# FILE COPY

Shaughnessy No.:059101

Date Out of EAB: JAN 24 1986

To: J. Ellenberger
Product Manager 12
Registration Division (TS-767)

From: Samuel M. Creeger, Chief
Review Section #1
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # : 464-448, 464-523 and 464-552

Chemical Name: Chlorpyrifos

Type Product : Insecticide

Product Name :

Company Name : DOW

Purpose : Reevaluation of photolysis on soil study for registration

Date Received: 11/6/85

Action Code(s): 306

Date Completed: JAN 24 1986

EAB #(s) : 6150-6152

Days: 1.75

Deferrals to:

____ Ecological Effects Branch

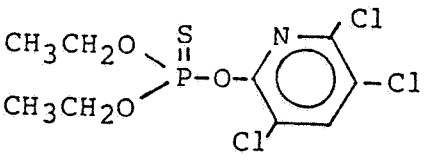
____ Residue Chemistry Branch

____ Toxicology Branch

Monitoring study requested by EAB: / /

Monitering study voluntarily conducted by registrant: / /

1. CHEMICAL: Chlorpyrifos



2. TEST MATERIAL: O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl-2,6-$^{14}$C) phosphorothioate having specific activity of 14.2 mCi/mmole and 99+% radiochemical purity.

3. STUDY/ACTION TYPE: Review of a Photolysis Study.

4. STUDY IDENTIFICATION: Photodegradation of Chlorpyrifos on Soil Surfaces.

5. REVIEWED BY:

Akiva D. Abramovitch, Ph.D.
Chemist
Environmental Chemistry Review Section 1/EAB/HED/OPP

Abramovitch
JAN 24 1986
Date:

6. APPROVED BY:

Samuel M. Creeger, Chief
Supervisory Chemist
Environmental Chemistry Review Section 1/EAB/HED/OPP

JAN 24 1986
Date:

7. CONCLUSIONS:

The registrant marginally satisfied the EAB data requirement for "Photodegradation on Soil" with the present study since chlorpyrifos did not undergo photolytic degradation when irradiated in the range in which chlorpyrifos absorbs sunlight radiation.

8. RECOMMENDATIONS:

The study under the reported experimental conditions is only marginally acceptable. For future uses of chlorpyrifos a new soil photolysis study will be needed using a light source that simulates sunlight in wavelength and intensity and apparatus that provides a constant flow of humidified air across the soil surface during irradiation. EAB recommends that a study protocol be submitted for evaluation prior to initiating future photolysis studies. The information in Zepp's review mentioned in section 10 E would be helpful in designing photolysis studies under sunlight and/or simulated sunlight conditions.

9. BACKGROUND:

A. Introduction: The presently submitted study was last discussed in the EAB review of Nov. 15, 1984 and was found deficient. Dow, as asked, is submiting additional information with regard to transmissibility of the glass plate used to cover the reaction chamber, the relationship of the artificial light intensity to that of natural sunlight and the UV absorption of Chlorpyrifos, as well as additional arguments in support of their conclusions.

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B. Directions for Use: See earlier EAB reviews.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

A. Study Identification: Photodegradation of Chlorpyrifos on Soil Surfaces. The study was conducted by P.R. Yackovich, P.J. McCall and J.H. Miller of the Agricultural Products Department of Dow Chemical.

B. Material and Methods:

A slurry of Commerce soil containing 36% sand, 50% silt, 14% clay and 0.68% organic matter was poured onto 9-cm glass plates. The plates were then air dried for four days. The soil on each plate was about 3 mm deep and weighed approximately 25 gm. The test chemical (see section 2) was applied randomly in 140 microliter of acetone to the soil layer (2,372,160 dpm/plate and 89914 dpm/microgram). The light source was a mercury arc lamp having energy spectrum through quartz glass window as shown in comparison to that of sunlight (see attachment). The temperature at the incubation chamber was maintained at 25°C and the air was passed through Drierite to remove moisture. Volatiles were trapped using a polyurethane plug and $^{14}CO_2$ with 100 ml of carbosorb. The parent radiolabeled chlorpyrifos and its radiolabeled degradates were analyzed by HPLC in reference to authentic samples of potential degradates. Identical samples were placed in the dark in order to determine the degree of degradation that chlorpyrifos will undergo in absence of light (also see EAB review of Nov. 15, 1984).

C. Reported Results:

Recoveries of $^{14}C$ material averaged 99% and little difference in behavior was observed between irradiated and non-irradiated samples of chlorpyrifos on Commerce soil and in both cases over 40% of the compound degraded in 3 days primarily to 3,5,6-trichloro-2-pyridinol. Light irradiation did produce 3% of 2-methoxy-3,5,6-trichloropyridine as a minor degradation product as indicated by the attached Fig. 8 and 9.

D. Study Author's Conclusions:

The study author concluded that photodegradation under sunlight on soil surfaces will be an insignificant environmental dissipative pathway for chlorpyrifos. The authors attributed the formation of pyridinol to degradation on soil surfaces in absence of light and noted that under normal field moisture conditions, the chemical degraded with a half life of 2-4 weeks at 25°C. However, under dry conditions degradation was accelerated to half lives of just a few days with production of pyridinol which did not undergo further degradation.

E. Reviewer's Discussion and Interpretation of Study Results:

The objective of the study is to determine the environmental fate of Chlorpyrifos under sunlight. The photolytic degradation study on soil was not conducted under sunlight conditions as indicated by the spectra of the the GE Mercury Arc Sunlamp #CG 4011 shown in Fig. 3. Since the reviewer was surprised that no radiation was shown below 300 nm in Fig. 3 (290 nm in

the text) as expected with a mercury arc lamp through quartz glass that is transparent to UV light, attempt was made to obtain further information about the lamp. Unfortunately, the GE customer service department was unable to locate a lamp # CG 4011 in their catalogs (past and present). However, we were told that their mercury lamps radiate from the 280 nm range and even lower as also noted in discussions in Experimental Approaches to Environmental Photochemistry by R. G. Zepp, pp. 24-29 in the Handbook of Environmental Chemistry, Volume 2/Part B edited by O. Hutzinger.

In the event photolytic degradation was reported in this study, we would have been unable to determine whether it was due to radiation under sunlight conditions in the range above 300 nm or below 300 nm.

These difficulties were overlooked in this particular situation since the study author was able to convince this reviewer that virtually identical degradation took place in the first three days of the study in both dark and photolyzed samples, indicating that no significant degradation can be attributed to radiation at the range chlorpyrifos absorbs in the sunlight range (see Fig. 13 in the attachment).

The reviewer noted (as previously noted by the EAB review of Nov. 15, 1984) that the rate of degradation of the photolyzed sample was somewhat faster than that of the "dark" soil sample. In fact on day 12, only 40% of the chlorpyrifos in the "photolyzed" sample was still present versus 55% in the "dark" sample (see Figures 8 and 9) while the registrant insisted that photodegradation did not take place. Since the difference in the degradation rate is only noted from day 3-12 (and not before), the reviewer can see some merit in the author's argument. The increased rate in the "photolysis" study could have been attributed to a decrease in the soil moisture content during the photolysis study since a decrease in soil moisture would induce faster degradation according to the study authors (see remarks in section D, above). However, this point was not studied in this experiment and the authors did not report the soil moisture content during the study as they should have obviously done in this case in order to explain the different rates. Further support to the author's claim that all the degradation observed on the soil was due to the soil and not to radiation could have been provided by additional photolysis studies on glass surface.

11. COMPLETION OF ONE LINER: Not yet completed.

12. CBI APPENDIX

None

Page_____ is not included in this copy.

Pages 5 through 11 are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

✓ FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

_____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

"RSM"

The product covered in this report is a self-ballasted sunlamp designed for operation on 115-125 volts A.C. Housed inside the reflector-bulb is a 100-watt mercury arc tube, a 175-watt tungsten filament ballast, and a bi-metallic starting switch. The lamp is equipped with a mogul screw base. No parts are replaceable, and a fracture of the outer bulb renders the lamp inoperative. This product is to be sold in combination with a lampholder as a sunlamp kit, and also as a replacement lamp for those kits. Photographs are attached.

Outer glass bulb is blown in a reflector shape with the reflector portion aluminized on the inside. The reflector is in the shape of a parabola and has a reflectance of from 87 to 89 per cent over the wavelength range of from 260 to 320 nanometers. As the reflecting surface is sealed into the bulb, it is not subject to deterioration from outside elements.

Reflector is an integral part of lamp. If bulb breaks, lamp becomes inoperative in 30 seconds or less due to filament oxidation.

The outer bulb is blown from borosilicate glass and acts as a filter for the radiation generated by the mercury arc tube in the lamp. This glass transmits strongly in the 300 to 320nm. region (52 to 56% at 302nm.) and greatly attenuates radiation of wavelengths under 280nm.

The bulb is an integral part of the lamp. If it is broken, the lamp becomes inoperative in 30 seconds or less due to filament oxidation.

We recommend eye protection to prevent sunburning of the eyes and lids through the use of goggles. As this is a replacement bulb, goggles are not supplied with it. The goggles we recommend are Lucas #LSS. See supplementary report on our RSK-5 sunlamp kit which includes a pair of these goggles.

At 30 inches, the exposure time with this lamp for minimum perceptible erythema for fair skin is 4 minutes. Exposures at distances less than 30 inches would result in shorter times that would be difficult to control with accuracy. Similarly, as the distance of exposure becomes shorter, the accuracy of its measurement becomes more critical. For these reasons, we warn that this lamp should not be used at distances closer than 30 inches.

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All of these will be covered in the instructions to users imprinted on the carton. See 2.15.

"Warning Ultraviolet - Read Caution Notice" appears on face of bulb.

Sunlamps of the RS-type are primarily purchased and used in an attempt to obtain cosmetic tanning similar to that produced from exposure to sunlight. Pigmentation of the skin following exposure to either solar radiation or ultraviolet radiation from artifical sources is a normal photochemical response which involves two distinct processes. There is an immediate pigment darkening effect which results from the oxidation of bleached pre-formed melanin granules upon absorption of long-wave ultraviolet radiations ( 320nm) and those in the visible region. Primary melanization occurs after there is sufficient exposure to the ultraviolet radiations between 280-320 nanometers to produce an erythemal response. Radiations below wavelengths 280nm. are not particularly effective in initiating melanogensis because of their inability to penetrate into the basal-cell region of the epidermis.

On the basis of the above, we believe that an effective sunlamp to produce cosmetic effects should emit (a) sufficient radiations in the erythemetogenic region of the ultraviolet (280-320nm.) to initiate the delayed pigment darkening effect, and (b) radiations in the near ultraviolet and the visible (320-750nm.) to produce the immediate pigment darkening effect (IPD) and/or to augment the tanning effect.

The instructions to the users of our sunlamps are designed to permit the gradual production of skin darkening over a period of time without the development of either initial or recurring skin "sunburn." Accordingly the emission levels recommended are based on the degree of exposure required to elicit a minimal perceptible reddening of the skin. The criterion for this level is the irradiance of solar ultraviolet to produce this minimal effect in an exposure period of 15 minutes, equated to the effectiveness of the different ultraviolet wavelengths in the production of erythema. Thus, the average irradiance in the beam of the GE RS-Sunlamp at a distance of 1 meter from the lamp face is about $2.65 \times 10^{-4} W \cdot cm^{-2}$ but the erythemally weighted irradiance using the Coblentz Action Spectrum data is $0.63 \times 10^{-4} W \cdot cm^{-2}$ @ 1M. This action spectrum ispredicated upon the development of a more persistent erythema, and equates all wavelengths to maximum effectiveness at 297nm. This irradiance value in the wavelength region 280-320nm. is desirable in order to produce a minimum perceptible erythemal exposure on the average skin in periods of less than 10 minutes.

No definitive data are available on the exposure parameters required to elicit the "immediate pigment darkening" effect. The total average irradiance from the RS Sunlamp in the wavelength region 320-750 nanometers is around 15 x $10^{-4}$ $W \cdot cm^{-2}$ at a distance of 1 meter.

Sunlamp exposure without medical advice and proper supervision not recommended for:

Debilitated persons
Infants and small children
Persons with skin diseases
Photosensitive individuals
People under medication

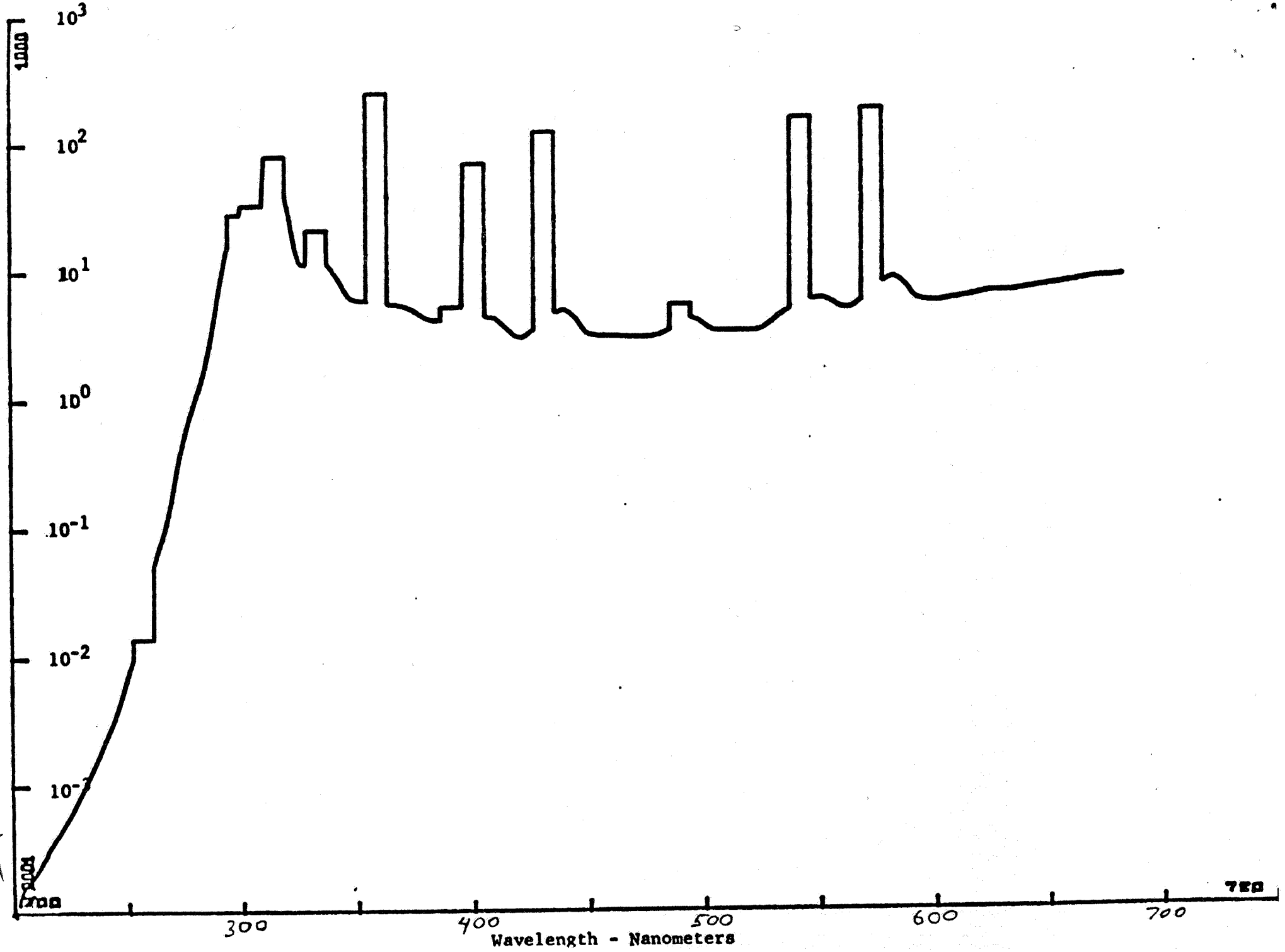
General Electric's RS Sunlamp (only the medium base version available at the time) was accepted by the Council on Physical Medicine of the American Medical Assoc. on Oct. 5, 1946. The Council has requirements for acceptance and regulations to contr advertising of sunlamps sold to the public. The Council distinguishes between sunlamps and therapeutic lamps, and points out that the spectral radiation characteristics of acceptable sunlamps are such that they are suitable for home use by persons familiar with the action of natural sunlight, without the supervision of a physician. The requirements state that the ultraviolet spectral energy distribution of a sunlamp shall be comparable in biologic effectiveness, to the ultraviolet emission of natural sunlight, with the spectral range limited largely to 290.0nm. to and including 313.2nm. and shall not include an appreciable amount of ultraviolet of wavelengths shorter than 280.0nm. To comply with the requirements for minimum intensity, the lamp shall be able to produce a minimum perceptible erythema on average untanned skin in not more than 60 minutes at a minimum distance of 24 inches. AMA approval was based on data be

| Wavelength Angstroms | Microwatts per $cm^2$ at 30 inches |
|---|---|
| 3129 | 120 |
| 3022 | 38 |
| 2967 | 15 |
| 2925 | (Intensity too low to measure) |
| 2894 | |
| 2804 | |
| 2753 | |

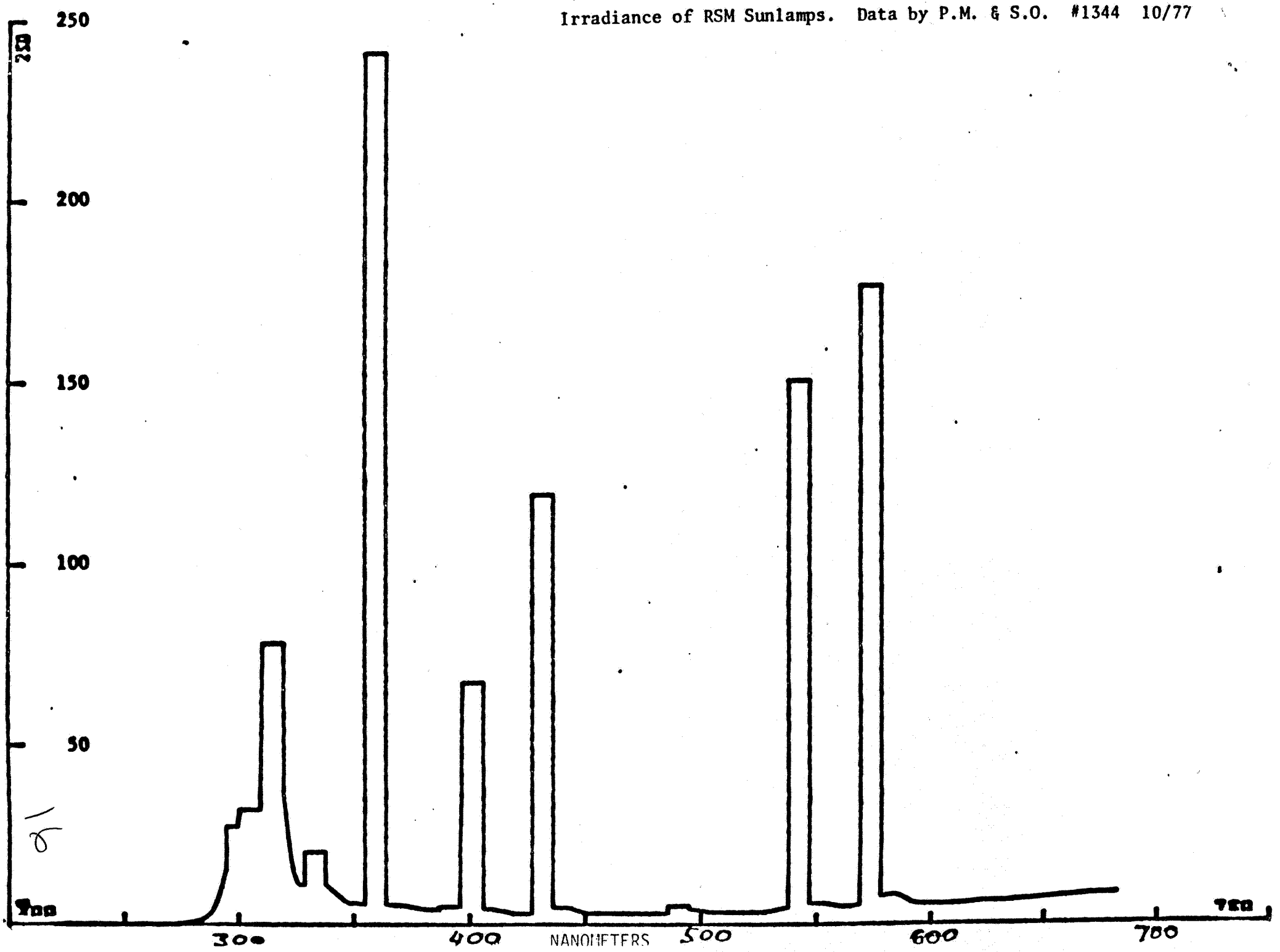
(for wavelengths 2,925°A and shorter, the output is insignificant.)

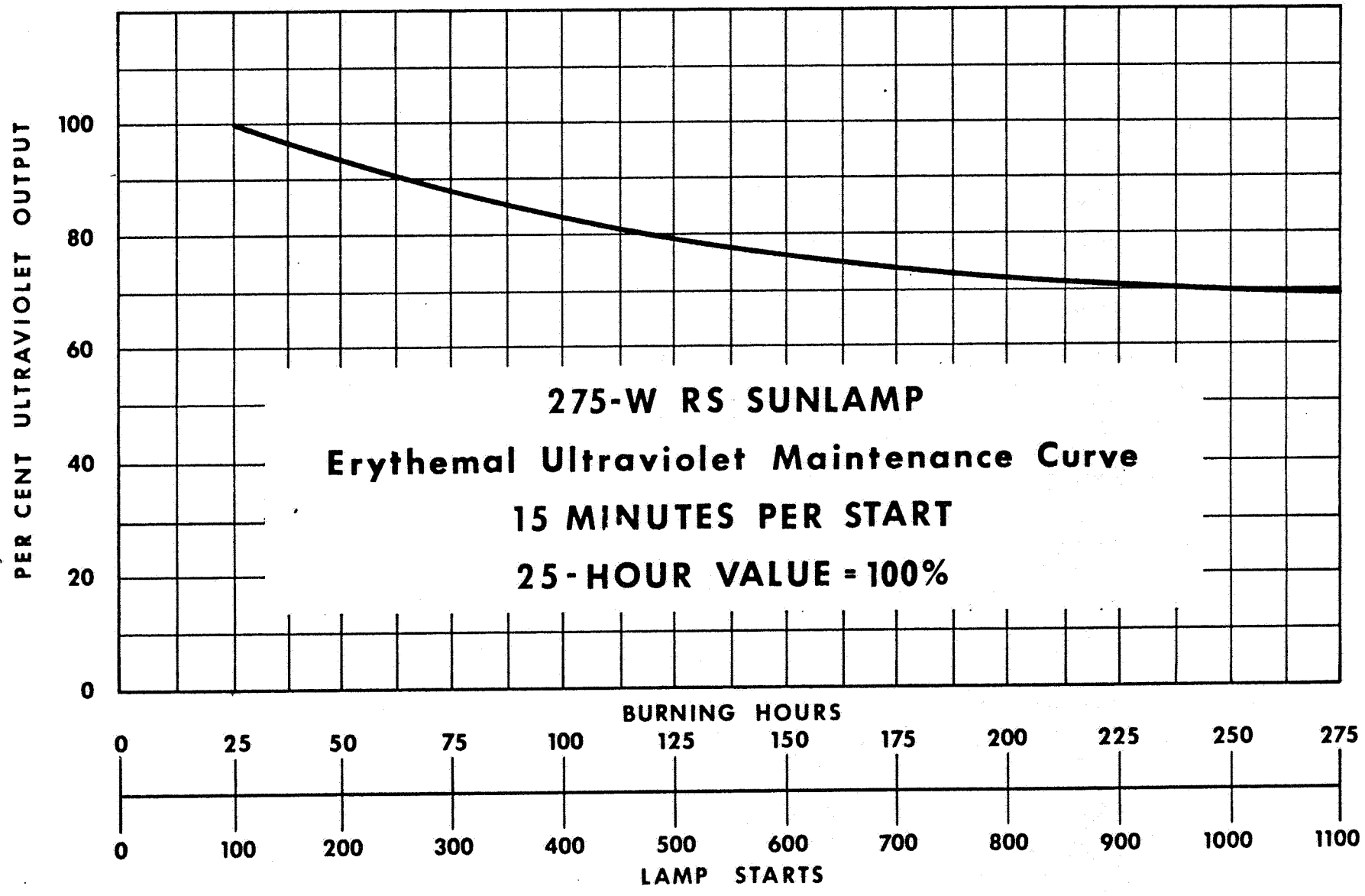
Above is from Journal of American Medical Association, October 5, 1946, page 283.

Irradiance of RSM Sunlamps. Data by P.M. & S.O. #1344 10/77



Irradiance of RSM Sunlamps. Data by P.M. & S.O. #1344 10/77




PER CENT ULTRAVIOLET OUTPUT
100
80
60
40
20
0
275-W RS SUNLAMP
Erythemal Ultraviolet Maintenance Curve
15 MINUTES PER START
25-HOUR VALUE = 100%
BURNING HOURS
0
25
50
75
100
125
150
175
200
225
250
275
0
100
200
300
400
500
600
700
800
900
1000
1100
LAMP STARTS

LINE CHANGED FROM 292 TO 293 BY

DATA BY: PHOTOMETRIC MEASUREMENTS AND STANDARDS OPERATION, 1344

| FILE NO. | DATE: | TYPE | NO. |
|---|---|---|---|
| 1099 | 12/14/79 | GE SUNTANNER | MFG.CODE 84 |

COMMENT: 120.0V*/2.42A/279.9W/30IN./0 HRS/HORZ.

LAMP MEASURED AT 76.2 CM.
DETECTOR AREA = 3.55CM2
DATA FOR 10NM BANDPASS CENTERED ON GIVEN WAVELENGTH
MEASURED WAVELENGTH RANGE: 170 - 429
UV IRRADIANCE RATIO ( 175 -260/261-320): [redacted]

| BRH RECOMMENDED WAVELENGTH RANGE | UV-C 175-~~280~~ 260 | UV-B ~~280~~ 260-320 | UV-A 320-400 | TOTAL 175-425 | SPECIAL 320-420 |
|---|---|---|---|---|---|
| LINES | .0025 | 159.6023 | 470.2811 | 763.2111 | 603.6063 |
| CONTINUUM | 2.9239 | 114.6206 | 126.8591 | 242.5787 | 144.6373 |
| TOTAL | 2.9313 | 274.2229 | 597.1402 | ******** | 748.2436 |

| NANOMETERS | A | B | A*B | C | A*C |
|---|---|---|---|---|---|
| LINES | MCW/CM2 | NIOSH | MCW/CM2 | SEC | MCW/CM2 |
| 257 | .002490 | .578 | .001439 | .480 | .001195 |
| 303 | 7.887855 | .167 | 1.315694 | .566 | 4.464526 |
| 314 | 151.714399 | .006 | .940629 | .040 | 6.129262 |
| 334 | 28.113597 | | | | |
| 366 | 442.167534 | | | | |
| 405 | 133.325216 | | | | |

159.602254

| CONTINUUM | MCW/CM2/10NM | NIOSH | MCW/CM2/10NM | SEC | MCW/CM2/10NM |
|---|---|---|---|---|---|
| 180 | .000000 | | | | |
| 190 | .001275 | | | | |
| 200 | .000022 | | | | |
| 210 | .000172 | | | | |
| 220 | .000003 | | | | |
| 230 | .000232 | | | | |
| 240 | .000694 | | | | |
| 250 | .015600 | .420 | .006552 | .570 | .008892 |
| 260 | .121613 | .650 | .079048 | .420 | .051077 |
| 270 | .386865 | 1.000 | .386865 | .140 | .054161 |
| 280 | 2.402369 | .880 | 2.114085 | .060 | .144142 |
| 290 | 9.257095 | .640 | 5.924541 | .310 | 2.869699 |
| 300 | 56.989598 | .300 | 17.096879 | .830 | 47.301366 |
| 310 | 28.765878 | .015 | .431488 | .110 | 3.164247 |
| 320 | 17.205705 | .001 | .017206 | .005 | .086029 |
| 330 | 14.747470 | | | | |
| 340 | 13.941201 | | | | |
| 350 | 10.803131 | | | | |
| 360 | 24.214005 | | | | |
| 370 | 20.711363 | | | | |
| 380 | 7.833988 | | | | |
| 390 | 9.871697 | | | | |
| 400 | 7.530508 | | | | |
| 410 | 12.555847 | | | | |
| 420 | 5.222291 | | | | |

115.007510

0.139616 + 0.002490 = .142106

.142106
274.609764
[redacted]

115.007510 + 159.602254 = 274.609764

18

NIOSH TIME (0.003 J-SEC/CM2) = 106.0 SEC. 1.77 MIN. .03 HR