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on

SPACE SHUTTLE NONMETALLIC MATERIALS AGE LIFE PREDICTION

to

NASA-LYNDON B. JOHNSON SPACE CENTER

August, 1975

by

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SPACE SHUTTLE NONMETALLIC MATERIALS AGE LIFE PREDICTION

by

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INTRODUCTION

Space vehicles are an extraordinarily complex assembly of components with varied composition. The useful service life of these components is of great importance since the conditions of their use often makes repair impossible, or at best inconvenient and costly.

Adoption of meaningful age prediction tests for polymers has been slow because present methods do not correlate very well with natural aging results. Most, if not all present test methods accelerate the aging process by increasing temperature, oxygen partial pressure or both. Such test techniques may lead to large age life prediction errors since reaction mechanisms may be completely changed from the normal aging reaction mechanisms.

A technique such as chemiluminescence, which provides a capability to examine the reactions which occur at room temperature, can be of great value since kinetics of reactions can be studied and age life predicted under identical conditions. Light emitted by the aging reactions as they proceed may provide the necessary elements upon which an accurage predictive technique can be developed.

The development of an accurate age life prediction technique can provide for a better selection of materials, which can result in lower program costs both initially and long-term.

In this program we have shown that the chemiluminescence emission from polymeric materials is a sensitive function of its temperature, environment, composition, and mechanical and chemical history. Correlations between these variables have been obtained as a first step toward useful age life prediction of the polymeric materials.

SUMMARY

The chemiluminescence, or emission of "cold-light", from samples of cis-polybutadiene, Viton, Teflon, Silicone, PL 731 Adhesive, and SP 296 Boron-Epoxy composite was measured at temperatures from 25 to 150 C (77 to 302 F). Excellent correlations were obtained between chemiluminescence and temperature. These correlations serve to validate accelerated aging tests (at elevated temperatures) designed to predict service life at lower temperatures.

In most cases, smooth or linear correlations were obtained between chemiluminescence and physical properties of purified polymer gums. The physical properties included tensile strength, viscosity, and loss tangent, The latter is a complex function of certain polymer properties. Data were obtained with far greater ease by the chemiluminescence technique than by the conventional methods of study.

The chemiluminescence from the Teflon (Halon) samples was discovered to arise from trace amounts of impurities, which were undetectable by conventional, destructive analysis of the sample.

Milling on a rubber mill of five polymer gums produced chemiluminescence due to the mastication. This result confirms the possibility of studying the effects of mechanical deformation on polymers by the chemiluminescence technique.

Experimental

The Chemiluminescence Apparatus

An artist's rendition of the chemiluminescence apparatus appears in Figure 1. The heart of the apparatus is an RCA Model 4501/V4, 12-stage photomultiplier whose output can be displayed in analog (strip-chart recorder) or in digital (counts/seconds) form. Below the photomultiplier head are a sequence of shutters focusing lens, and a wheel containing filters. The sample is placed in the inner chamber of a two-compartment oven.

The inner chamber is provided with electric heating elements, while the outer chamber is cooled continuously to avoid heating the aluminum box that contains mechanical controls. Provisions are included for metering in two gases into the sample oven at rates read from flow meters.

Background counts with no sample in the oven were found to be a function of temperature (increasing with increasing temperature) and were larger in oxygen than in argon. This increase turned out not to be significant because the sample counts exceeded those from background by several orders of magnitude.

Chemiluminescence in argon at 100 C (212 F) and 150 C (302 F) showed an initial rise associated with warming of the sample, and the data were taken after the counting rate achieved a constant or nearly constant value (Table 1).

Color filters (2" x 2") were placed in some of twenty slots in an aluminum wheel mounted between the sample oven and the photomultiplier tube (Figure 1). Filters were changed by remote control. Slots without filters alternated with slots containing filters, in order to minimize the time to obtain filtered and unfiltered counting rates. The change from one filter to an adjacent one required about 10 seconds, followed by at least 30 seconds observation to obtain an averages count. This procedure is satisfactory except when the counting rate was changing too fast for a linear interpolation from unfiltered counting rates at the beginning and end of each determination. As a consequence most of the filtered data had been obtained in later stages of runs.

The data is given in the figures in terms of $f(\lambda)$, the fraction of the unfiltered emission rate observed with a cutoff filter whose O.D. is 0.50 at λ nm. The values cannot at present be translated directly into a spectral distribution, since a correction for the spectral sensitivity of the photomultiplier is necessary. For the purposes of detecting subtle changes in chemiluminescence emission, however, the $f(\lambda)$ values are adequate and probably more useful. Their accuracy in most cases reported here is believed to be ± 0.01. When filtered counts were near the unfiltered value or near the background level, they obviously contained larger errors. Background emission was significant in many cases although in most cases emission rates from samples were far greater than background. Significant background counts were subtracted out when reporting data.

Several procedures were developed to examine chemiluminescence from the samples being evaluated. This was necessary because the properties of the processed polymers differed markedly from those of uncured gums. The different procedures, which will be referred to in the text by the appropriate letter, are described in the following paragraphs.

Procedure A. Samples of the commercial, compounded, and cured polymers were cut into rectangles (40 x 37 mm), mounted on aluminum holders for 35 mm slides, and placed in the oven of the apparatus. The aluminum holders alone gave off relatively little chemiluminescence under these conditions. The same sample of material was examined first at 25 C (77 F), then at 70 C (158 F), and then at 53 C (127 F) in an oxygen atmosphere. A new sample of each material was examined at 100 C (212 F) in oxygen. At 150 C (302 F) we anticipated changes may have occurred during warm-up if it took place in oxygen, so samples were placed in the oven of the photon-counting apparatus in argon, and oxygen was admitted when the photon count (under argon) had reached a nearly constant level. This required 10-15 minutes at the two higher temperatures. On admitting oxygen at 150 C (302 F) to the sample under argon, the photon count increased by 1-2 orders of magnitude within 5-10 minutes and typically then increased or decreased by 1-2%/minute after that.

Procedure B. Polymer samples were loaded onto shallow pyrex dishes and introduced into the chemiluminescence apparatus preset at the desired conditions of temperature and atmosphere. Chemiluminescence data were calculated in terms of counts per gram-sec.

Procedure C. A sample of polymeric material was compressed between two clean aluminum sheets at 1400 psi for about 30 minutes. One sheet was peeled off and the other, bearing a film of polymer, was trimmed to fit a 35-mm aluminum slide holder. The sample was then examined as in Procedure A.

Procedure D. A solution of the polymer and any other desired ingredient was prepared, filtered, and concentrated to a small volume. A portion of the solution was placed in a tared aluminum cup. Attempts to dry the polymer by evacuating a dessicator containing concentrated polymer solutions led to boiling and highly irregular surfaces. Therefore, the solvent was evaporated in a dessicator equipped with an inlet to admit a stream of argon or nitrogen. The sample, which was smooth and regular, was handled and measured by Procedure C.

The polymer samples we examined in this project included the following:

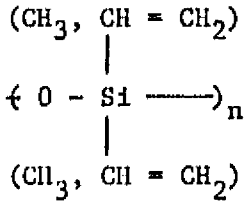
Polymer	Source	State
	Processed Polymers	
cis-Polybutadiene 1203	Phillips	Compounded cured sheet
cis-Polybutadiene	Battelle-Polymer Sec.	Cured gum sheet
SBR-1500	Firestone	Compounded cured sheet
Methyl Phenyl Siloxane RTV 560	General Electric	Compounded material; was cured into sheet according to supplier's directions.
Viton E60-C	DuPont	Compounded cured sheet
Natural Rubber (Malaysia)	Malaysian Rubber Producer's Assoc.	Compounded cured sheet
Natural Rubber SMR-5	Battelle-Polymer Sec.	Cured gum sheet
Teflon G-80	Allied	Molded sheet
Teflon G-10	Allied	Powder
Polyurethane "Estane" 5703	B. F. Goodrich	Granules
PL 731 Adhesive	NASA-Johnson	Thin sheet and as film on titanium
SP 296 Boron-Epoxy Composite	NASA-Johnson	Film on titanium, film with SP-296 on titanium
Viton A	DuPont	Colorless lumps
Silicone W-96	General Electric	High viscosity oil
cis-Polybutadiene	Phillips	Brown lumps.

Purification of Commercial Polymers

Commercially available polymers contain a wide variety of additives and impurities. In an attempt to separate the CL behavior of the various polymers from the impurities contained in them, they were purified by various methods.

Silicone Gum W-96. The colorless high viscosity liquid was dissolved in argon-flushed benzene (20 cc/g) and precipitated with argon-flushed methanol in a nitrogen atmosphere. The precipitation was repeated twice more, and the final product evacuated overnight at 25 C (74 F) with oil-pump pressure. The product was stored in the dark in an argon atmosphere.

The structure of this polymer is that of a vinyl-containing methyl silicone, the vinyl groups being introduced deliverately to facilitate cross-linking during the curing process.



$$\begin{array}{c} (CH_3,\ CH = CH_2) \\ | \\ \leftarrow\!(\,O - Si \text{ ——})_n \\ | \\ (CH_3,\ CH = CH_2) \end{array}$$

For chemiluminescence studies the sample was examined by Method B. The sample of material was removed after the experiment and stored in a bottle in the dark until rheological experiments were made.

Viton A. A 10 g-sample was dissolved in acetone (100 cc) and precipitated with excess distilled, argon-flushed water in a nitrogen atmosphere. The process was repeated twice more, and the residual, white polymer was evacuated at oil-pump pressure at 25 C (74 F) for 48 hr. Samples were examined by Method B. The final product was not suitable for direct study of rheological properties, so excess acetone was added to the samples. After standing at least 24 hr in the dark, the solute was decanted from any insoluble material present and concentrated (1) to dryness if not all of the material dissolved, or (2) to a 20% solution for viscosity measurements.

Estane 5703. A telephone call to Mr. Richard Loveless at B. F. Goodrich Co. in Cleveland yielded some information on the material we were studying. Estane 5703 is a linear, aromatic-type polyester containing a linear diol. The product is sold without additives or antioxidants. The material is dusted with talc, which can be removed easily by filtration of a solution of the polymer.

We experienced great difficulty in obtaining desired amounts of this polymer by solvent precipitation from benzene with hexane, or from acetone with water. In view of information from Goodrich, we felt adequate purification was to dissolve the material in acetone, filter, and concentrate to dryness followed by evacuation with an oil pump. The product was examined by Methods B, C, and D.

cis-Polybutadiene. Samples of brown cis-BR gum were dissolved in benzene and precipitated with methanol. The treatment did not change the color of the samples.

Teflon. Halon G-10 was extracted in a soxhlet extractor with a 1:1 benzene-2-butanone mixture for 24 hr., dried in a vacuum of 0.1 torr, and examined for chemiluminescence. The extracted material was extracted an additional 24 hr. with fresh solvent mixture. The Halon was dried and examined for chemiluminescence. The results appear in Table 4 and in Figure 28.

The solvent from the extraction, which had acquired a yellow-brown color, was removed at reduced pressure to give a sticky, yellow-brown material, 0.14% of the original weight of Halon G-10. The material showed chemiluminescence under the conditions of the original experiment, but it was not examined further.

Tensile Strength Measurements

A cured gum sample of cis-BR rubber prepared in the Polymer Section of Battelle-Columbus Laboratories, was cut into dumbbell-shaped sections that were aged at 150 C (302 F) in an oven in air for various lengths of time.

The tensile strength of virgin and aged samples was obtained in the usual fashion with an extension rate of 5.08 cm (2.0 in.) per minute.

Viscosity Measurements

Values of tangent (θ) and the viscosity functions were determined on a Weissenberg rheogoniometer using a cone-and-plate assembly. Changes in viscosity reflect changes in polymer chain length and in the degree of crosslinking. Tangent θ, or the loss tangent, is the ratio of viscous to elastic response in a material.

Milling Study

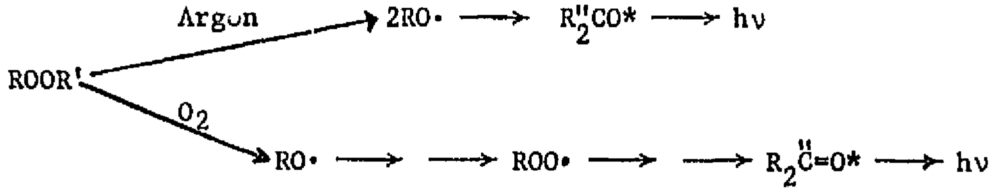
Fifty-gram samples of polymer gums were milled for 20 minutes. The mill was operated at 50 C (122 F) in air with a gap of 0.051 cm (20 mil) and a differential speed between the rolls of 15 rpm. The chemiluminescence of each sample in oxygen at 50 C (122 F) was determined before and after milling by Procedure B. The results are given in Table 8.

RESULTS AND DISCUSSION

The results of the work performed on this project can be divided into two main parts. The first concerned chemiluminescence emission from standard compounded sheets of polymeric materials supplied by the manufacturer. Correlations were made between observed chemiluminescence and physical property measured and data supplied by manufacturer.

In the second part of the program, uncured, purified polymers were treated by physical and chemical techniques, and the changes both in chemiluminescence and in physical properties were measured over extended times. Correlations were made between the two sets of data so obtained.

The lower values of chemiluminescence under argon than under oxygen (Table 1) at the same temperature indicates beyond doubt that most of the chemiluminescence we observe is due to an ongoing oxidation process, and not merely the decomposition of some component of the polymers that produces light emission. The residual sample counts under an argon atmosphere is real and significant, however, and it may be the result of the decomposition of peroxides present in the sample, by way of radicals that terminate to give excited states. In the presence of oxygen, these peroxide decompositions, along with other nonchemiluminescent reactions serve to initiate the usual radical-chain decomposition:



The apparent linearity of most of the plots of log (counts/sec) vs T_{abs}^{-1} (Figures 2-11) is an interesting and somewhat unexpected feature. The values at 25 C (77 F) (furthest right point) are uncertain within ±2 counts for statistical reasons, and the value at 150 C (302 F) is suspect because of the rapid changes at this high temperature. Moreover, changes in counting rate of the order of 1-2%/minute even after temperature equilibration make the selection of the "true" count difficult. In view of these approximations, and of the complex nature of the materials under study, the results are gratifying. The energy of activation for chemiluminescence in the temperature range 25-150 C (77-302 F) in at least seven of the 10 samples, is similar, consequently the mechanism of oxidative degradation is possibly similar.

Our analysis of the data follows that of Lundeen,(1) derived for hydrocarbon oxidation in the liquid phase. A steady-state concentration of hydroperoxide was assumed to form by the process:

$$2ROOH \longrightarrow RO\cdot + (H_2O + ROO\cdot)$$

$$RO\cdot + R'H \longrightarrow R'\cdot + ROH$$

$$R'\cdot + O_2 \longrightarrow R'OO\cdot$$

$$R'OO\cdot + R'H \longrightarrow R'OOH + R'\cdot$$

$$\frac{dROOH}{dt} = 0$$

---

(1) G. W. Lunden, Thesis, University of Minnesota, 1964.

The maximum emission of light in a sample occurred when the steady-state concentration of ROOH had been reached. We have no way to verify whether this approach is correct (an alternate treatment could be based on the assumption that a relatively constant concentration of some initiator is present at all temperatures). It is reasonable to assume the same set of reactions will also be present in polymer oxidation, and can be subjected to similar mathematical treatment.(1) A second point is that the values of activation energy (E_a) obtained, i.e., 18 ± 1 kcal/mole in seven cases, lie close to a value of 20.8 ± 1.9 obtained by Lundeen(1) for the spontaneous oxidation of tetralin. From his analysis, the principal terms comprising $E_{I_{max}}$ are

$E\alpha + 2E_3 - E_3$, where

$E\alpha \approx 3$ for $2ROO\cdot \longrightarrow R'_2C{=}O^* + ROH + O_2$

$E_3 \approx 8\text{-}15$ for $RO_2\cdot + RH \longrightarrow R\cdot + ROOH$

$E_4 \approx 1$ for $2RO_2 \longrightarrow R_2C{=}O + ROH + O_2$

Initial Rate of Chemiluminescence Emission

At temperatures above room temperature the emission rate always increases initially. With extended times the rates in some cases begin to fall. Figures 12-21 show the chemiluminescence from polymer samples in the as-received condition at 70 C (158 F) in oxygen and chemiluminescence from the same samples after thermal aging. For most there is no pronounced peaking of light emission within 15 minutes, as is often the case with liquid hydrocarbons under these conditions. Cis-Polybutadiene (O_2 and Ar), Viton E60-C (Ar), Halon G-80 (O_2), and perhaps Silicone RTV-560 (Ar) show gradually increasing emission rates with time, and in some cases may reach a maximum after extended times. For practical reasons we have not used longer observations. In part this is based on the fact that any rapid screening technique for polymers would be limited severely by a requirement for long examination times for each sample.

After aging, the initial emission rates are constant for cis-polybutadiene, Viton E60-C, SBR-1500, and Silicone RTV-560 in argon. The emission rates increase for Halon G-80 (under Ar) and for Silicone RTV-560 in oxygen. The initial emission rates for Halon G-80 in oxygen decreased with heat-aging.

Correlations of Chemiluminescence from Polymer Samples with Aging Data

Samples of cis-polybutadiene, Viton-E60-C, Halon G-80, SBR-1500, Natural Rubber (Malaysia), and Silicone RTV-560 were aged for various times in air at elevated temperatures. The aging times were selected to correspond to physical property data given to us from the suppliers of the polymers, although quantitative data were not available in every case.

Our most satisfying results were obtained from natural rubber supplied by the Malaysian Rubber Producer's Research Association. Curves of chemiluminescence versus time are shown for rubber and after aging, on Figures 22-24. With aging we note an increase in the initial intensity of light emission under argon, and the development of a maximum in the sample after 48 hours. The steady-state intensity under oxygen increases from time zero to 24 hours, and then decreases at 48 hours, though not to the value observed originally.

Tensile strength data for this rubber show a continuous decrease with age at 125 C (257 F). Clearly the I_{max} in oxygen will not correlate with tensile strength, since the former first increases and then decreases (Figure 25). On the other hand, deterioration in polymer properties will be the cumulative result of oxidation reactions, and may be expected to correlate with the total light emitted. This is proportional to the number of chain terminations in the sample, which is proportional to twice the radical chains that have taken place. Figure 26 shows the plot of tensile strength versus relative light emitted from the sample. A fairly smooth curve is obtained.

This figure would allow one to predict the tensile strength of a rubber sample from its chemiluminescence versus time behavior. Predictive behavior at lower temperatures would require additional data at other temperatures, of course.

Attempts were made to improve the correlation for this polymer by examining the chemiluminescence at 100 C (212 F) rather than 70 C (158 F), the same temperature as the aging. Measurements were determined initially in the unaged condition and after aging for times corresponding to literature data on the mechanical properties. Data for the samples appear in Table 3. The aging and chemiluminescence measurement temperatures match in this case. For plotting on Figures 26A data from samples 1 and 3 were normalized to agree with Sample 2 by multiplying their fractional decrease in counting rates by the initial counting rate of Sample 2.

Attempts to duplicate the result for natural rubber (Malaysia) with other polymer samples were less successful. The chemiluminescence from Halon G-80 decreased sharply from time zero to 24 hours (Figure 27). In this time the weight loss, indicated by the top curve, was given by the manufacturer as 0.0002%/hour. The sample, however, contained surface contaminants, and the relationship between the light emission and changes in the polymer could not be determined with any certainty.

Pure polytetrafluoroethylene should not give rise to luminesence by any plausible oxidative mechanism. However, measurements of as-received Halon G-10, a powdered material, showed repeated counting maxima at 80 C (176 F) of 49 and 54 cps. Extraction treatment reduced the maximum to 21 cps, and the count decreased to half of this value after 60 minutes. Two extractions gave a product that displayed a counting maximum of 14 cps. This count decreased to 4 cps after 40 minutes. The simplest explanation for this result is that an oxidizable material that gives chemiluminescence is removed slowly by solvent extraction. The residual counting rate of Sample 4 (Table 4 and Figure 28) may be due to small amounts of unextracted material that, due to the sensitivity of our apparatus, gives rise to measurable luminescence.

Untreated Halon G-80 sheet supplied by DuPont under these conditions gave a maximum of 173 and 150 counts/sec. The counting rates decreased to a quarter of these values on extended observation (Table 4) at 80 C. A fresh sample of Halon G-80 was prepared by abrading the surface with a razor blade until surface contamination was no longer evident. This process reduced the counting maximum to 46 (Sample 7), a value close to that observed for untreated Halon G-10 (Samples 1 and 2). We suggest that the bulk phase of Halon G-80 contains oxidizable material, and that the abrasion process simply removes an excess of contaminant on the surface from the extraction of Halon G-10.

A sample of Halon G-80 was submitted for combustion analysis. The results did not differ from those expected from pure polytetrafluoroethylene. It is thus possible to detect impurities in Teflon at far lower concentrations than are with destructive analysis, and with a technique that does not destroy the sample.

A sample of cis-BR rubber (prepared at BCL) contining carbon black was heat aged in an attempt to repeat correlations obtained with the BR-1203 sample. The emission rates were low (<100 cps) and nearly constant at 150 C (302 F) in air during a 38-hr observation period. This result correlated very well in a qualitative fashion with the physical measurements, which also showed little change on aging (Table 6).

Two samples each of SBR-1500 and silicone RTV-560 were aged at 100 C (212 F) and 316 C (600 F), respectively. Chemiluminescence was observed from all samples. Further observations for longer periods will be necessary to obtain correlations for the SBR-1500. It will be necessary to obtain aging data for Silicone RTV-560 to obtain age-life correlations.

Mechanical Treatment and Chemiluminescence

In Table 7 is presented the results of mechanical treatment of two samples of SBR polymer on the chemiluminescence intensity in oxygen at 14 C (57 F). The increases are significant and indicate the chemiluminscent technique will be useful for studying autoxidation processes initiated by mechanical deformation.

Physical stress on polymeric materials can induce degradation by rupture of bonds which then causes further damage by radical-induced oxidation. This mechanically-induced oxidation can be detected by chemiluminescence techniques.

This effect was demonstrated more systematically for a series of polymer gums that were milled under identical conditions (Table 8). The chemiluminescence increases in every case. The chemiluminescent emission [illegible] Viton A is absent originally and induced entirely by the milling treatment.

Effect of Compounding on Chemiluminescence

A dramatic effect of compounding on chemiluminescence intensity was shown for different cis-butadiene samples. It is suspected that the low counting rates for commercial polymers stemmed from the presence of carbon black and other compounding agents in the polymer samples. These absorb light strongly and reduce the amount of chemiluminescence that is detected with the photomultiplier. Table 9 demonstrates the effect of compounding on light emission from different samples of cis-polybutadiene. The large decrease noted in the compounded and cured material results in part from the absorption effect, and partly, of course, from the presence of stabilizers that reduce the rate of oxidation.

Correlation of Polymer Stability With E_{Imax} for Chemiluminescence

Values of E_{Imax} were obtained from the slopes of lines drawn through points of an Arrhenius plot. The Arrhenius figures were made by plotting the log of chemiluminescence emission obtained by procedure A vs. 1/T. It is apparent from Table 2 that there is no simple correlation between polymer stability and E_{Imax}. The Halon G-80 and natural rubber samples have E_{Imax} identical within error, as do the Viton E60-C and polybutadiene samples, although each pair differs greatly in stability.

Also there does not appear to be a simple correlation between chemiluminescence intensity and polymer stability at any temperature, although the Viton and silicone samples are expected to be the most stable and do show the least light emission. Part of the reason is the presence of carbon black as pigment in the polybutadiene, SBR-1500, Viton E60-C, silicone rubber, and probably other samples. Self-absorption will reduce light output, and the measured intensity will not be the intrinsic intensity.

Viton E60-C displayed a very low counting rate in oxygen at 70 C. The chemiluminescence-aging data are shown in Figure 29 together with tensile strength given for the same aging times. There is no clear correlation between mechanical strength and either with counting rate or with the area under the intensity versus time curve.

cis-Polybutadiene displayed behavior similar to Viton, as shown in Figure 30. There was little change in counting rate with time at 100 C (212 F), and the counts did not change systematically. The tensile strength decreased in a linear fashion at these temperatures.

Chemiluminescence from *cis*-Polybutadiene 4-1203

The improved condition with Natural Rubber when the aging and chemiluminescence were done at the same temperature, encouraged us to try with *cis*-BR as well. Four cured samples of *cis*-polybutadiene 4-1203 (Phillips Petroleum) were examined for chemiluminescence at 100 C (212 F) in oxygen. Two samples were aged in air at 100 C (212 F) for 24 hr and two for 72 hr. At the end of the aging periods the samples were examined for chemiluminescence under the same conditions of the original examination. The results are given in Table 5.

Plots of counts/sec observed for the samples vs time of aging, and of normalized total relative emission vs tensile strength appear in Figures 31 and 32, respectively. The results are of uncertain significance because of the limited amount of data, but the linear relationship observed in Figure 32 is encouraging.

Chemiluminescence of Purified Polymers

The preceding results were encouraging, but the complexity of the commercial products limited what we could say about the chemiluminescence emission. We therefore studied a series of pure polymers, that is, uncured and without fillers, pigments, or antioxidants, in order to establish a base set of data. The effect of additives and processing could then be studies, we felt, in a more systematic fashion.

Silicone W-96

Striking changes in light emission were found for Silicone W-96 gum as a function of time. The curves are shown in Figures 33-36, and the conditions of aging for this and other gums are summarized in Table 10. We ascribe the initial rise in chemiluminescence, which is on the order of the warm-up time, to increased terminations at the high temperature. The radical source is not known, but is presumably peroxidic material present in the sample. The decrease after the rise may be due to consumption of these peroxides, which results in a decreased termination rate. Development of absorbing impurities may be a small factor in the decrease in emission, but the samples at 193 C (379 F) remained visibly without color.

The slow rise after the minimum in Run 41 (Figure 34) may be due to the development of an emitting species (fluorescer) among the degradation products. The increase was not seen at 150 C (302 F) Figure 36).

The greater chemiluminescence at 150 C (302 F) than at 193 C (392 F) is consistent neither with our expectations nor with past experience. We suspect that an impurity was present in the batch of silicone used for the lower temperature runs. The impurity may be either an emitter or a substance more easily oxidized than the silicone itself. (A similar case was found for Halon G-10 and G-80). Alternatively a quenching impurity may have reduced the chemiluminescence from the sample at 193 C (379 F). The viscoelastic properties of the two samples (Figures 37 and 38) differed little. This indicates that chemiluminescence is a more sensitive technique than conventional methods for measuring polymer properties.

A free-radical process in the silicone gum will increase its modulus (stiffness) by crosslinking. Peroxides are in fact recommended for this purpose by the manufacturer, and the monomer contains vinyl groups to facilitate the process. Although the complex modulus did not change greatly with heat aging (Figures 38-42), values of tangent (θ), which is the ratio of viscour to elastic response, clearly showed the expected effect of cross-linking (Figures 43 and 44). A linear relation between total chemiluminescence emission at 193 C (379 F) and tangent (θ) at 10 $\sec^{-1}$ appears in Figure 45. The corresponding plot for aging at 150 C (302 F) was curved (Figure 46).

The physical measurements on heat aged silicone show, as expected, less change at 150 C (302 F) (Figure 44) than at 193 C (379 F) (Figure 43).

Viton A

Significant effects of temperature, time, and antioxidant chemiluminescence from Viton A were discovered in our work. Chemiluminescence-time curves for Viton A appear in Figures 47-51. At 150 C (302 F) Viton A samples showed the typical pattern of rapid rise to a maximum, followed by a slow decrease (Figures 47 and 48). The two runs agreed well in general features. The wavelength distribution changed little with time (Figure 48). and was similar at both temperatures, although samples visually discolored under these conditions. This paradox is easily resolved if the colored material absorbs at all wavelengths about equally (the decrease from 1.00 to 0.90 with the 354 nm filter may not be significant). The decrease may also result from consumption of an emitter, or of oxidizable impurities.

At 200 C (392 F) the emission maximum decreased more rapidly than at 150 C (302 F) (Figure 49). We ascribe the increase at both temperatures to increased termination rates brought on by the increase in temperature. The spectral distribution (Figure 49) is shifted to slightly longer wavelength at 193 C (379 F) than at 150 C (302 F).

With antioxidant present a higher maximum per unit weight of polymer was reached (Figures 50 and 51), but the counting rate decreased more sharply. The antioxidant, N-phenyl-2-naphthylamine, can itself function as a fluorescer, which may explain the higher maximum.

Aromatic amines also produce highly colored products on oxidation. This may explain why the samples appeared jet black after heat aging.

The absorption spectrum of these products may account for the shift toward shorter wavelengths (Figure 50) of chemiluminescence compared with Viton A without antioxidant (Figure 49).

The chemiluminescence intensity decreases at a constant rate after extended reaction times (Figure 48-50). The constant drop in luminescence is in part due to the increase in color of the polymer with time. The color will absorb some of the light being emitted. If the drop in emission is entirely due to the colored product, it is being formed at a constant rate when a constant slope is reached. The slope is higher at the higher temperature because the colored material is formed faster.

The weight losses in the Viton A samples were all small and irregular (Table 11). There may be a compensating effect from loss of solvent and absorption of oxygen. No consistent trend is apparent either from temperature or time.

The samples were in the form of hard crusty pieces after the aging process, which made them unsuitable for direct measurement of viscoelastic properties. The aged material was accordingly treated with a large excess of acetone for 24 hr at room temperature. The solvent was decanted from any solid or gel and concentrated to dryness. The weights of the gel and of the soluble material were noted. If the entire sample dissolved after 24 hr, it was concentrated to 20 ± 1% by weight and the viscosity determined.

The viscosity data appear in Figures 52-54, and the solubility results in Table 12. The sample from run 51, although it appeared soluble in acetone, gave erratic results on attempting to measure the viscosity of the solution. The rheological data could not be obtained from this sample, although fairly smooth curves were obtained with solutions of starting Viton, and samples heat-aged at 150 C (302 F).

The changes in viscosity with aging at 150 C (302 F), however, are not uniform. Between time zero and 0.8 hr the viscosity at the high-shear rate (10 sec^{-1}) drops, and then remains unchanged after total 3.3 hr. At the lower shear rate (0.2 sec^{-1}) the viscosity increases at short aging and falls to values much lower than those of unaged material. This behavior indicates that the changes in the sample even at 150 C (302 F) are rather complex. We did not attempt correlations with chemiluminescence emission for this reason.

The solubility data (Table 12) show that gel formation is more apparent at 200 C (392 F) than at 150 C (302 F), presumably because rates of free radical cross-linking in the sample are faster, or at least compete more effectively with other reactions at the higher temperature.

We obtained less gel formation with N-phenyl-2-naphthylamine (antioxidant) present (Table 12). This is an expected result due to the inhibition of free-radical chains by the amine. The amount of acetone absorbed into the gel is nearly identical in the presence or absence of antioxidant. This suggests they may be similar in character, and this is expected if the antioxidant functions only to postpone the crosslinking process until the amine is consumed. After the amine is consumed the reaction proceeds as usual.

The presence of amine antioxidant reduced the chemiluminescence intensity at 200 C (392 F) about five-fold (Figures 49 and 50). Although the reduced chemiluminescence correlates with the reduced crosslinking (as evidenced by decreased gel formation), a simpler explanation is preferred. The samples with antioxidant became black, increasing the amount of self-absorption.

Estane 5703

Large differences in chemiluminescence intensity with increasing aging time were found for Estane 5703. The polyurethane polymer showed behavior similar to Viton when heated in oxygen at 150 C (302 F) (Figures 55-58). Part of the decrease after the maximum can be ascribed to development of colored products, since the initially yellow polymer was brown after aging.

Conclusions

We observed linear Arrhenius plots with nearly identical slopes for chemiluminescence from commercial polymeric materials in eight of ten cases. This is consistent with a common mode of oxidative degradation over the temperature range 25-150 C. This result is of great importance in that it supports the validity of service life measurements taken at high temperatures and extrapolated to low ones.

The smooth correlations obtained from plots of total emission vs tensile strength are an empirical result, but extremely interesting from a practical standpoint. The best correlations are obtained from *cis*-polyisoprene and *cis*-polybutadiene based polymers, which among those examined are the most likely to undergo antioxidative degradation.

The chemiluminescence from Halon samples is the result of oxidizable impurities present in very small amounts. The sensitivity of our chemiluminescence technique is so great that we can detect residual amounts of emission even after exhaustive solvent extraction of a sample.

The correlations of physical properties and chemiluminescence that have been obtained for some purified polymer gums are no better than those obtained from commercial polymeric samples. The influence of antioxidants on chemiluminescence from gums can be explained in a qualitative way.

Future Work

The chemiluminescence behavior of commercial samples of polymeric materials, and of purified polymers are both complicated. In view of (a) the satisfactory correlations of physical properties of rubbers with chemiluminescence data (in particular Figure 26A, natural rubber), and (b) the large amount of work necessary to obtain physical data on heat-aged, purified polymers, we suggest that attempts to predict service life be restricted to finished, commercial polymeric materials.

We feel the best polymers for study are those that undergo deterioration in properties primarily by a free-radical, oxidative route. These include polyethylene, polyisoprene, natural rubber, styrene-butadiene, polystyrene, and related polymers. A second desirable criterion is that extensive heat-aging data should be available, since our experience in the current project indicates that aging data for polymer physical properties is much more difficult and expensive to obtain than is data from the chemiluminescence measurements.

The most suitable polymers we know of in this respect are Natural Rubber and cis-Polybutadiene. Time restrictions did not permit us to use all of the literature aging data available for these compounds. We suggest that these materials should be studied extensively, in particular, measurements at different elevated temperatures should be carried out to extrapolate aging data, obtained at these temperatures, to ambient conditions.

Other hydrocarbon polymers will be studied in this intensive fashion, if sufficient aging data can be obtained from their manufacturers.

An alternate approach for study is to measure a precisely determinable property of a polymer that can be related directly to chemical changes that also produce chemiluminescence. This could involve, for instance, changes in molecular weight, determined by viscosity measurements, induced by the known rate of decomposition of an initiator grafted onto the polymer backbone. We have introduce such groups on to polymers in this laboratory with singlet molecular oxygen.

APPENDIX

The Autoxidative Degradation of Polymers

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The chemical changes in organic polymers as they undergo reaction with atmospheric oxygen are believed to occur by the same mechanism as liquids, that is, by a free-radical chain reaction.[2] The mechanism, now generally accepted for this process, is thought to be;

Initiation: $\text{Initiator} \xrightarrow{k_1} R\cdot$

Propagation: $R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot$

$RO_2\cdot + R'H \xrightarrow{k_3} R'\cdot + RO_2H$

Termination: $2RO_2\cdot \xrightarrow{k_4}$ Non-radical products.

$RO_2\cdot + R\cdot \xrightarrow{k_5}$

$2R\cdot \xrightarrow{k_6}$

Actually, this is a rather simplified scheme, and in the real situation there are usually a variety of initiators present (hydroperoxides) that decompose by unimolecular, bimolecular, or induced[3] processes. Such induced decompositions may be the result of almost any of the components of a formulated polymer and undoubted are the most significant in real life polymer degradation processes. The propagation step 2 is not rate-determining, while the rate of step 3 depends on the nature of the R'-H being broken. Of the termination steps, only 4 is considered of importance in the presence of oxygen under the conditions normally seen by polymers in service. However this may not always be the case in polymers if oxygen consumption is sufficiently fast compared with diffusion rates.

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[2] L. Reich and S. S. Stivala, "Elements of Polymer Degradation", McGraw-Hill Book Co., 1971.

[3] R. Hiatt in Organic Peroxides (D. Swern, ed.), Vol. II., Wiley-Interscience (New York, 1971), Chapter 1.

Two basic modes of inhibition of autoxidation are possible.

(1) Free radical chain breaking

Substances which react with peroxy radicals to form inactive products will inhibit oxidation since these radicals are the major chain carriers. With such inhibitors present, the following additional steps are required to complete the oxidation mechanism:

$$RO_2\cdot + InH \longrightarrow ROOH + In\cdot$$

$$\left.\begin{array}{l} RO_2\cdot + In\cdot \longrightarrow \\ In\cdot + In\cdot \longrightarrow \end{array}\right. \text{Stable products}$$

The chain length is large during the initial stages of autoxidation but when the reaction reaches its steady state rate the chain length is reduced to unity. Thus free radical chain breaking inhibitors will be most effective during the initial stages of the reaction.

(2) Preventive mechanisms

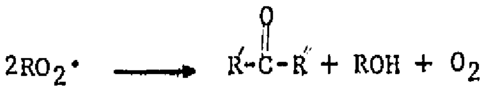
Two general types of reactions provide protection: (1) peroxide decomposition by reactions not producing radicals, and (2) deactivation of metal ions, generally by complex formation and/or stabilization of an inactive oxidation state of the metal.

Catalyst deactivators will be most effective during the initial stages of oxidation (catalysts serve to reduce the induction period but do not affect the steady state rate) while peroxide decomposers will be more effective during later stages of oxidation when the peroxide concentration is higher. Thus the different types of inhibitors complement one another.

Chemiluminescence Method

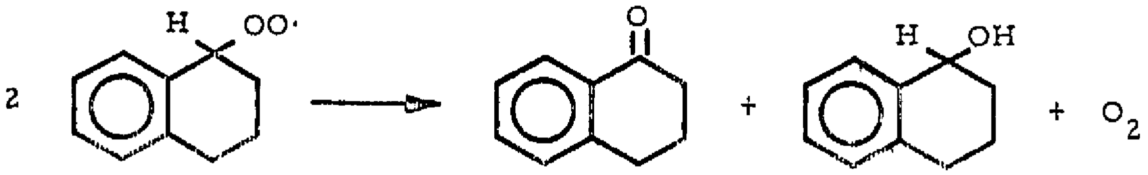
Although it has been known for many years that hydrocarbon oxidation and peroxide decomposition produce weak chemiluminescence, only recently has an understanding of the detailed mechamisms been gained. This understanding allows the use of chemiluminescence emission to follow the detailed course of these reactions. Much of the recent work in this area has been done by R. F. Vasil'ev and coworkers at the Institute of Chemical Physics, U.S.S.R., Academy of Sciences. Their work is summarized in several recent reviews.[4]

It is now well established that excitation occurs in the termination reaction in which disproportionation of peroxy radicals yields, a ketone, alcohol, and oxygen, e.g.,



$$2RO_2\cdot \longrightarrow R'-\overset{O}{\overset{\|}{C}}-R'' + ROH + O_2$$

Thus, for tetralin(4)



Recent studies indicate that this termination process involves a tetroxide intermediate R-0-0-0-0-R which rapidly rearranges to give the above final products. In this case spin conservation would require the formation of either singlet excited oxygen or triplet excited ketone. Generally, the chemiluminescence observed is a result of the small fraction of ketone molecules formed in their triplet state. The intensity of chemiluminescence is thus proportional to the rate of the termination step; $I = K[RO_2\cdot]^2$. The addition of chemically inert materials with high fluorescence efficiencies

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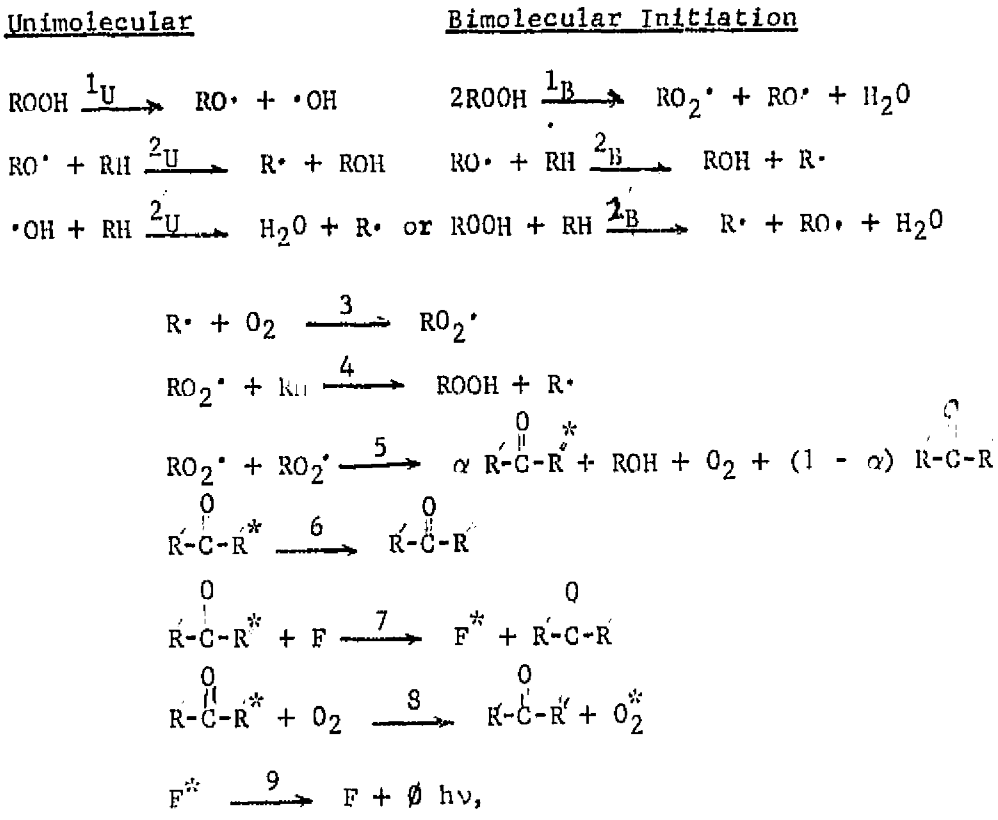
(4) (a) Vasil'ev, R. F., Progress in Reaction Kinetics, Vol. 4, p 305 (1967).

(b) Popisova, V. I., Shlyapentokl, V. Ya., Vasil'ev, R. F., Russian Chem. Rev. 34 (8), 599 (1965).

(c) Shlyapentokl, V. Ya., Russian Chem. Rev. 35 (4), 292 (1966).

(fluors) serves to increase the intensity due to energy transfer from the excited ketone to the fluorescent additive. This intensification increases the sensitivity of the chemiluminescence method by several orders of magnitude.

The current understanding of the mechanism, for chemiluminescence of hydrocarbon oxidation with added fluor is:



<u>Unimolecular</u> | <u>Bimolecular Initiation</u>

$ROOH \xrightarrow{1U} RO\cdot + \cdot OH$ | $2ROOH \xrightarrow{1B} RO_2\cdot + RO\cdot + H_2O$

$RO\cdot + RH \xrightarrow{2U} R\cdot + ROH$ | $RO\cdot + RH \xrightarrow{2B} ROH + R\cdot$

$\cdot OH + RH \xrightarrow{2U} H_2O + R\cdot$ or $ROOH + RH \xrightarrow{2B} R\cdot + RO\cdot + H_2O$

$$R\cdot + O_2 \xrightarrow{3} RO_2\cdot$$

$$RO_2\cdot + RH \xrightarrow{4} ROOH + R\cdot$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{5} \alpha\ R'-\overset{O}{\overset{\|}{C}}-R'^{*} + ROH + O_2 + (1-\alpha)\ R'-\overset{O}{\overset{\|}{C}}-R$$

$$R'-\overset{O}{\overset{\|}{C}}-R'^{*} \xrightarrow{6} R'-\overset{O}{\overset{\|}{C}}-R'$$

$$R'-\overset{O}{\overset{\|}{C}}-R'^{*} + F \xrightarrow{7} F^{*} + R'-\overset{O}{\overset{\|}{C}}-R'$$

$$R-\overset{O}{\overset{\|}{C}}-R^{*} + O_2 \xrightarrow{8} R'-\overset{O}{\overset{\|}{C}}-R' + O_2^{*}$$

$$F^{*} \xrightarrow{9} F + \emptyset\, h\nu,$$

where an asterisk indicates an excited state, α is the fraction of ketone produced in the excited state, and $\emptyset$ is the fluorescence yield of the fluor, F.

$$\mathrm{ROOH} \longrightarrow \xrightarrow{(\mathrm{Cat.})} 2\mathrm{R}\cdot$$

In this case the reaction rate goes through an induction period which corresponds to the time required to reach a steady state concentration of hydroperoxide. This induction period is conveniently measured in terms of $t_{1/2}$, the time required for the chemiluminescence intensity to reach half of its steady state value. From the above mechanism it can be shown that

$$t_{1/2} = \frac{1}{k_1 \ [\mathrm{Cat.}]} \ln \left\{ \frac{1 - \dfrac{[\mathrm{ROOH}]_o^{1/2}}{[\mathrm{ROOH}]_{oo}^{1/2}}}{1 - 1/\sqrt{2}} \right\},$$

where $[\mathrm{ROOH}]_o$ and $[\mathrm{ROOH}]_{oo}$ are the initial and steady state concentrations of hydroperoxide. Choosing $[\mathrm{ROOH}]_o$ $[\mathrm{ROOH}]_{oo}$ this reduces to $t_{1/2} = \dfrac{K'}{k_1 \ [\mathrm{cat}]}$ or

$$(t_{1/2})^{-1} = K \ k_1 \ [\mathrm{cat.}].$$

$t_{1/2}$ is a measure of the induction period. Since metal-ion catalysts shorten the induction period but do not affect the steady-state rate, this measure would be very useful for measuring stability of fuels which contain trace metal impurities.

The intensity of chemiluminescence is proportional to the oxidation rate, with the proportionality constant being a function of oxygen concentration, fluor concentration, nature of added fluor.

Compounds which deactivate metal ions would reduce the effective catalyst concentration and/or the value of k_1 and thus increase $t_{1/2}$. The steady state rate of oxidation is independent of catalyst so this type of inhibitor would not affect the steady state intensity or the steady state rate of oxygen consumption as measured by the "oxygen drop" method.

Materials which act as antioxidants by decomposing hydroperoxides via nonradical paths would reduce the steady state concentration of hydroperoxide, $[ROOH]_{oo}$, so $t_{1/2}$ will be slightly reduced. In this case, however, the steady state rate of oxidation will be reduced and thus the steady state intensity of chemiluminescence will be less and the rate of oxygen consumption, measured by the "oxygen drop" method, will decrease.

It is seen, then, that each type of oxidation inhibitor produced characteristic changes in the chemiluminescence accompanying free radical oxidation. Thus the chemiluminescence method offers the possibility of measuring the efficiency of each type of inhibitor in terms of the particular mechanism by which it operates. These measurements are summarized in the following table.

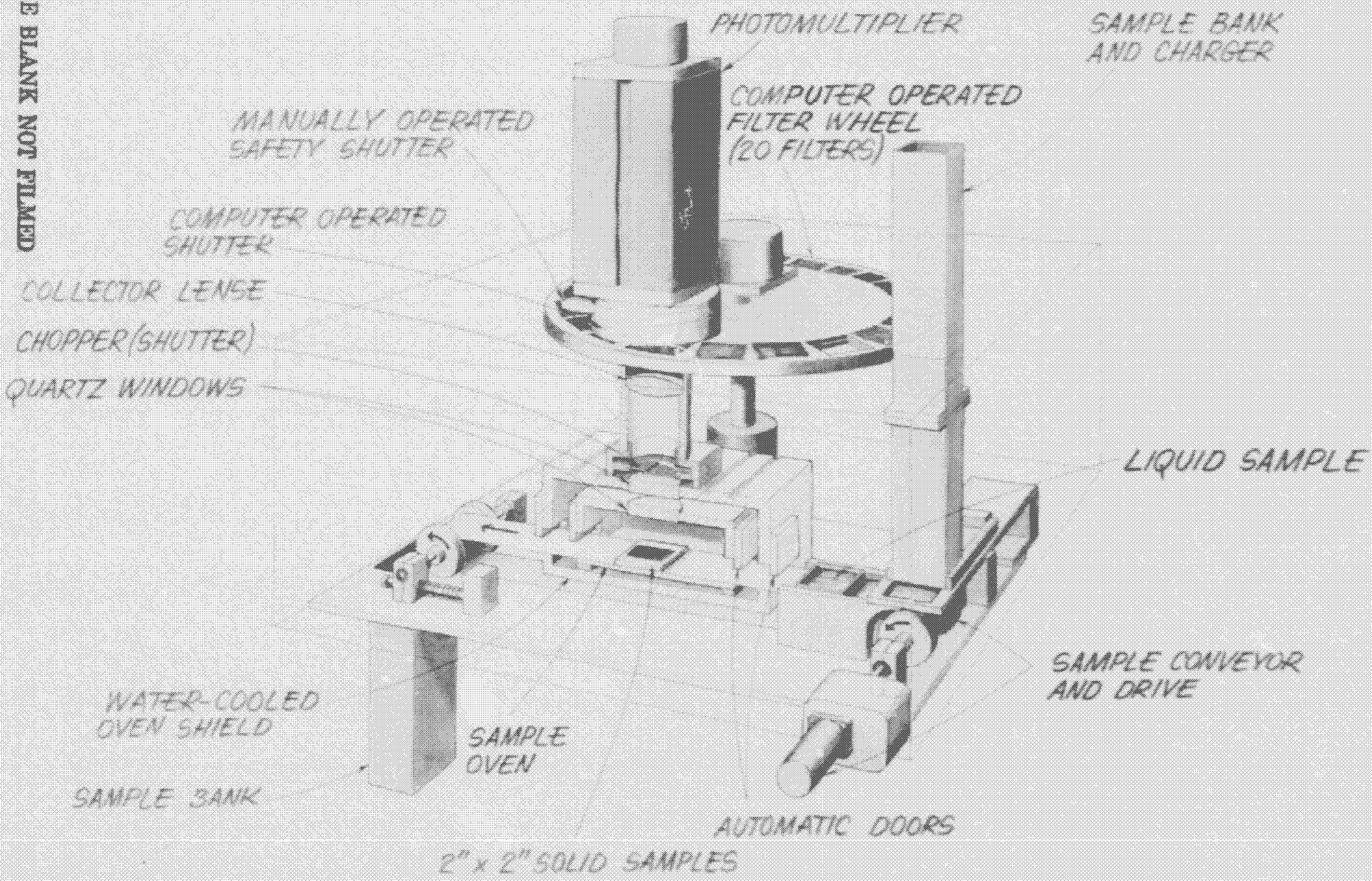
	Variables Measured	
Type of Inhibitor	Free Radical Initiated	Metal Ion Catalyzed
Radical chain breaker	$\sqrt{I/I_o}$, $k_8/\sqrt{k_5}$, $1/t_f$	
Metal deactivators		$t_{1/2}$
Peroxide decomposers		I/I_o, $1/t_f$

The chemiluminescence method provides instantaneous and continuous monitoring of the reaction rate in a form suitable for automatic recording. This permits the measurement of very short induction periods and other features of the initial stages of oxidation.

Typically the "oxygen drop" method requires the consumption of approximately 10^{-7} moles of oxygen per milliliter of solution, which is equivalent to about 0.002 ml of oxygen at atmospheric pressure. The measurement of oxygen absorption by the standard gas burette method would require approximately a 100 times longer reaction period in order to produce an accurately measurable change. In a polymeric, solid, material, the application of this method is possible in principle, but difficult from an experimental standpoint because diffusion into the bulk material can become rate-limiting.

FIGURE 1.

PHOTON COUNTING INSTRUMENTATION FOR CHEMILUMINESCENCE STUDIES



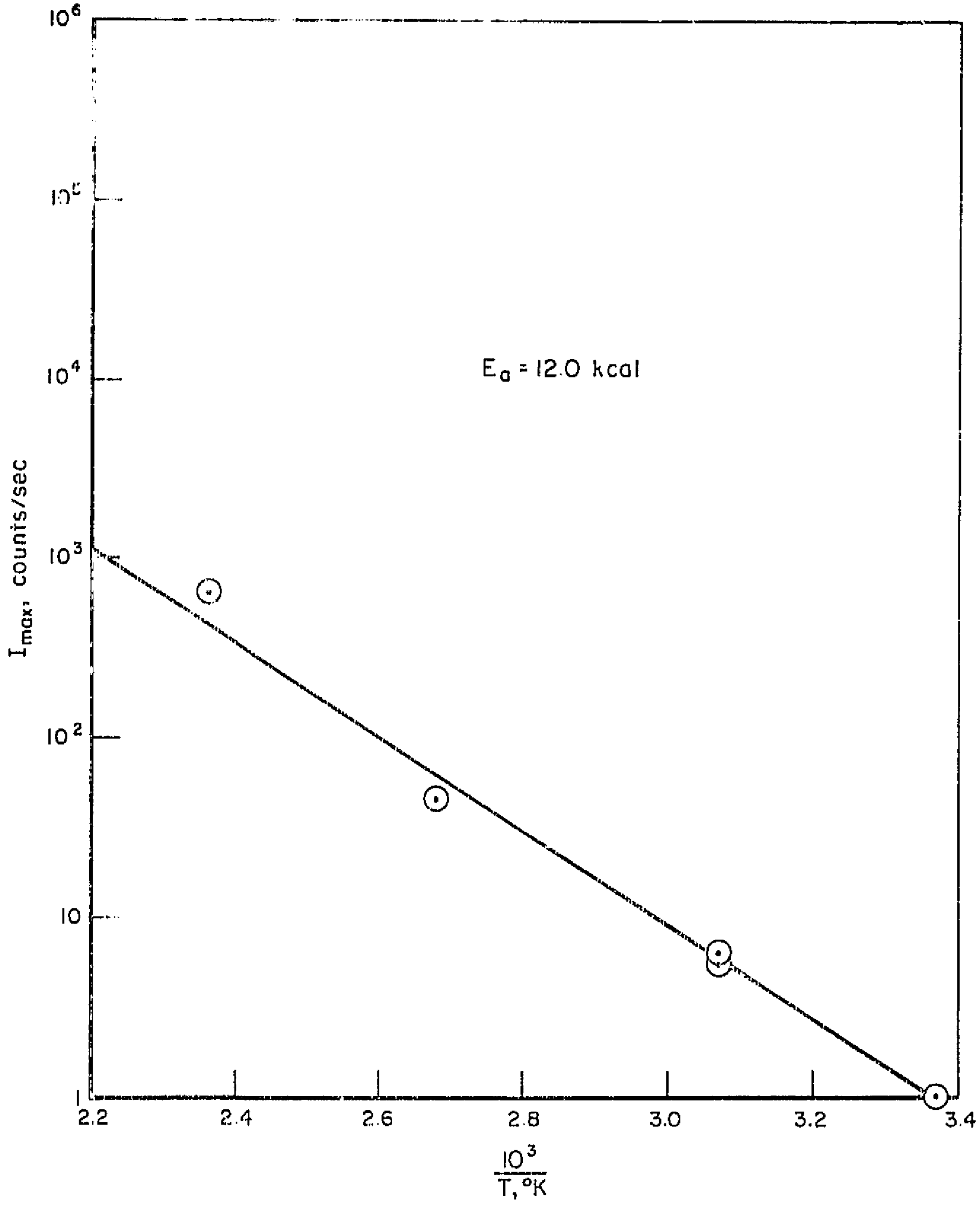


FIGURE 2. CHEMILUMINESCENCE FROM cis-POLYBUTADIENE 4-1203

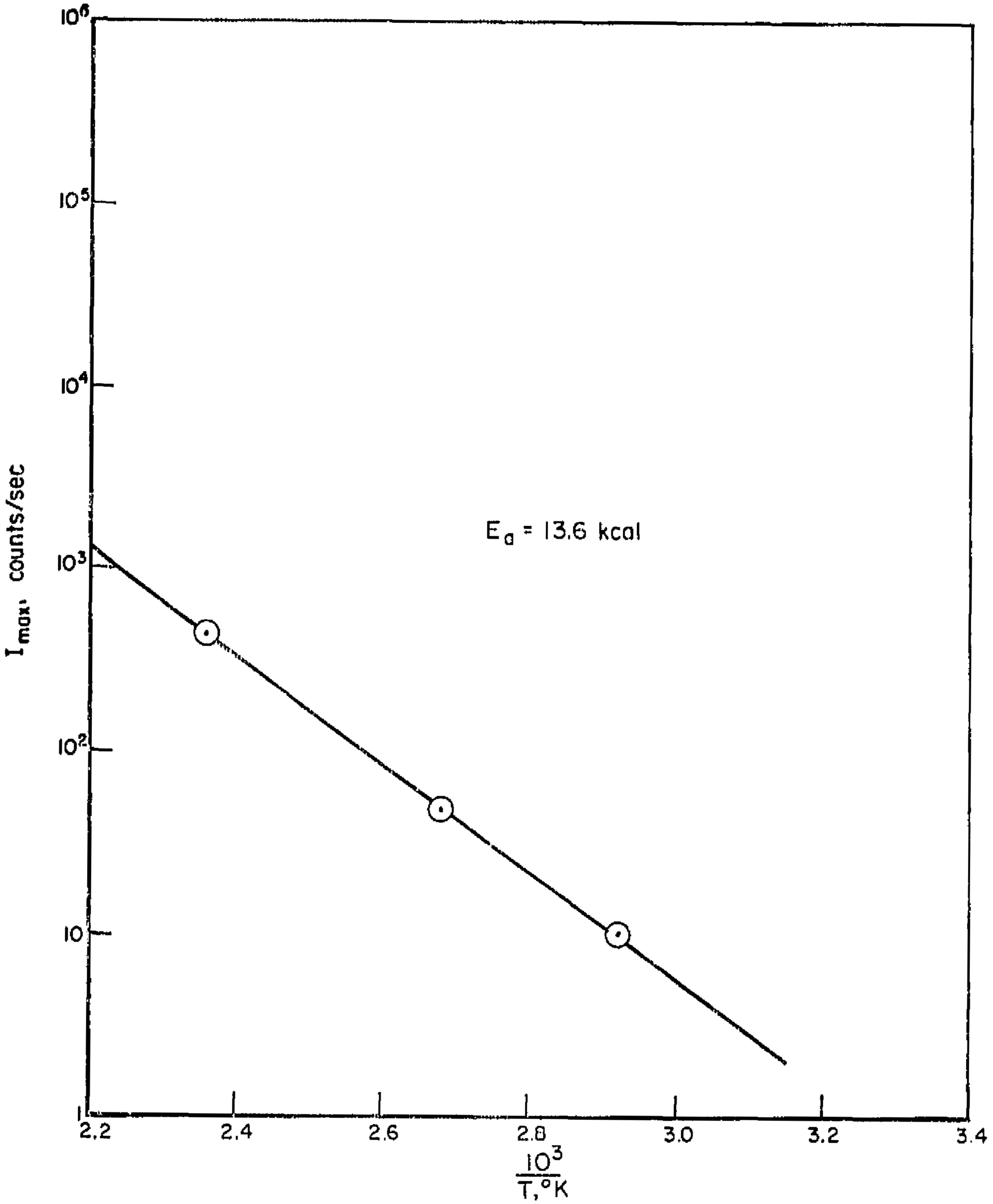


FIGURE 3. CHEMILUMINESCENCE FROM VITON E60-C

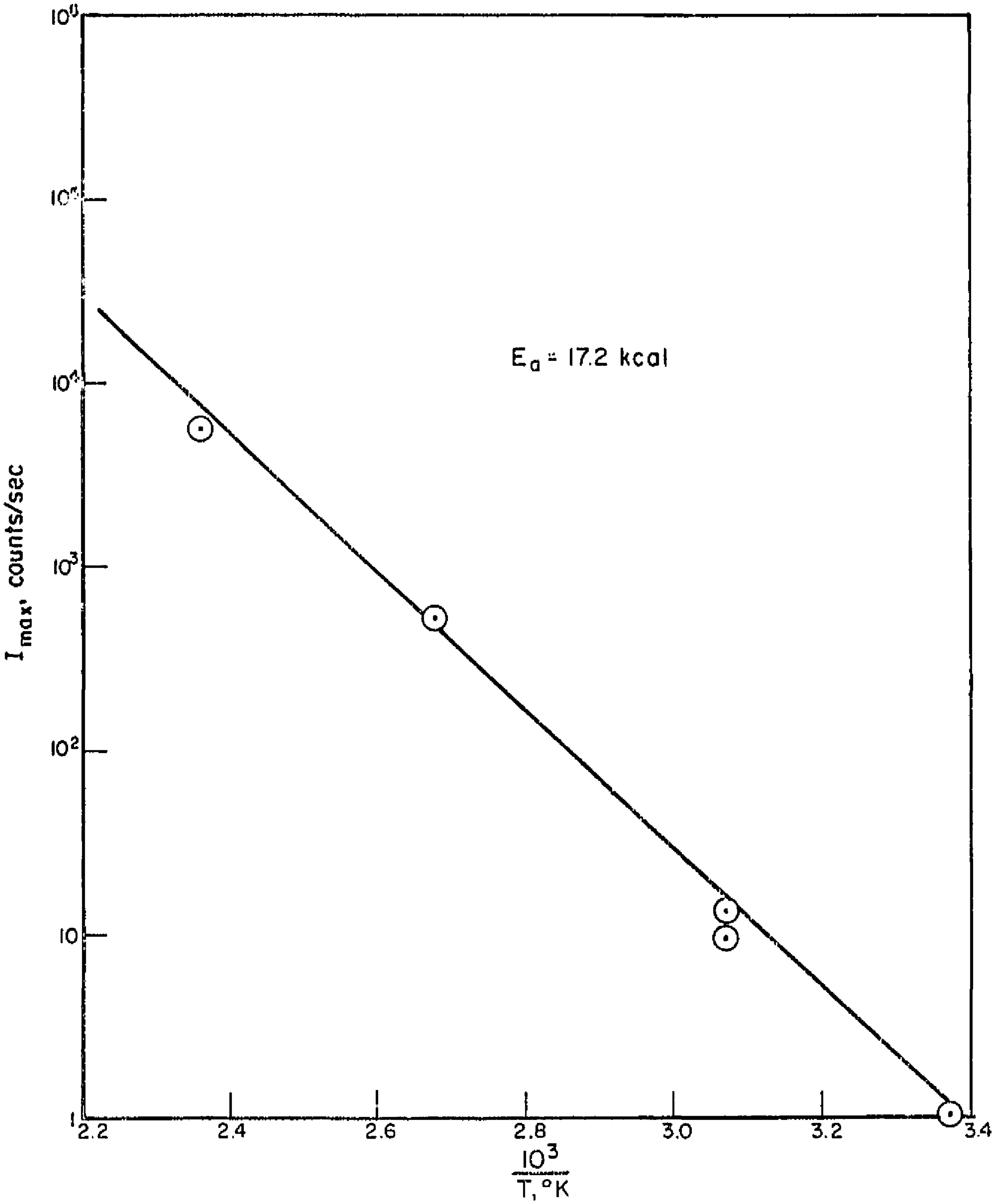


FIGURE 4. CHEMILUMINESCENCE FROM HALON G-80

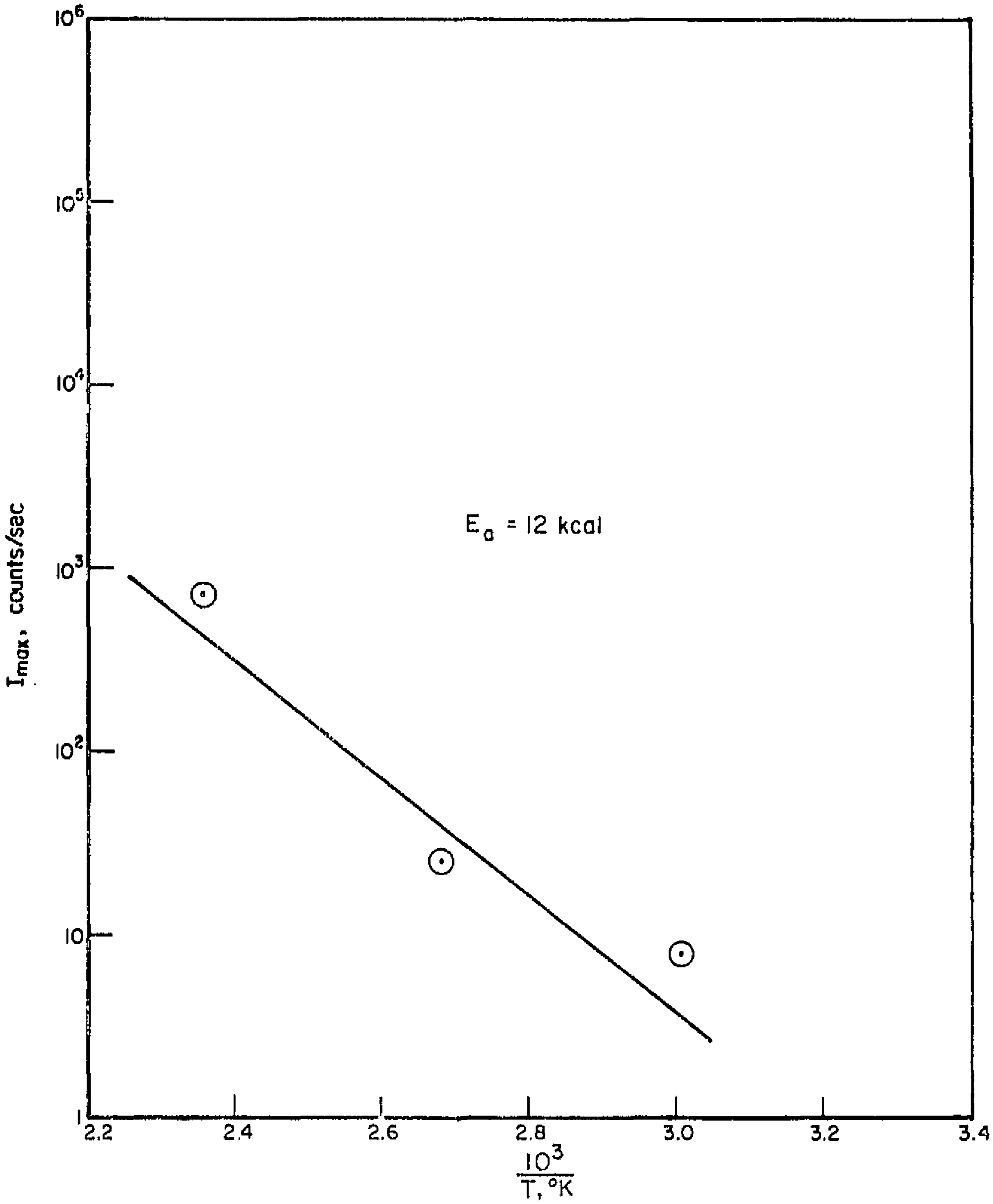


FIGURE 5. CHEMILUMINESCENCE FROM SBR-1500

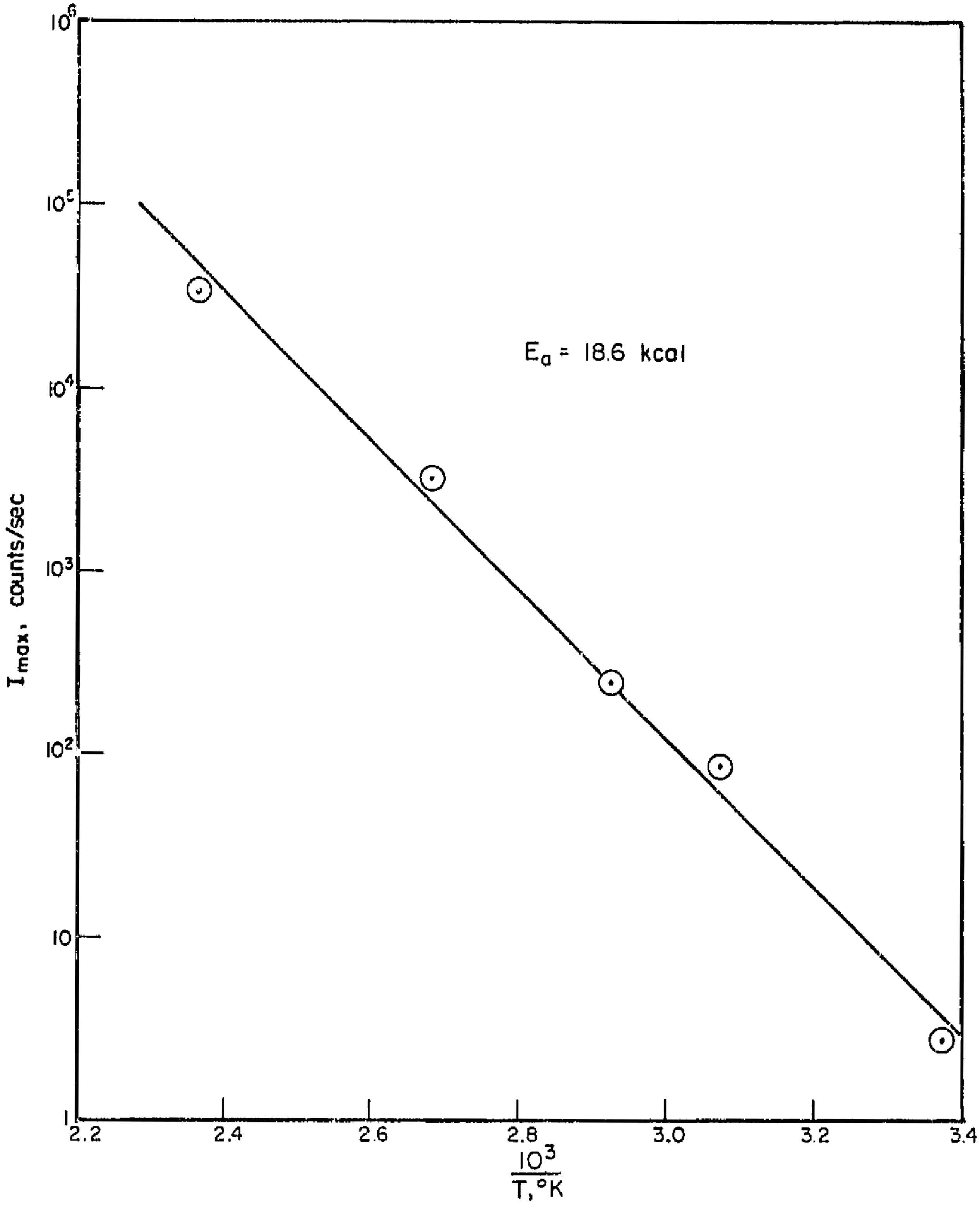


FIGURE 6. CHEMILUMINESCENCE FROM SMR-5 NATURAL RUBBER

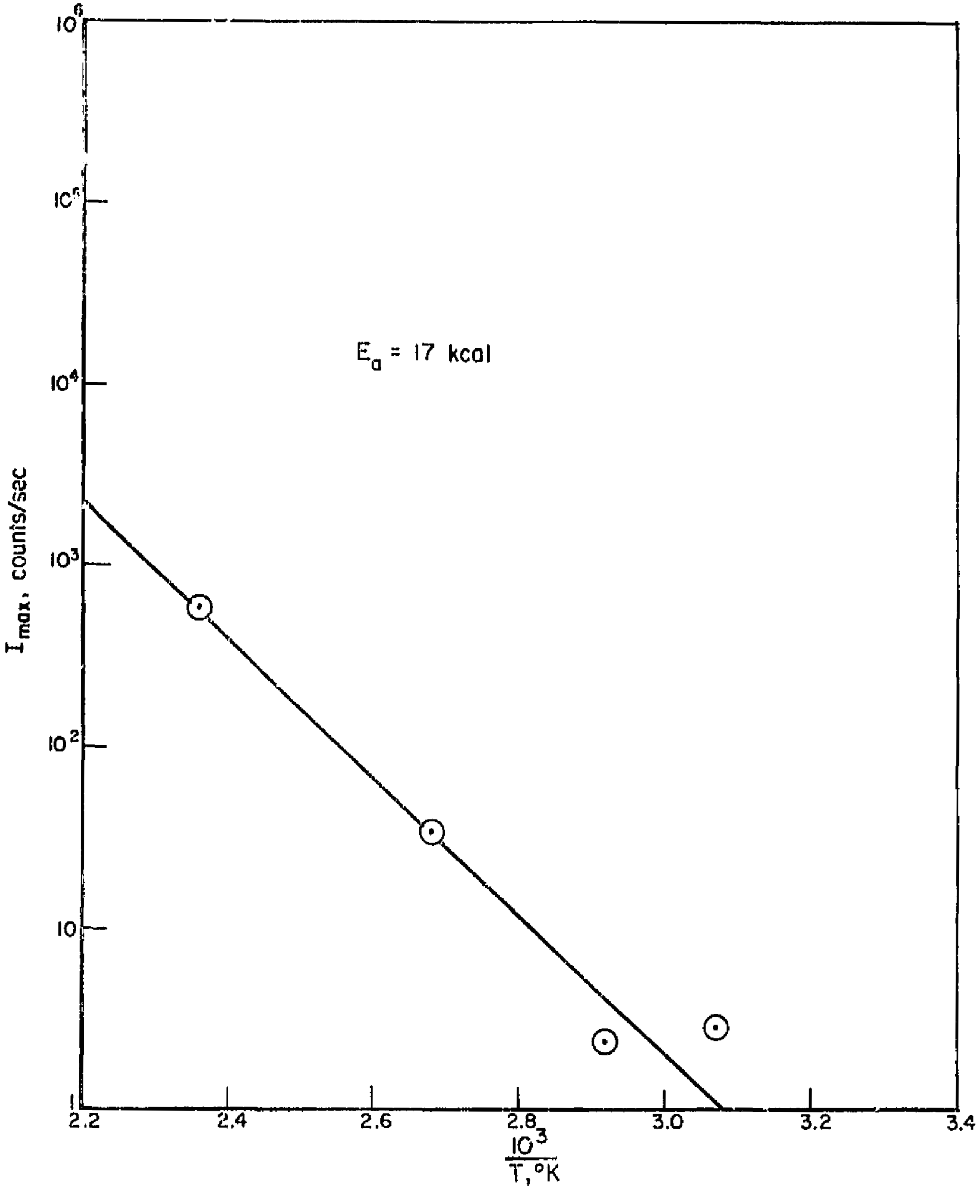


FIGURE 7. CHEMILUMINESCENCE FROM SILICONE RTV-560

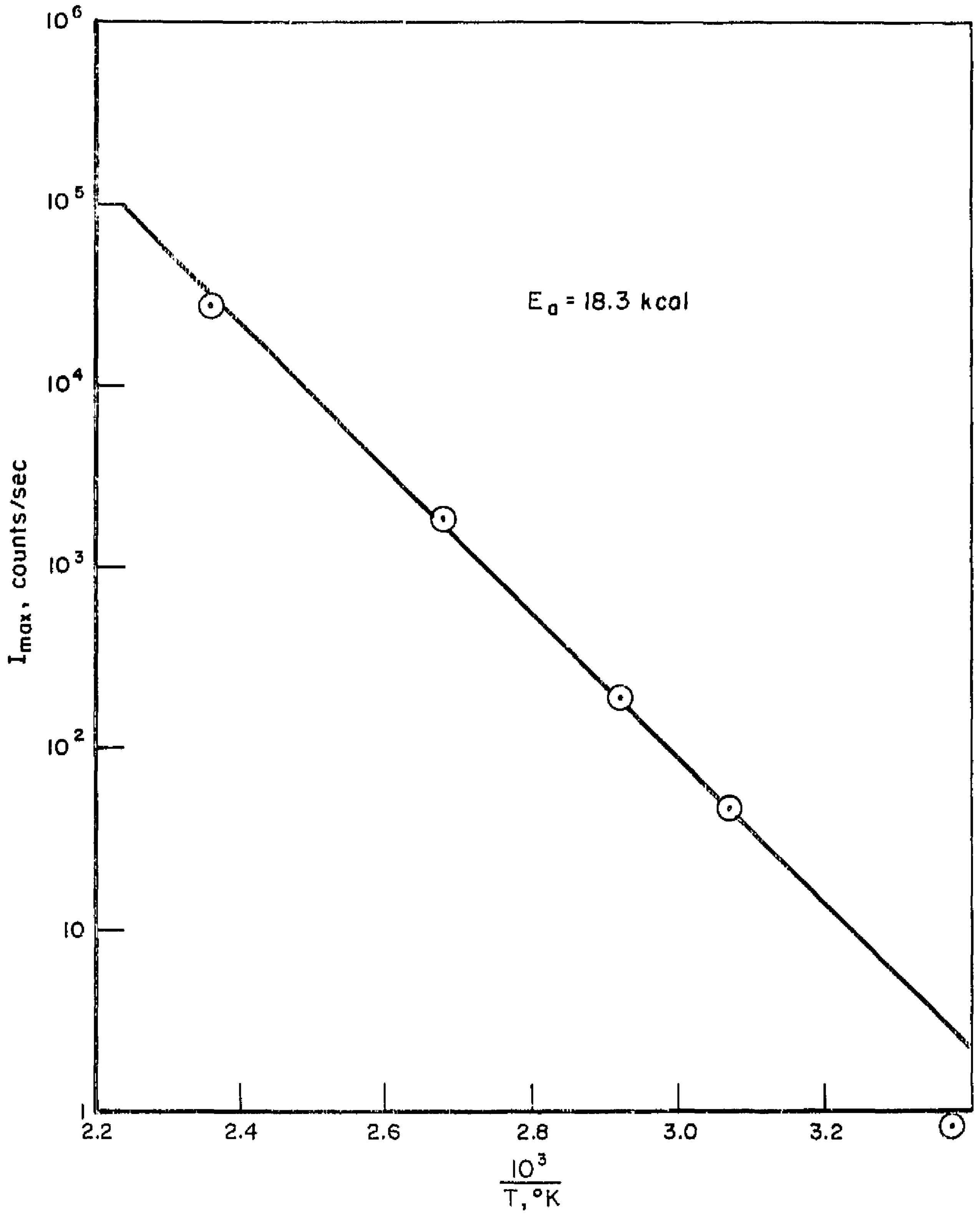


FIGURE 8. CHEMILUMINESCENCE FROM PL-731 ADHESIVE FILM

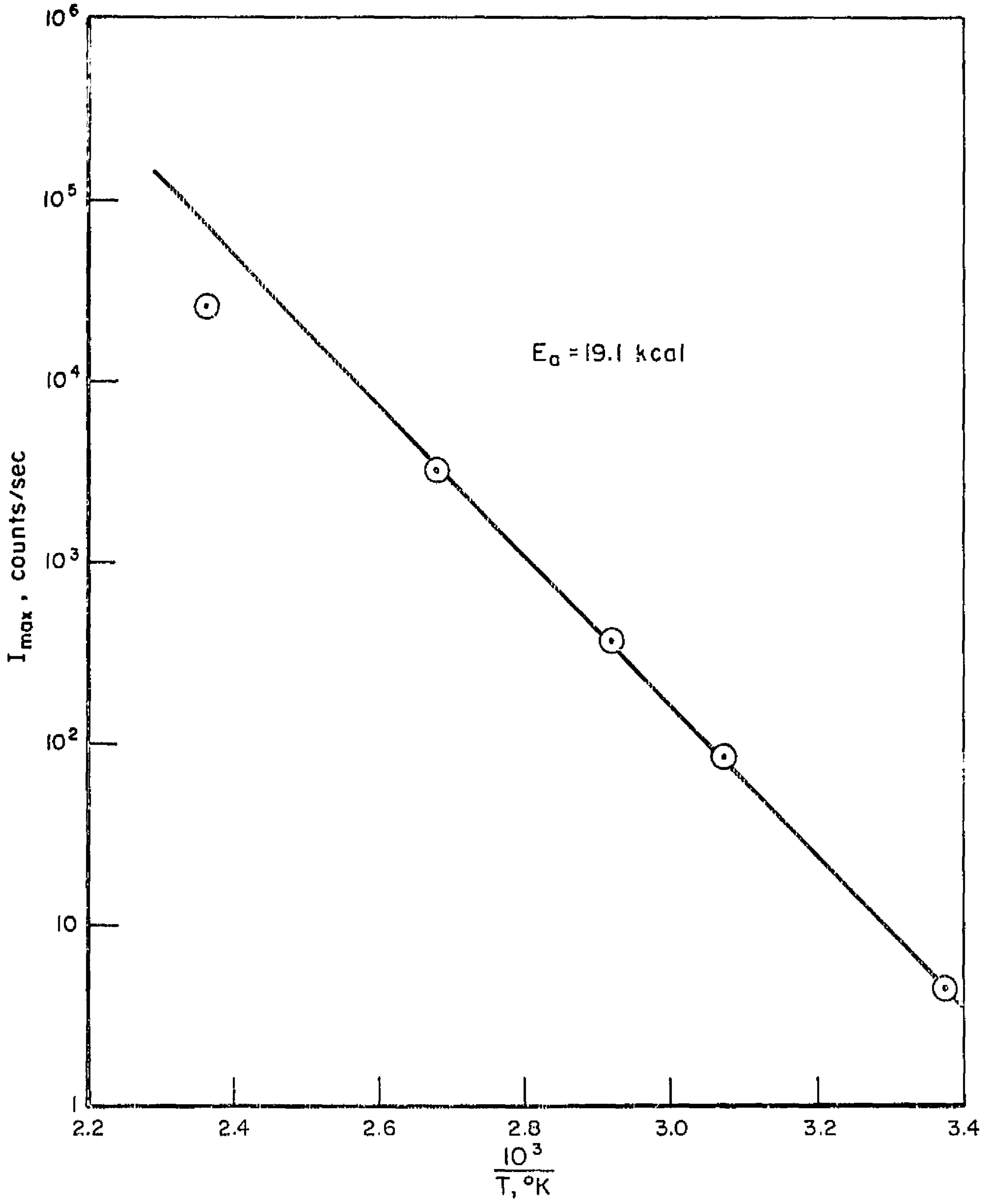


FIGURE 9. CHEMILUMINESCENCE FROM SP-296 COMPOSITE

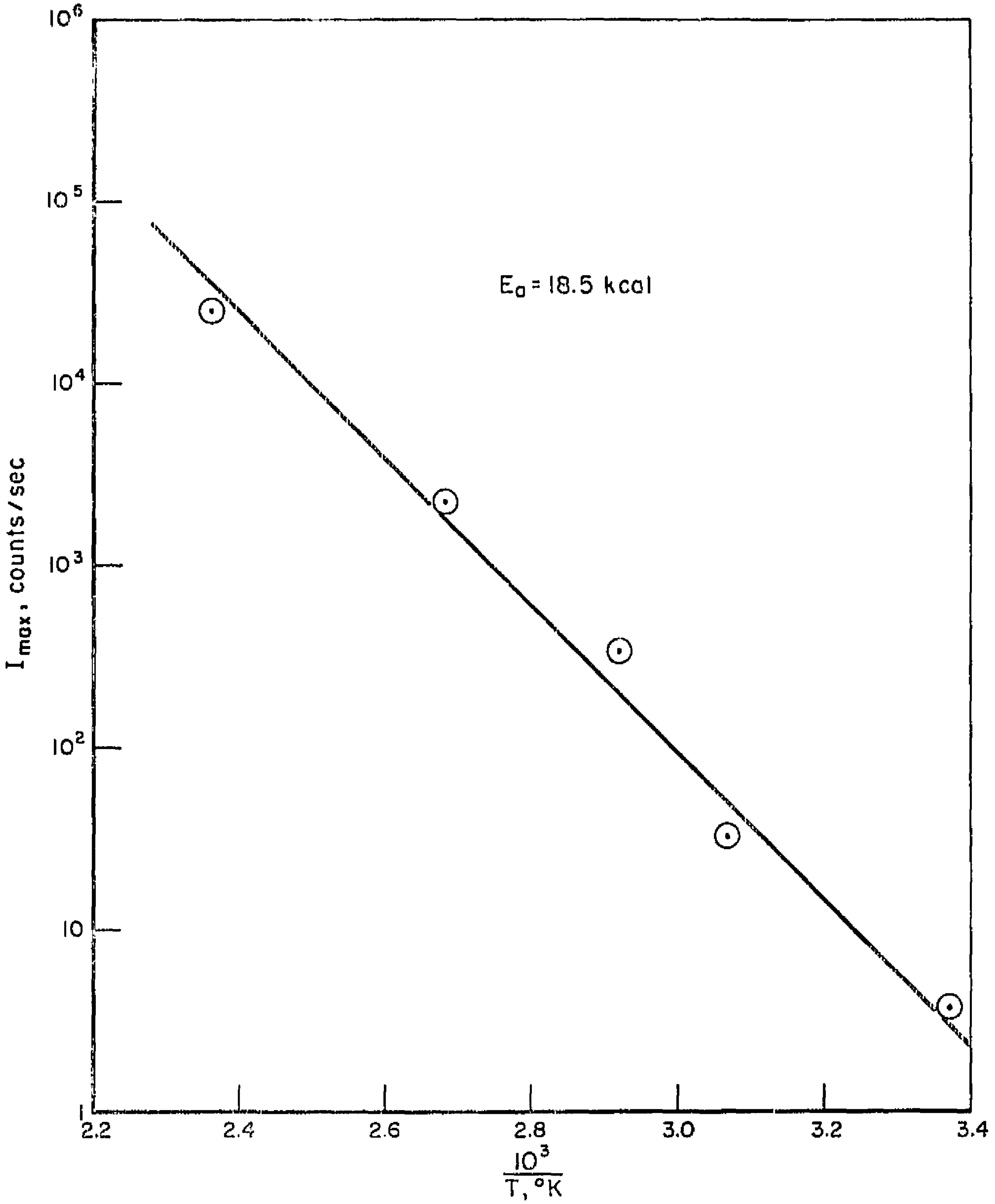


FIGURE 10. CHEMILUMINESCENCE FROM PL-731 AND SP-296 ON TITANIUM

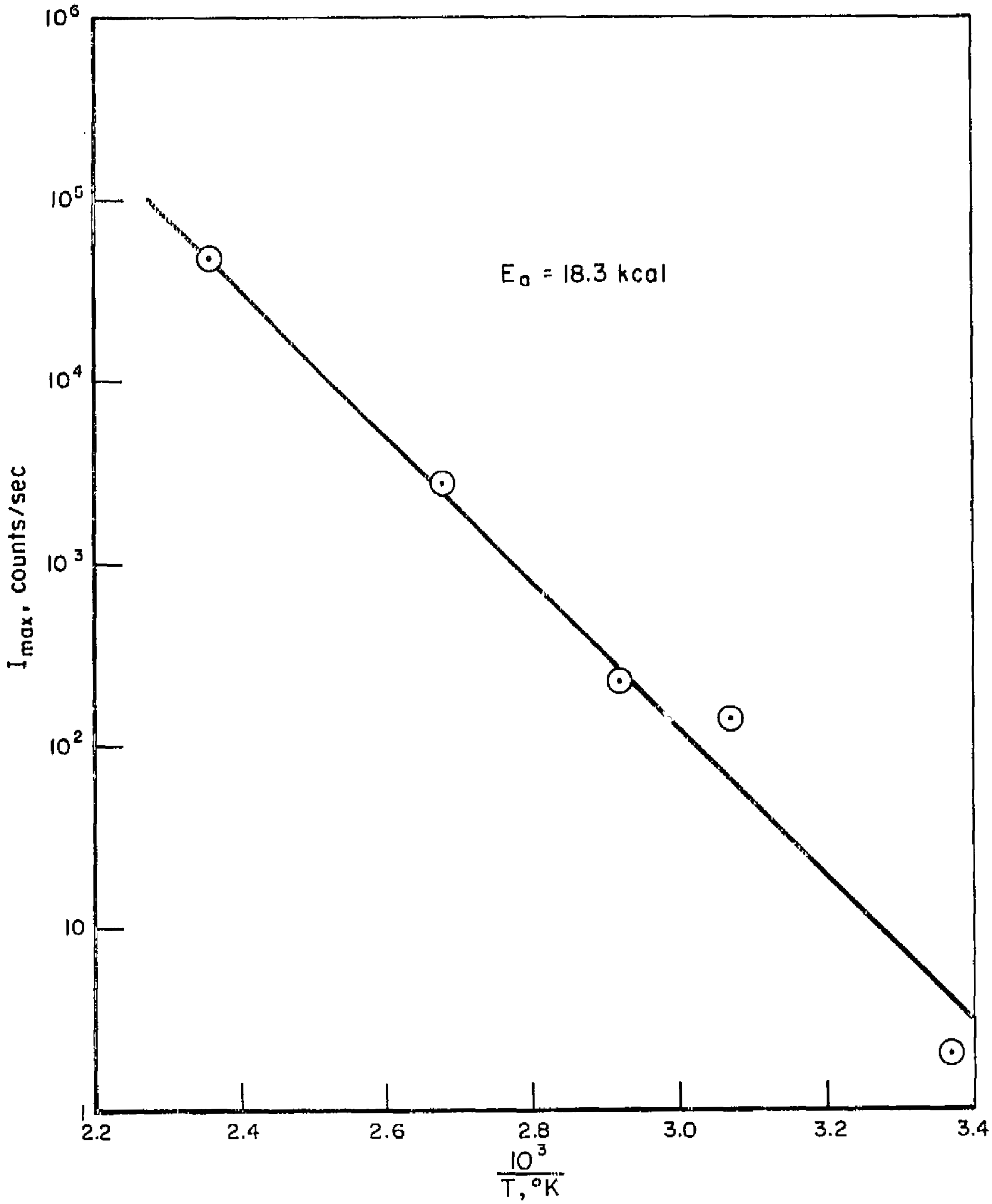


FIGURE 11. CHEMILUMINESCENCE FROM PL-731 CURED ON TITANIUM

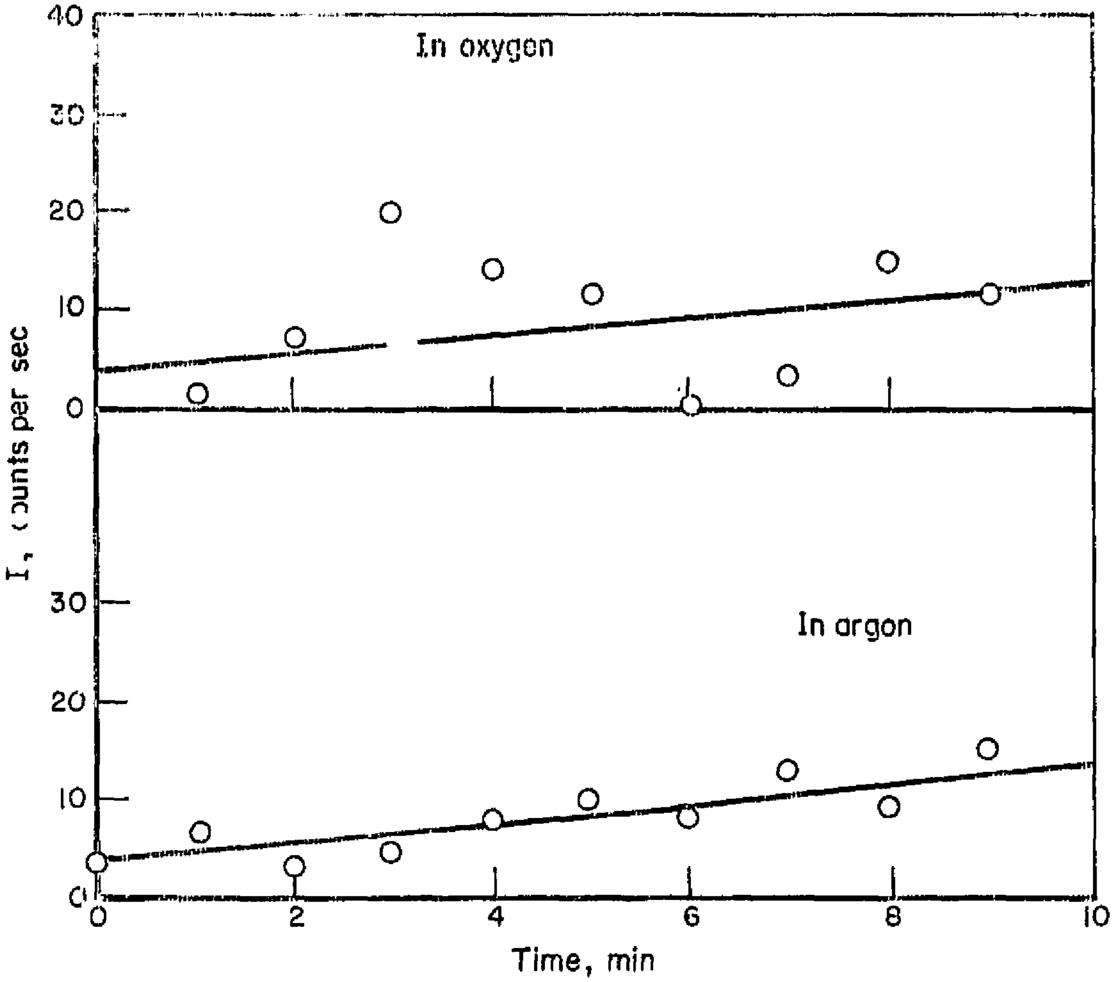


FIGURE 12. CHEMILUMINESCENCE FROM *cis*-POLYBUTADIENE 4-1203 AT 70 C (158 F)

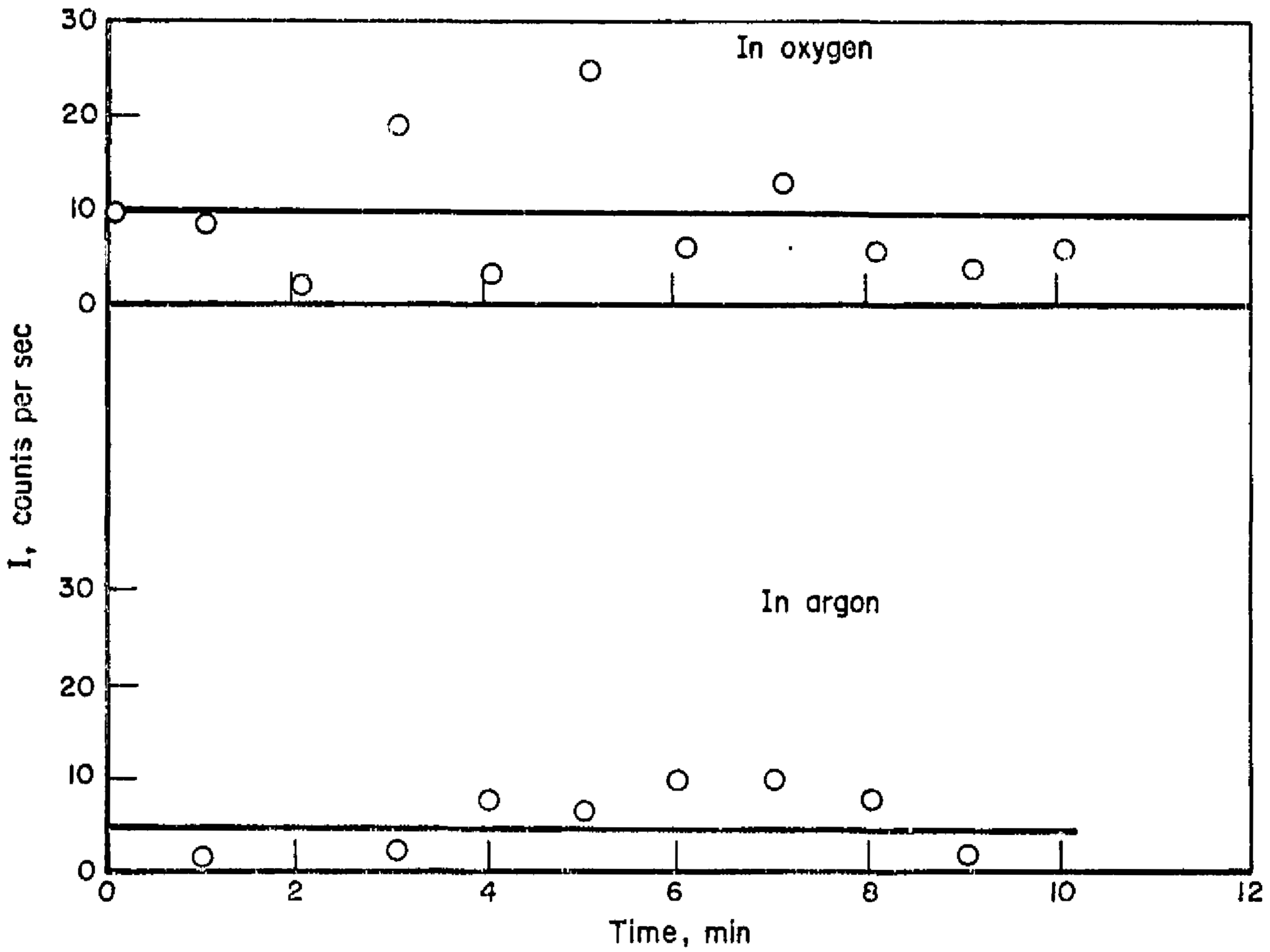


FIGURE 13. CHEMILUMINESCENCE FROM cis-POLYBUTADIENE 4-1203 [AGED 72 HR at 100 C (212 F)] AT 70 C (158 F)

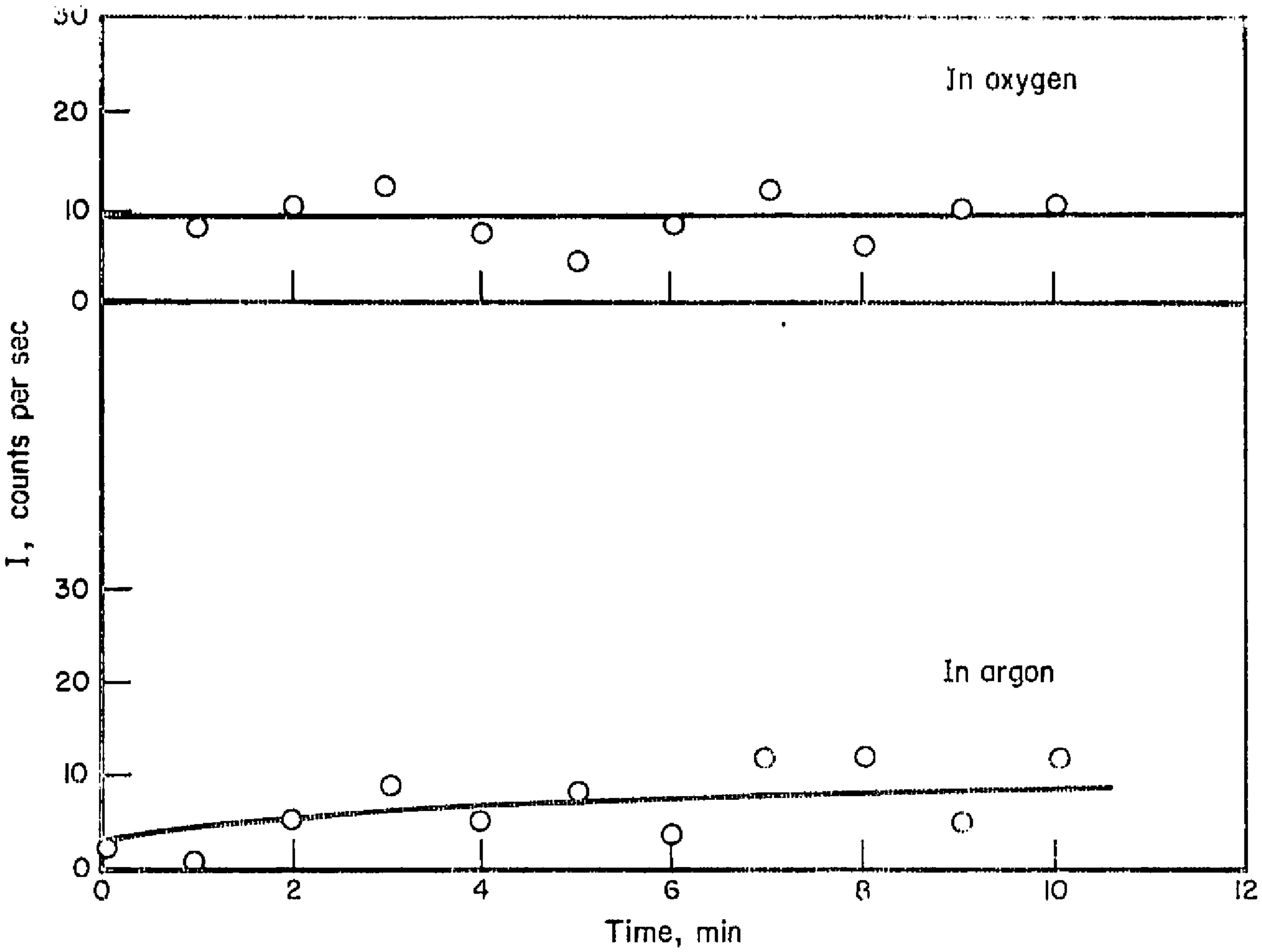


FIGURE 14. CHEMILUMINESCENCE FROM VITON E60-C AT 70 C (158 F)

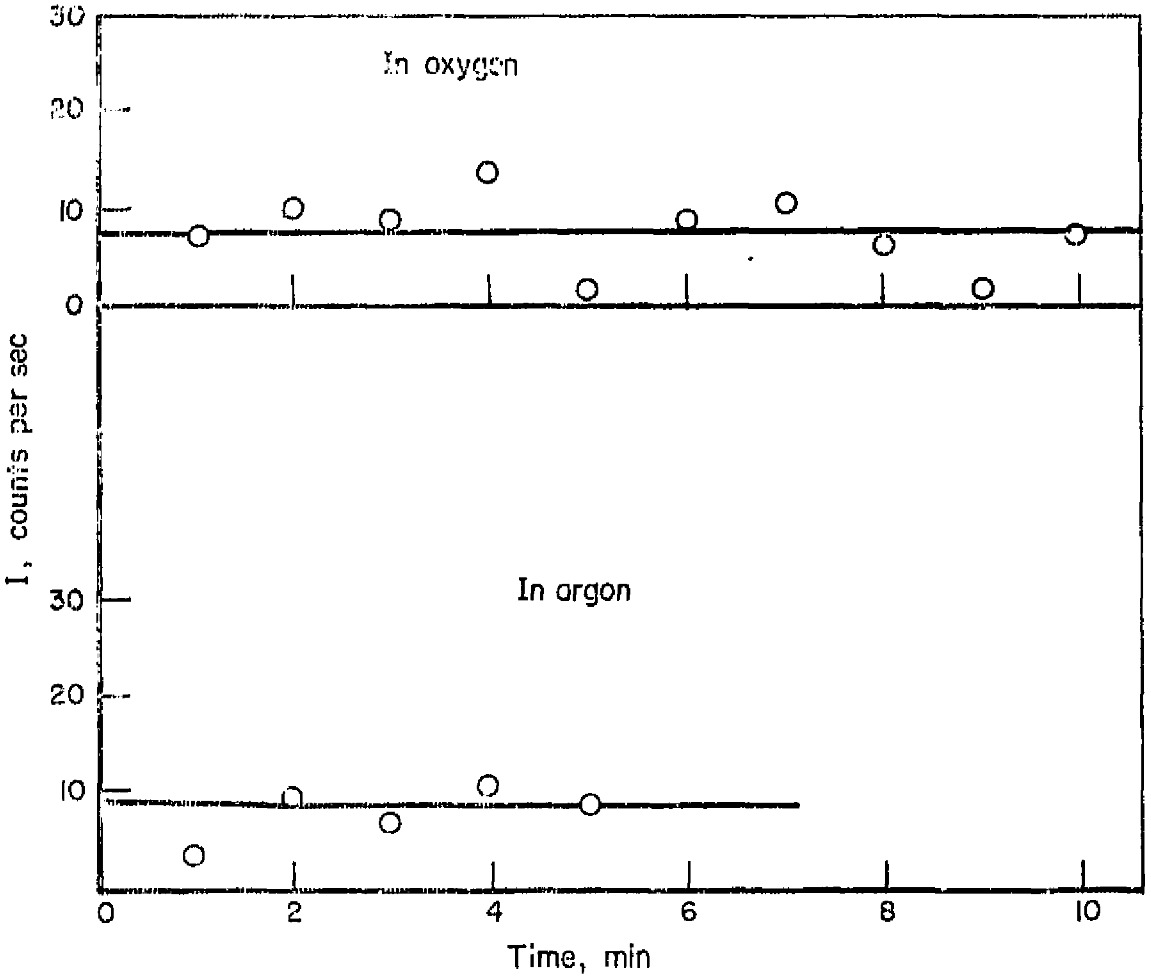


FIGURE 15. CHEMILUMINESCENCE FROM VITON E60-C
[AGED 48 HR at 316 C (600 F)]
AT 70 C (158 F)

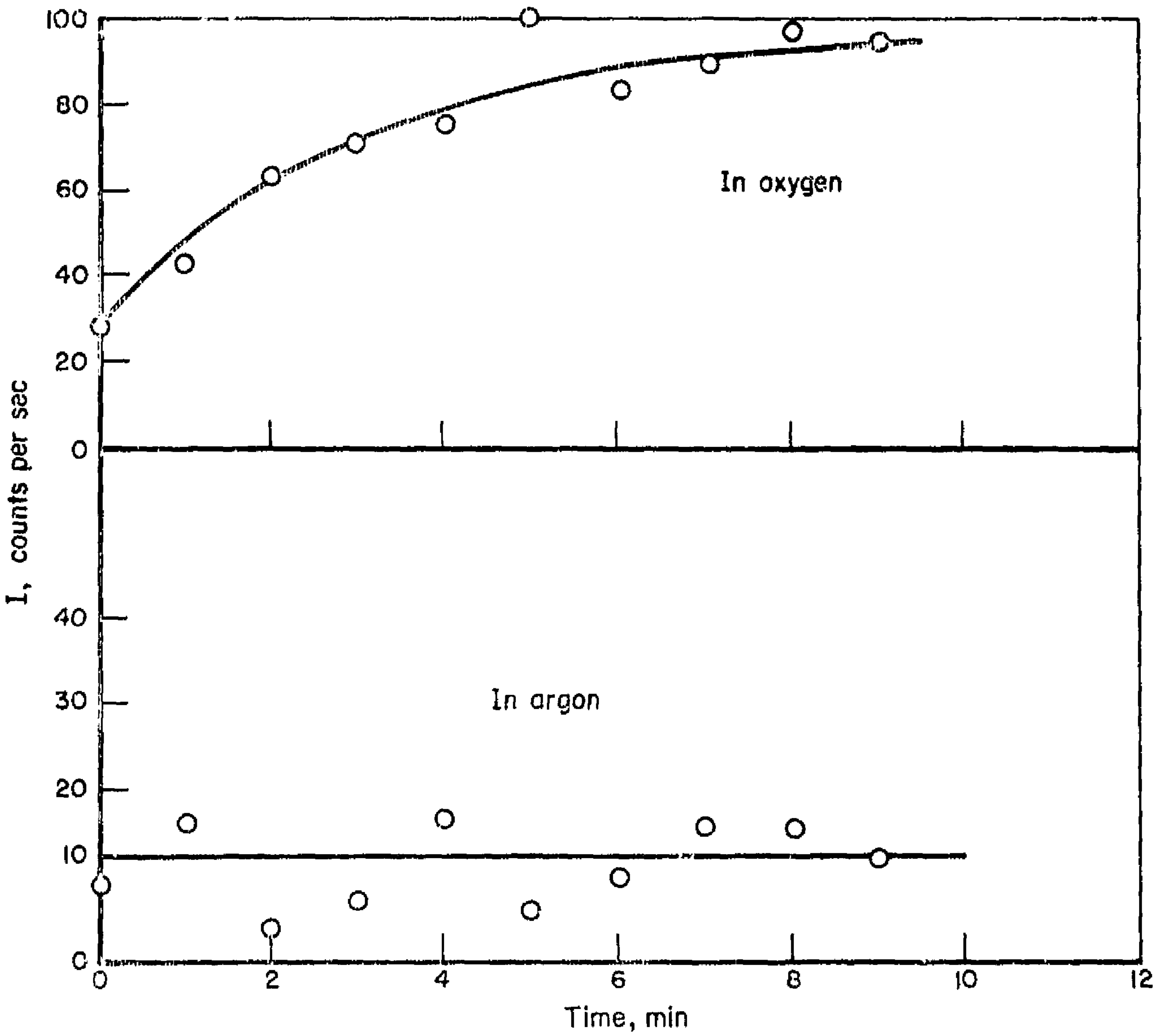


FIGURE 16. CHEMILUMINESCENCE OF HALON G-80
at 70 C (158 F)

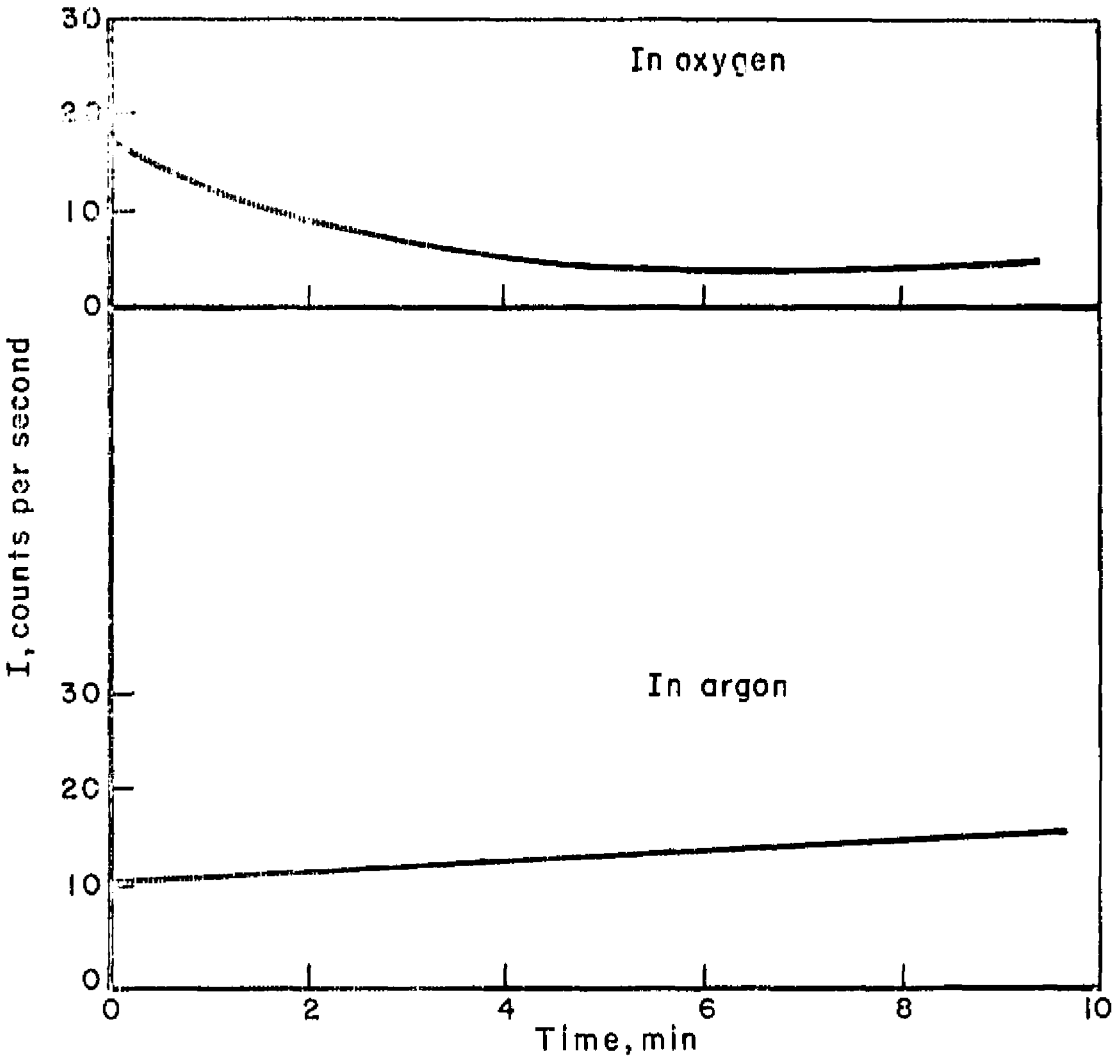


FIGURE 17. CHEMILUMINESCENCE OF HALON G-80 [AGED 48 HR at 232 C (450 F)] at 70 C (158 F)

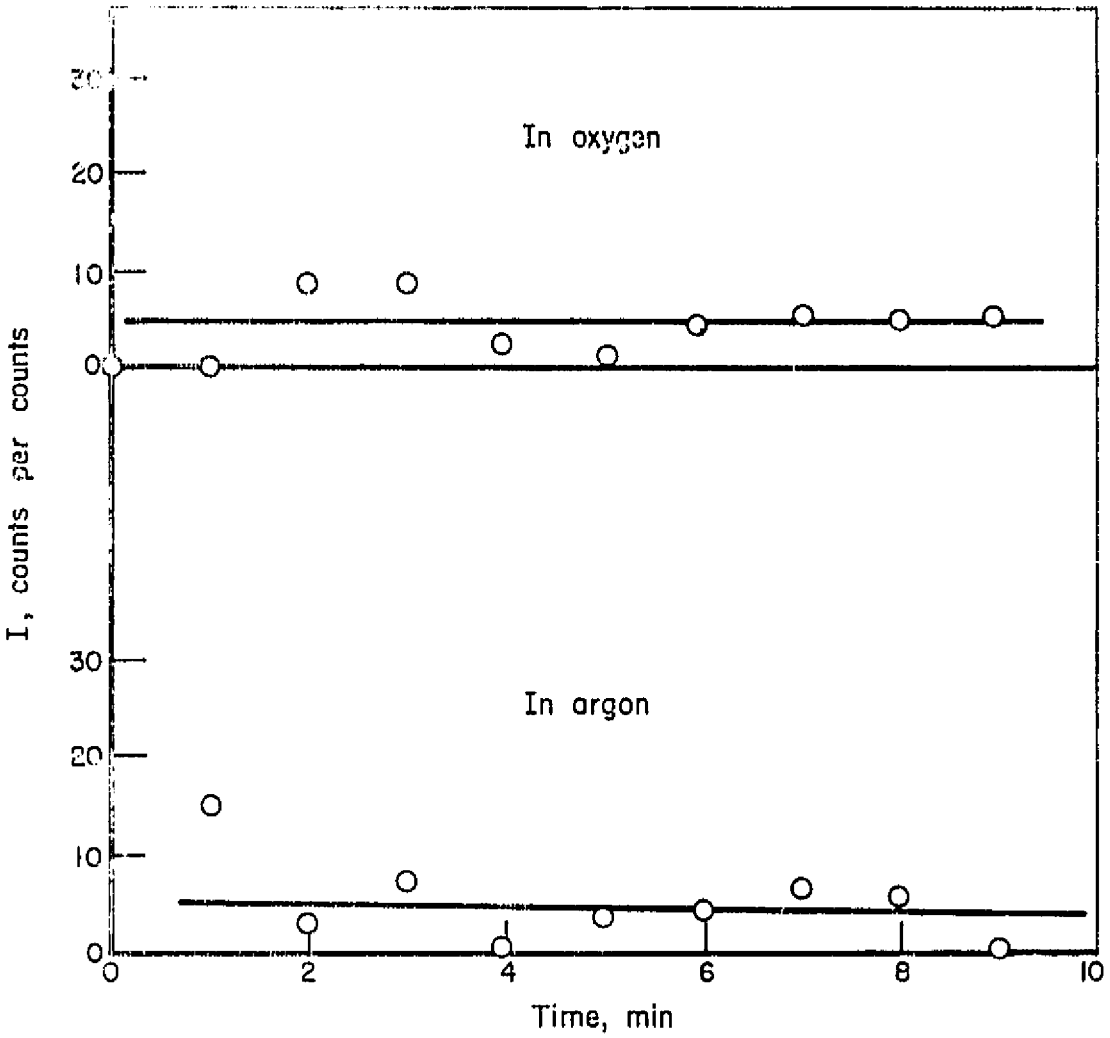


FIGURE 18. CHEMILUMINESCENCE FROM SBR-1500
AT 70 C (158 F)

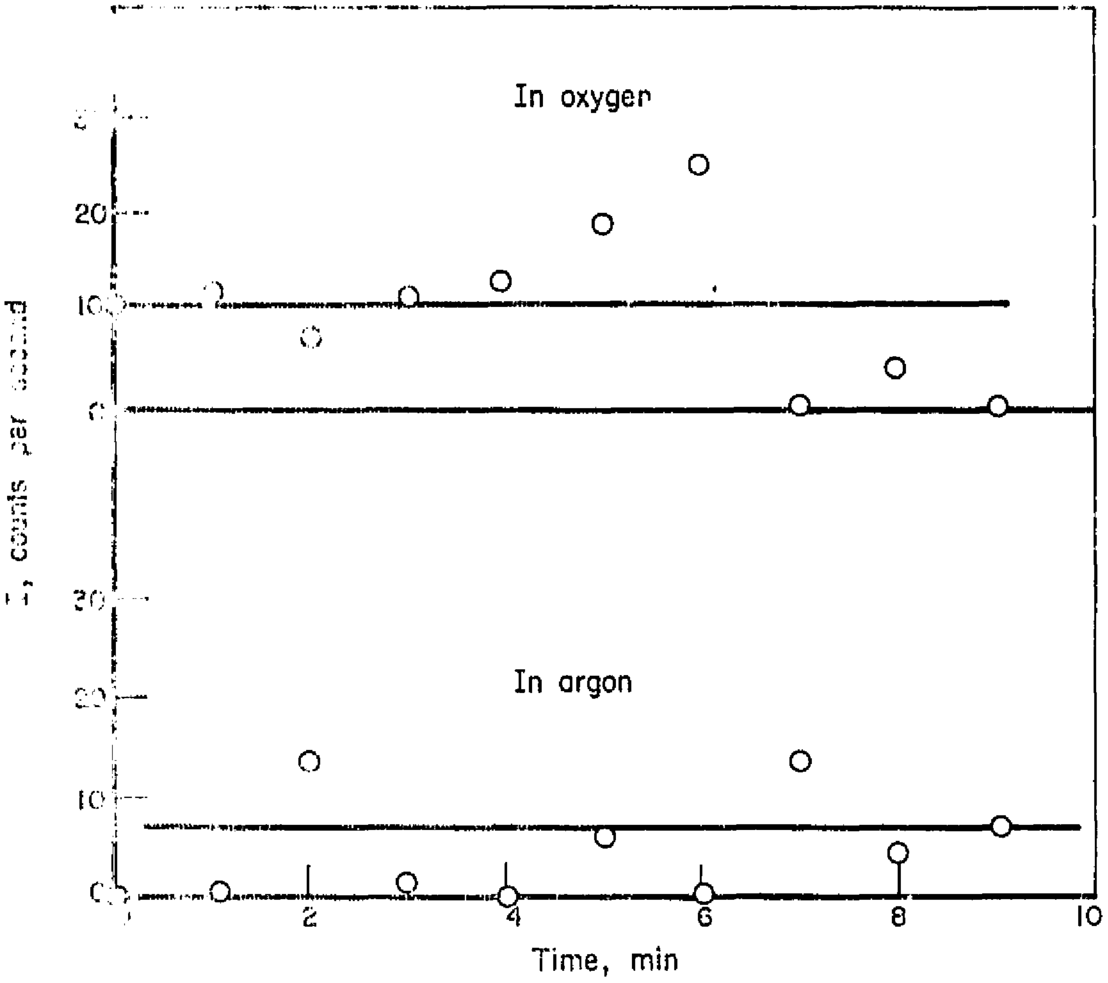


FIGURE 19. CHEMILUMINESCENCE FROM SBR-1500 [AGED 72 HR AT 100 C (212 F)] AT 70 C (158 F)

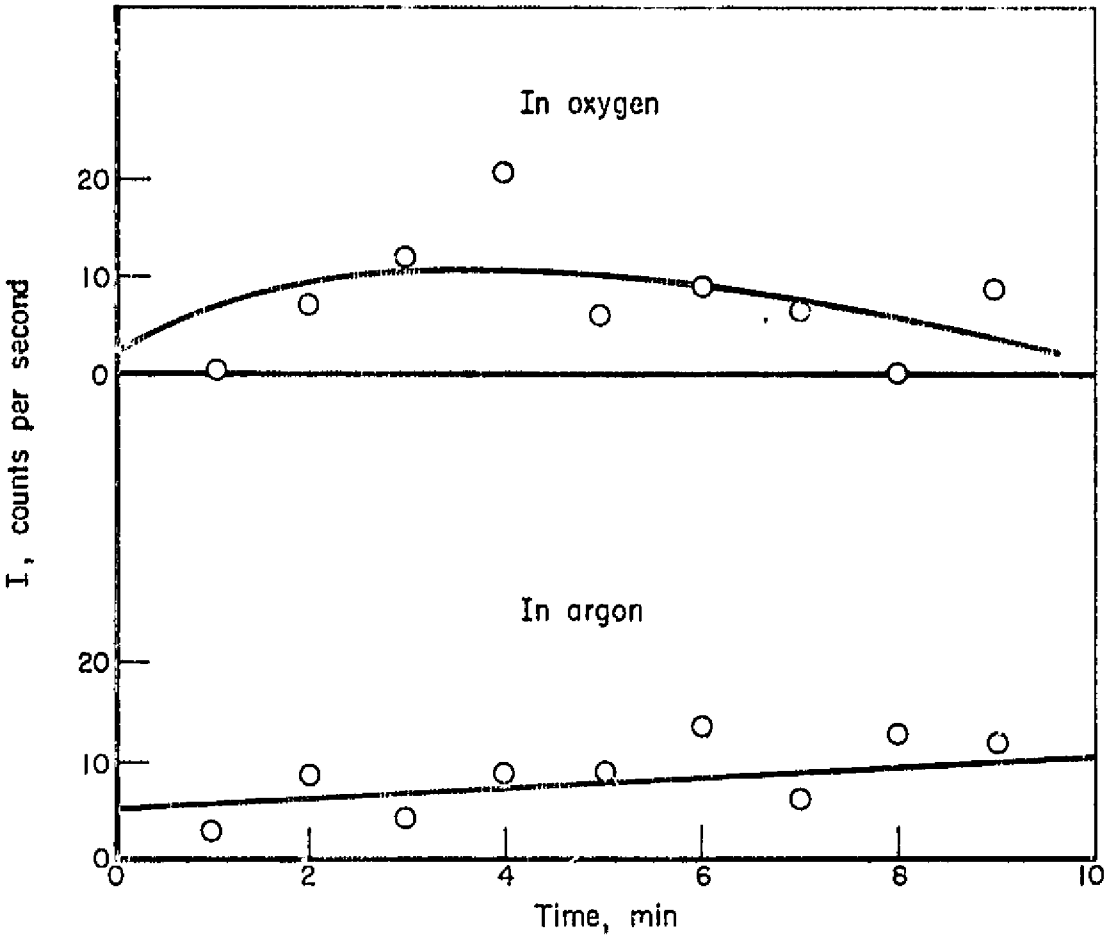


FIGURE 20. CHEMILUMINESCENCE FROM SILICONE RTV-560
AT 70 C (158 F)

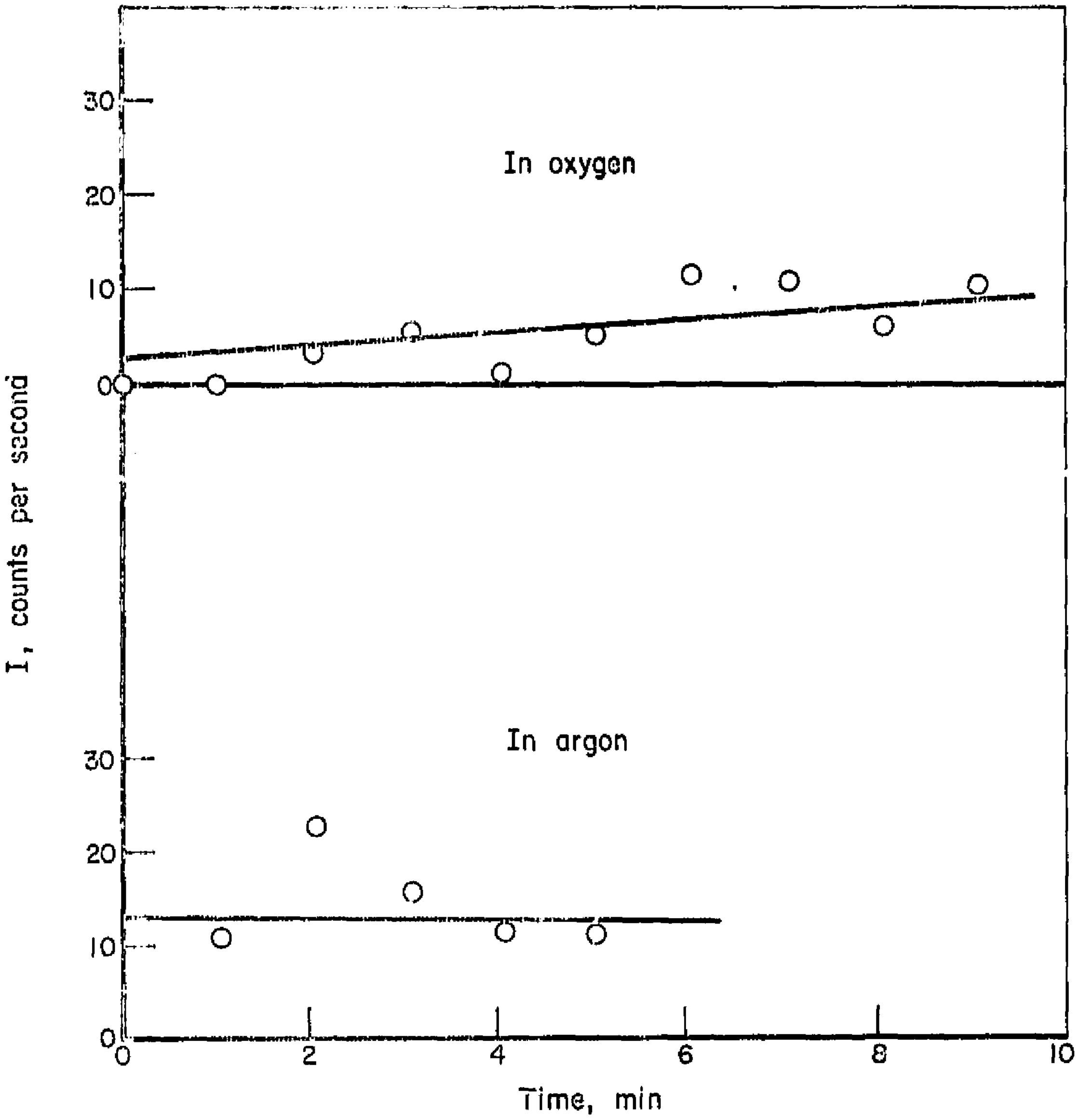


FIGURE 21. CHEMILUMINESCENCE FROM SILICONE RTV-560 [AGED 48 HR AT 316 C (600 F)] AT 70 C (153 F)

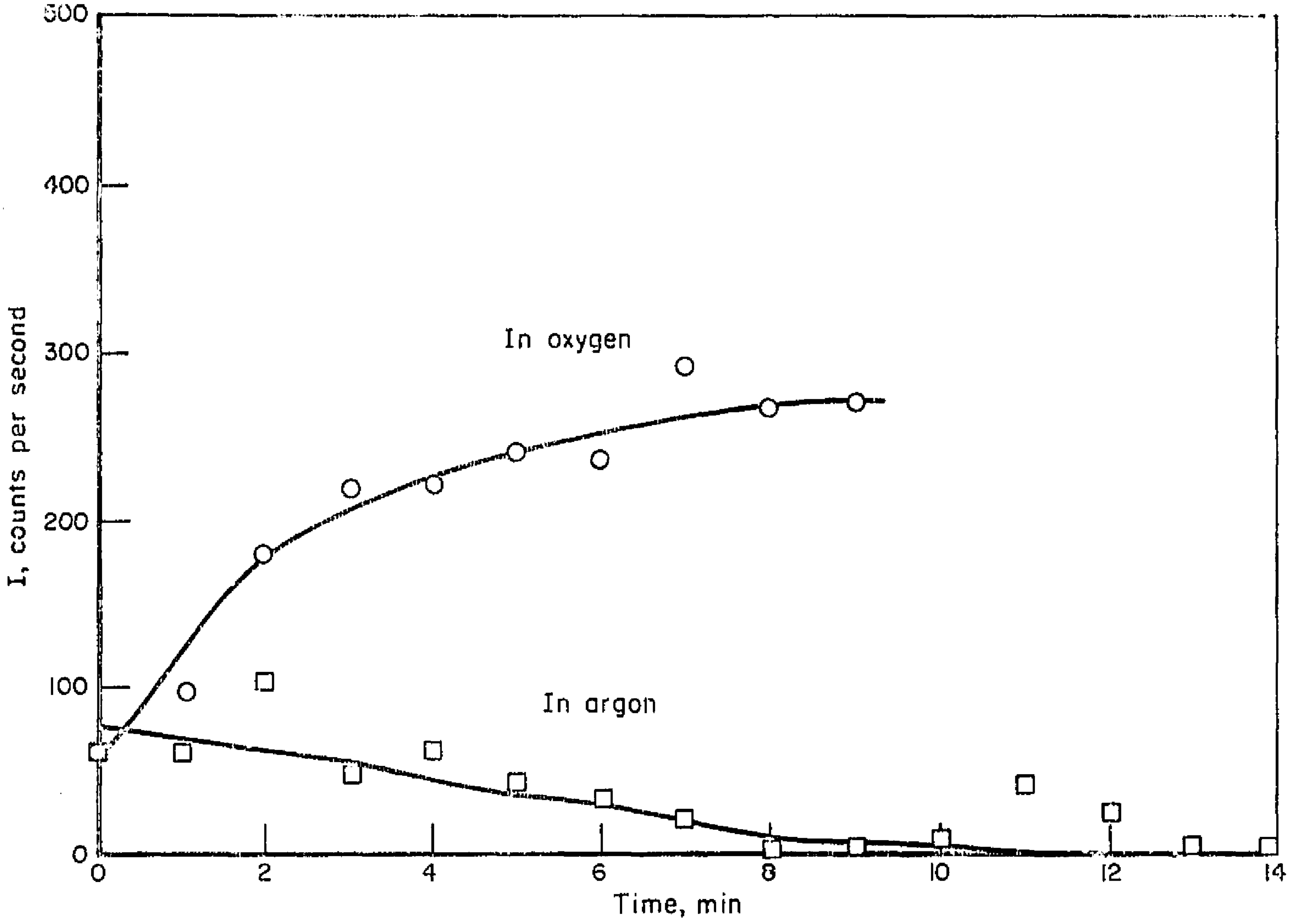


FIGURE 22. CHEMILUMINESCENCE FROM NATURAL RUBBER (MALAYSIA) AT 70 C (150 F)

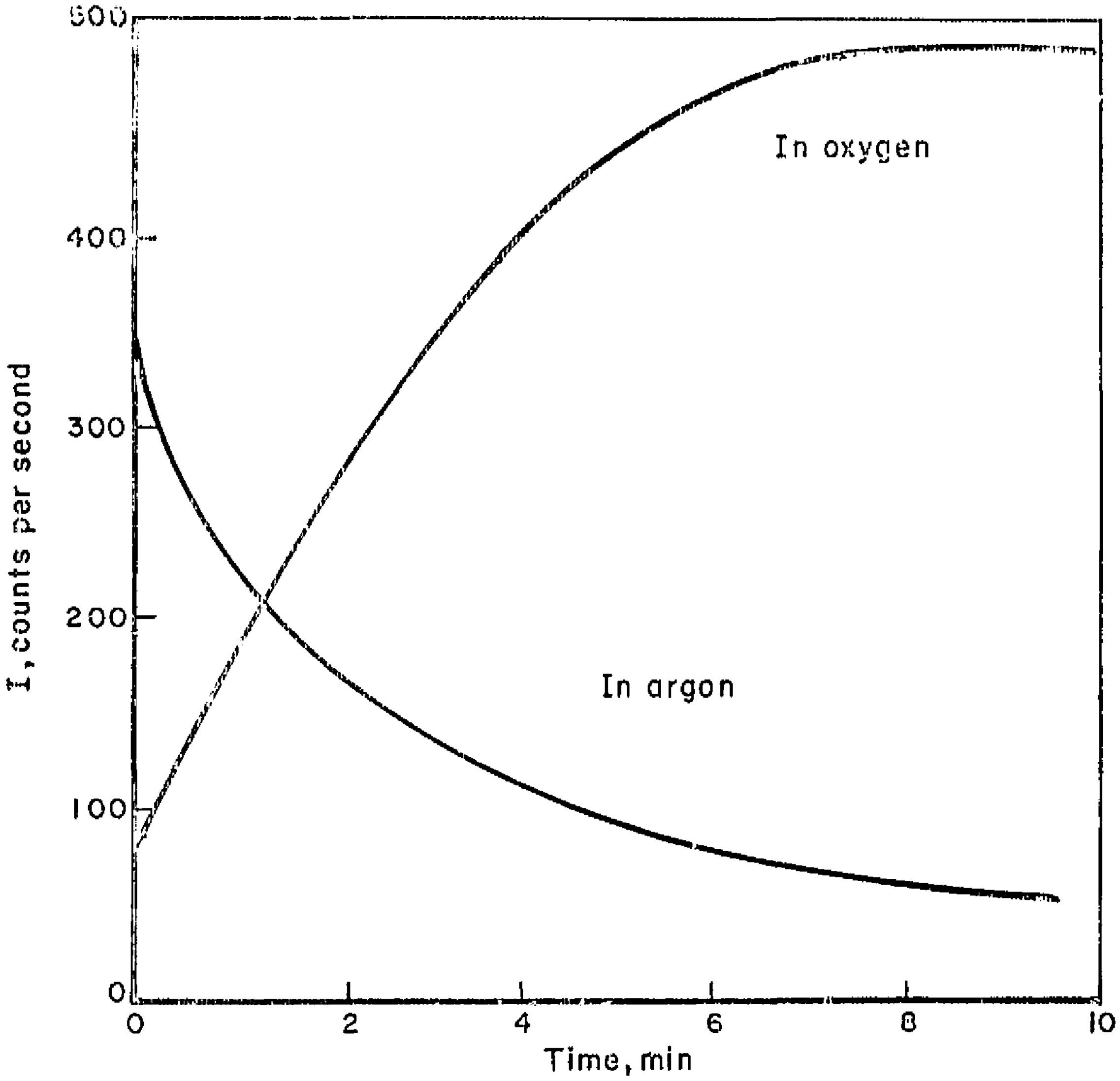


FIGURE 23. CHEMILUMINESCENCE FROM NATURAL RUBBER (MALAYSIA) AGED 24 HR at 125 C (257 F) AT 70 C (158 F)

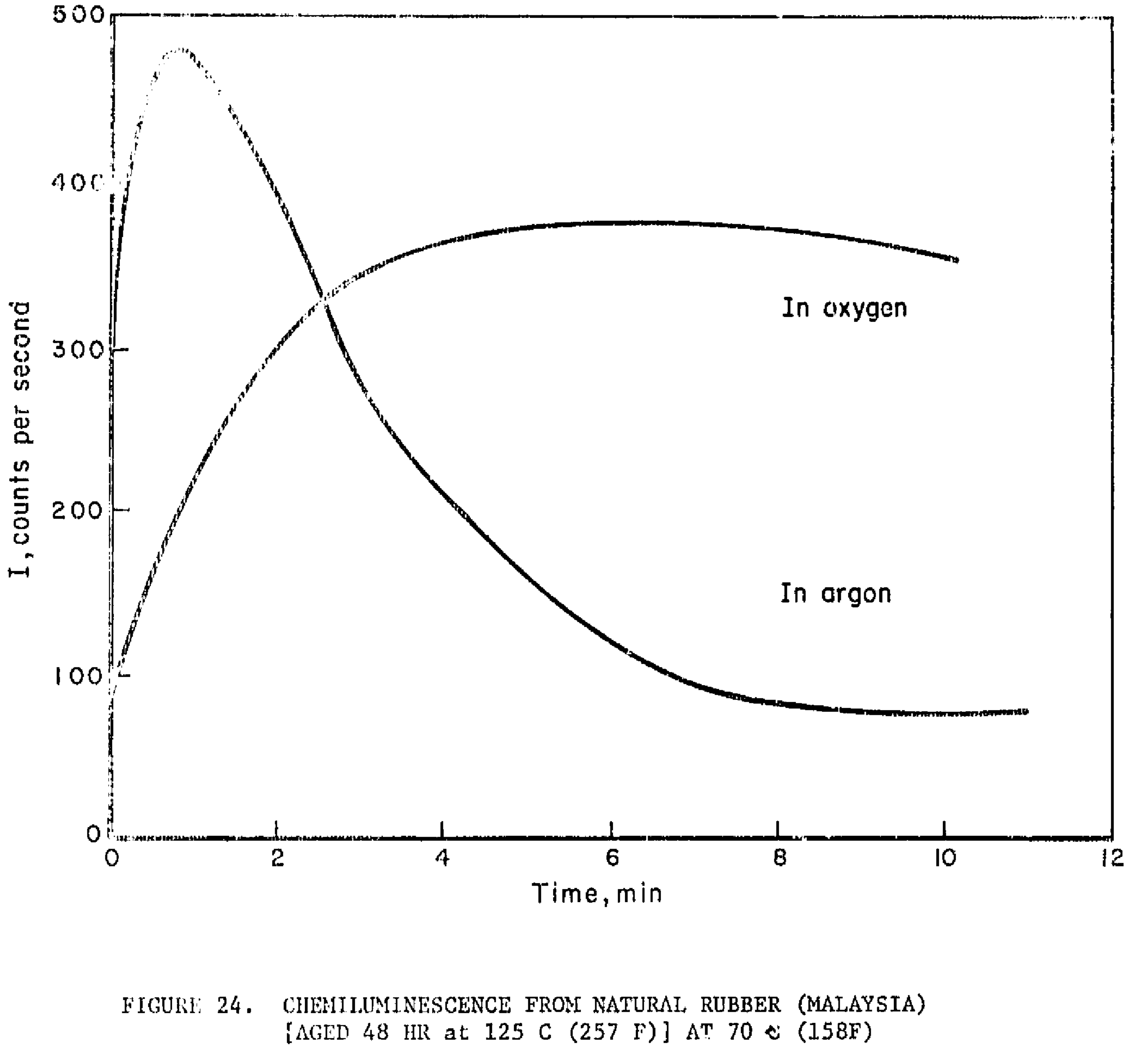


FIGURE 24. CHEMILUMINESCENCE FROM NATURAL RUBBER (MALAYSIA) [AGED 48 HR at 125 C (257 F)] AT 70 C (158F)

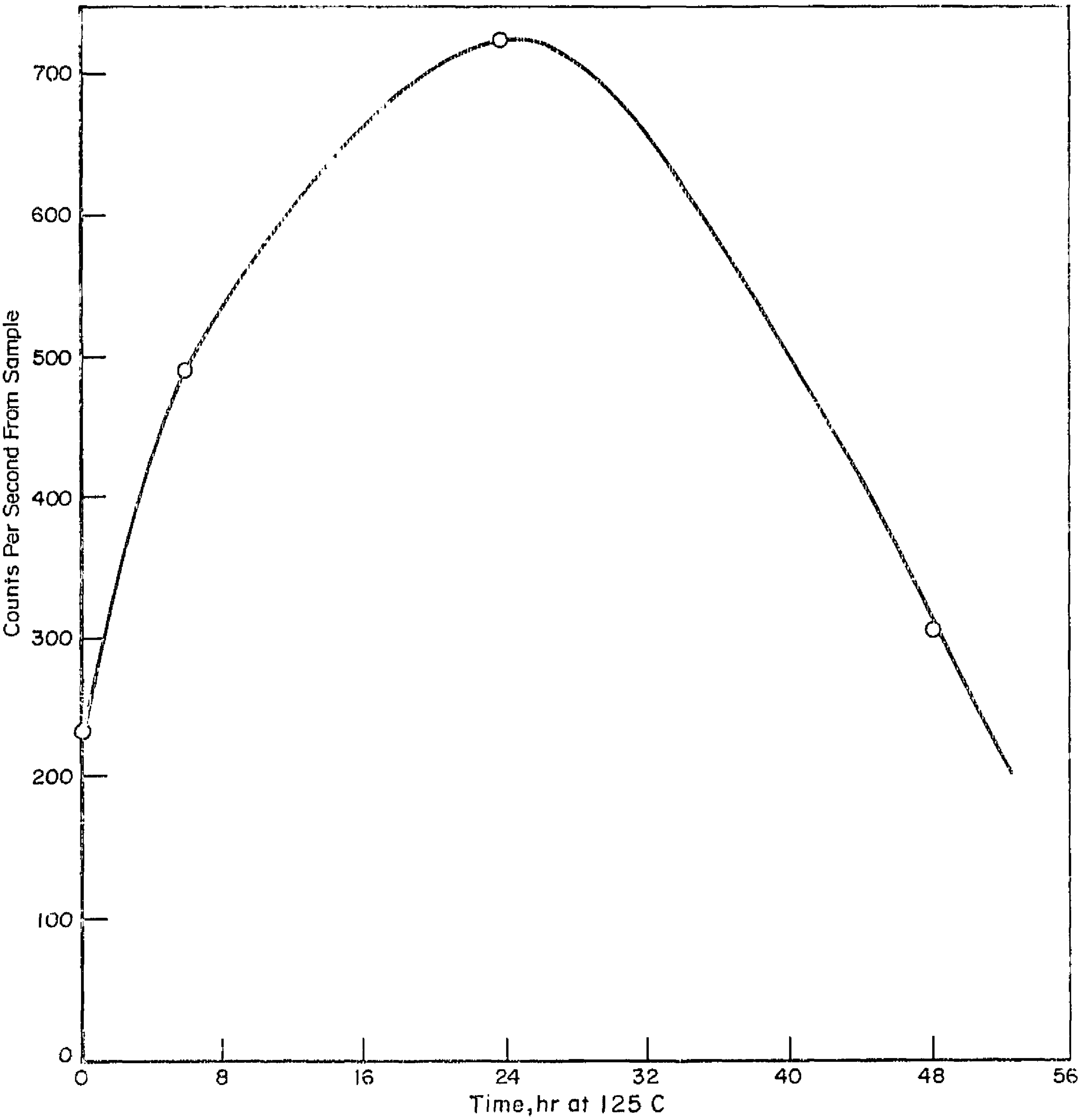


FIGURE 25. CHEMILUMINESCENCE OF NATURAL RUBBER [70 C (158 F) UNDER O_2] VS A FUNCTION OF AGING AT 125 C (257 F) IN AIR

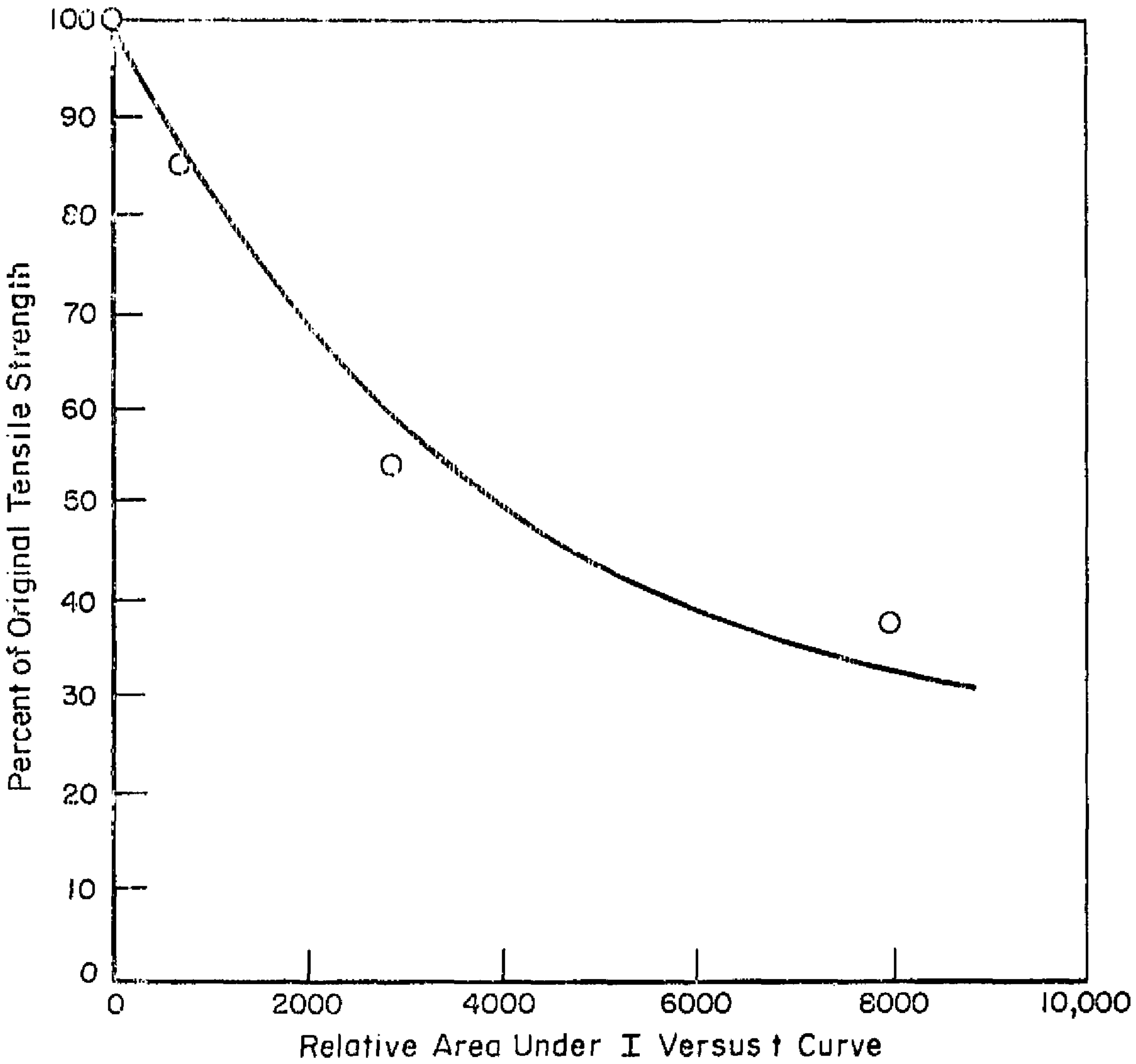


FIGURE 26. TENSILE STRENGTH OF NATURAL RUBBER (MALAYSIA) VS TOTAL CHEMILUMINESCENCE

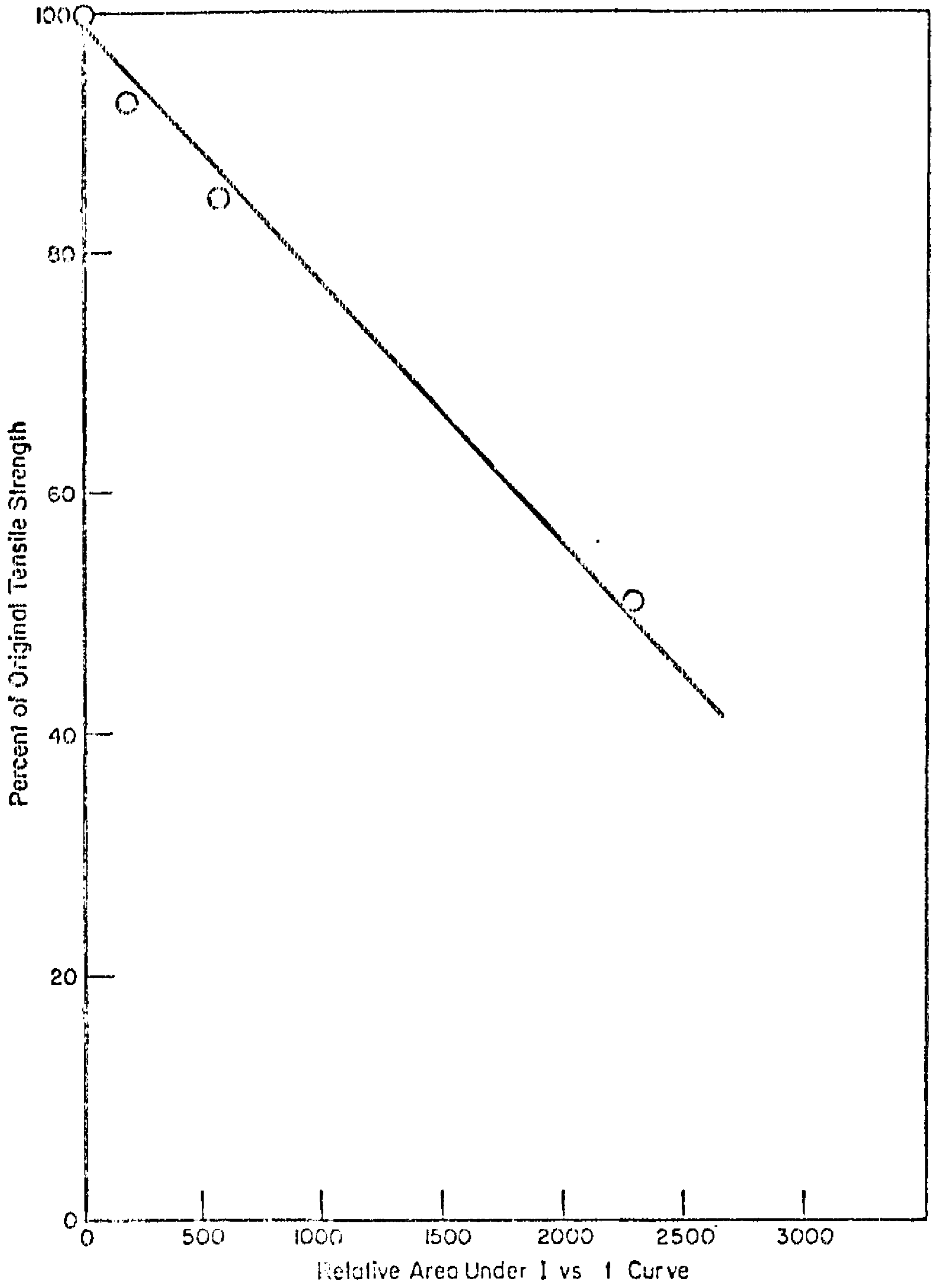


FIGURE 26A. LOSS OF TENSILE STRENGTH OF NATURAL RUBBER (MALAYSIA) AS A FUNCTION OF TOTAL LIGHT EMISSION AT 100 C (212 F)

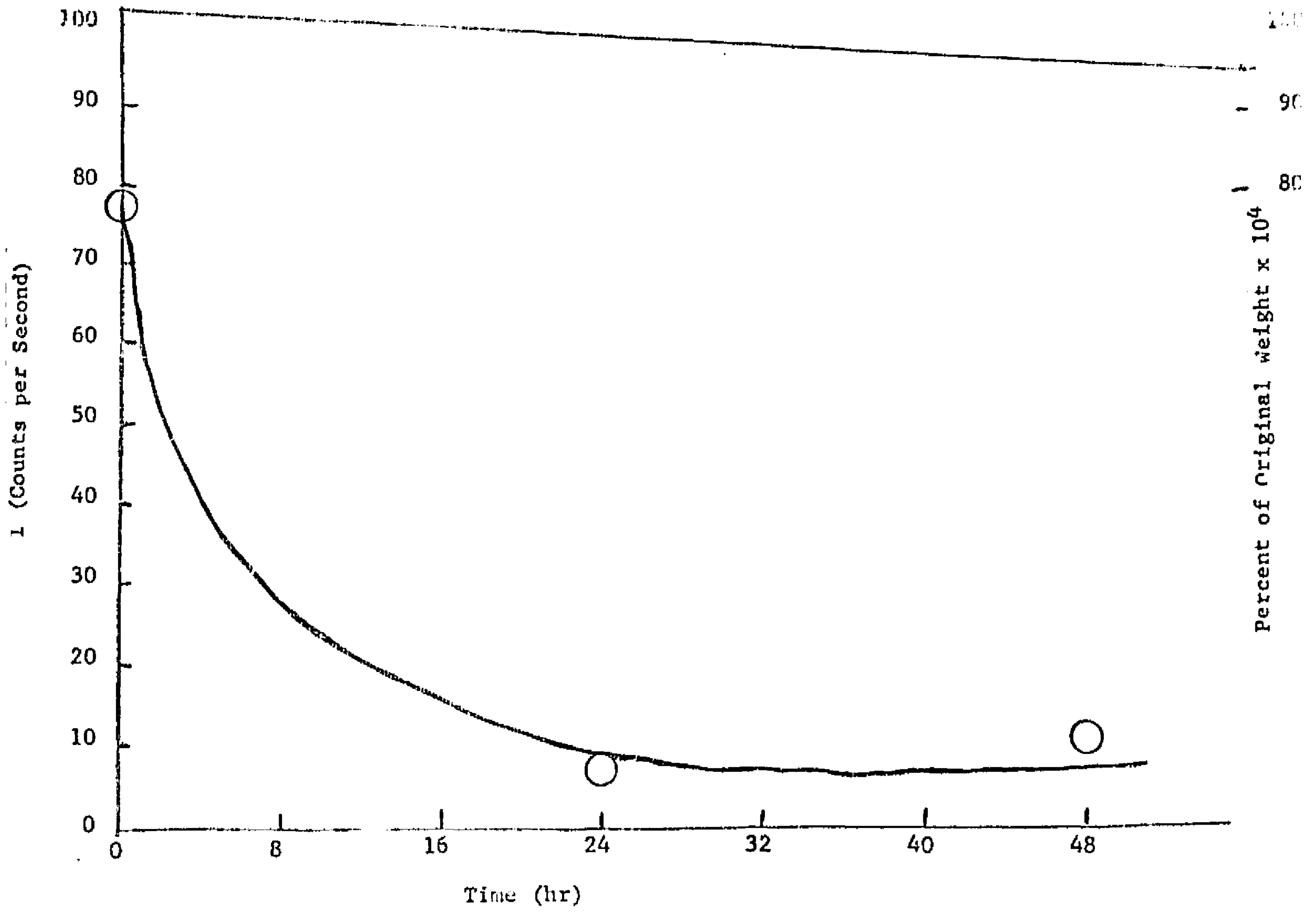


FIGURE 27. CHEMILUMINESCENCE OF HALON G-80 (IN O_2 AT 70 C) AS A FUNCTION OF AGING AT 232 C (450 F)

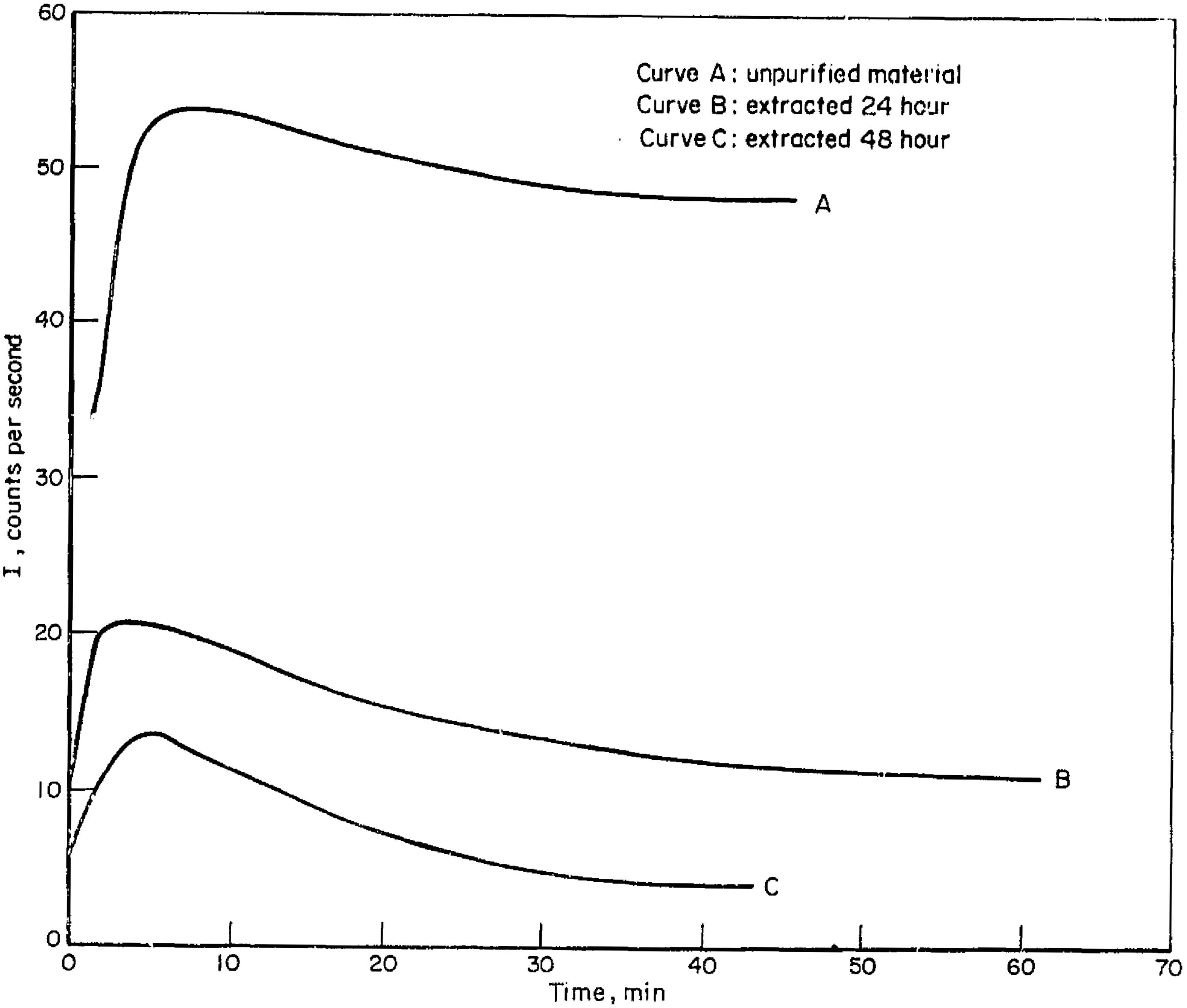


FIGURE 28. CHEMILUMINESCENCE FROM HALON G-10 $(CF_2)_n$.

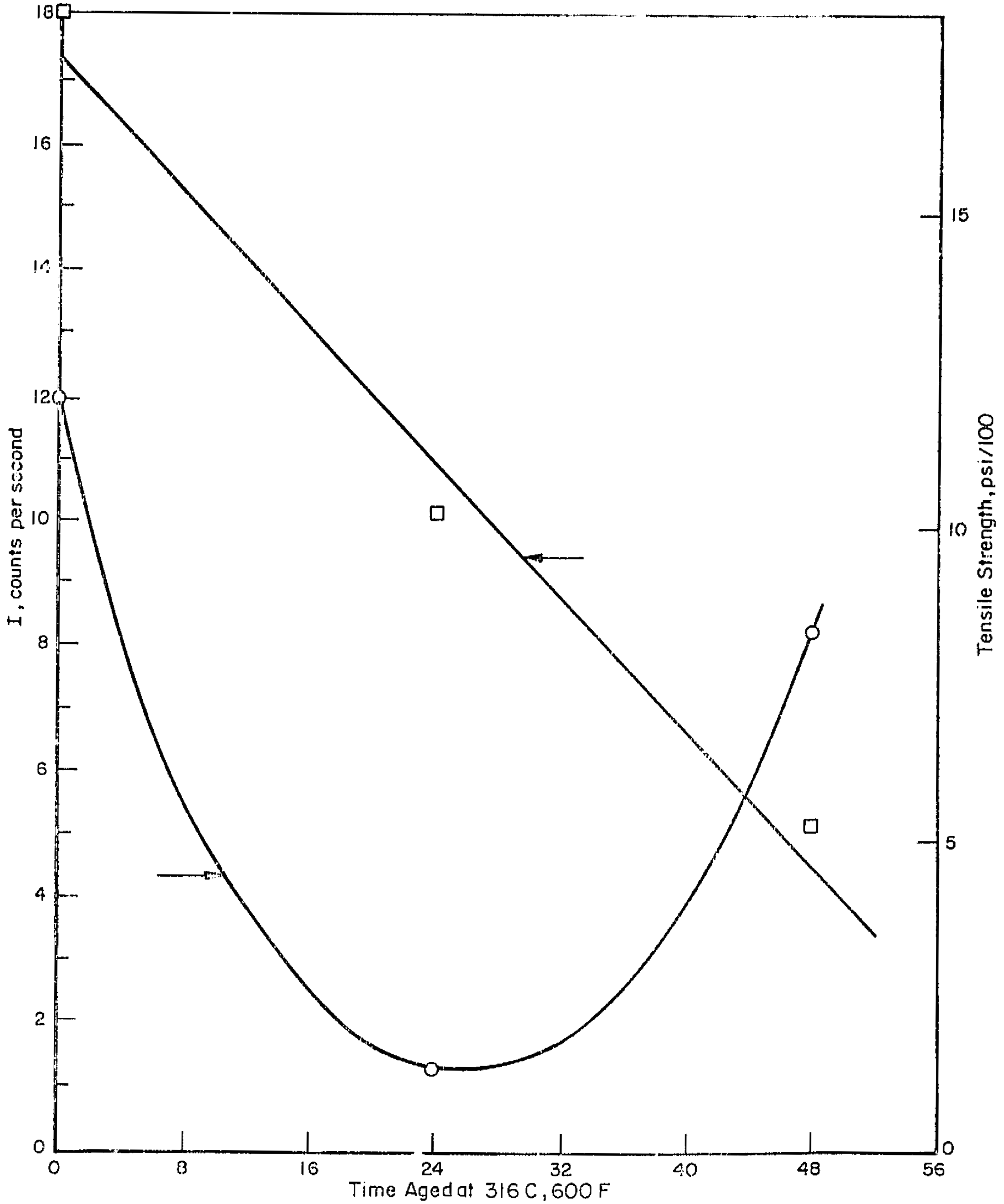


FIGURE 29. TENSILE STRENGTH AND CHEMILUMINESCENCE (AT 70 C IN OXYGEN) VS AGING OF VITON POLYMER

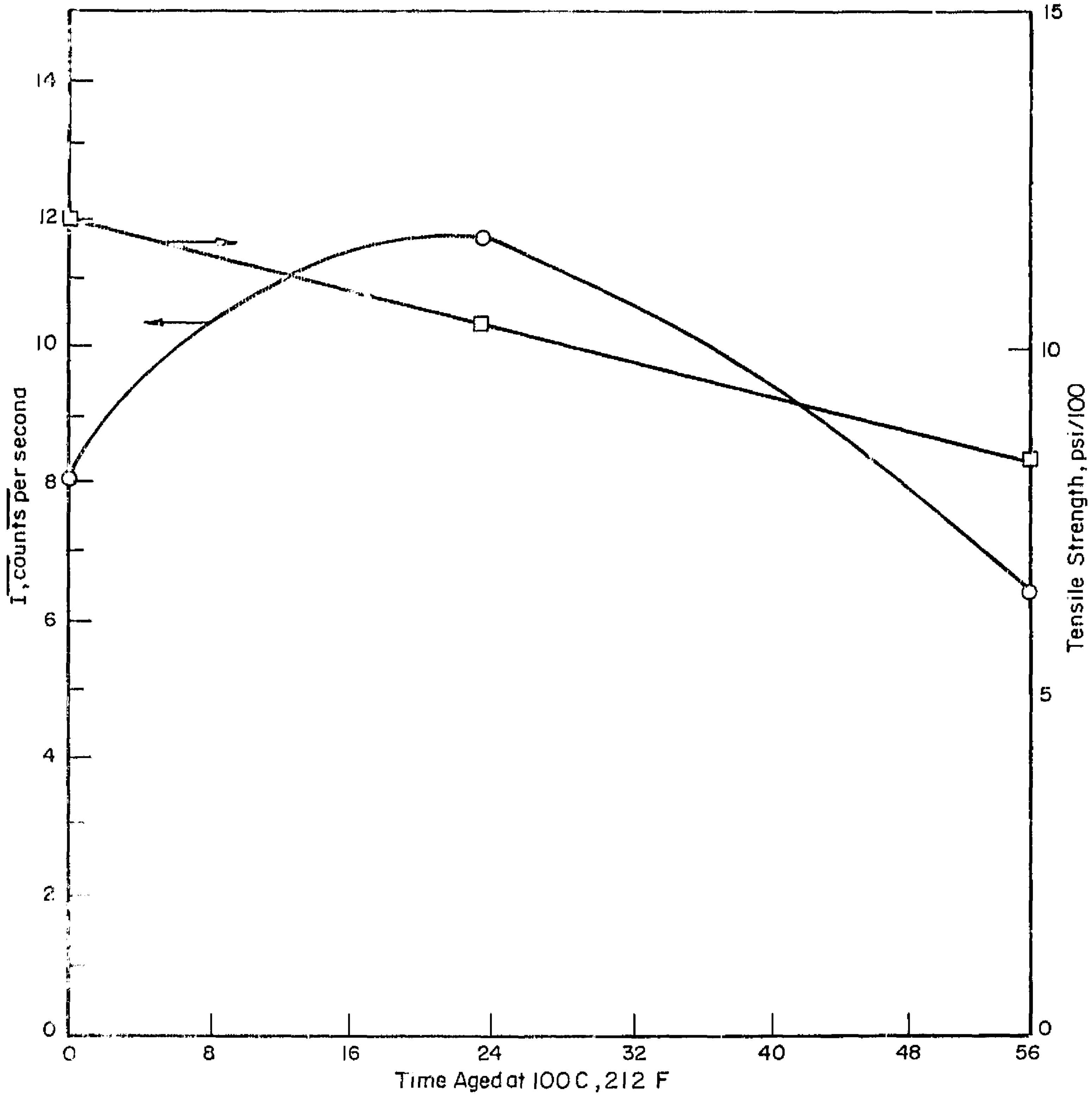


FIGURE 30. TENSILE STRENGTH AND CHEMILUMINESCENCE (AT 70 C IN O_2) OF cis-POLYBUTADIENE AS A FUNCTION OF AGING AT 100 C (212 F)

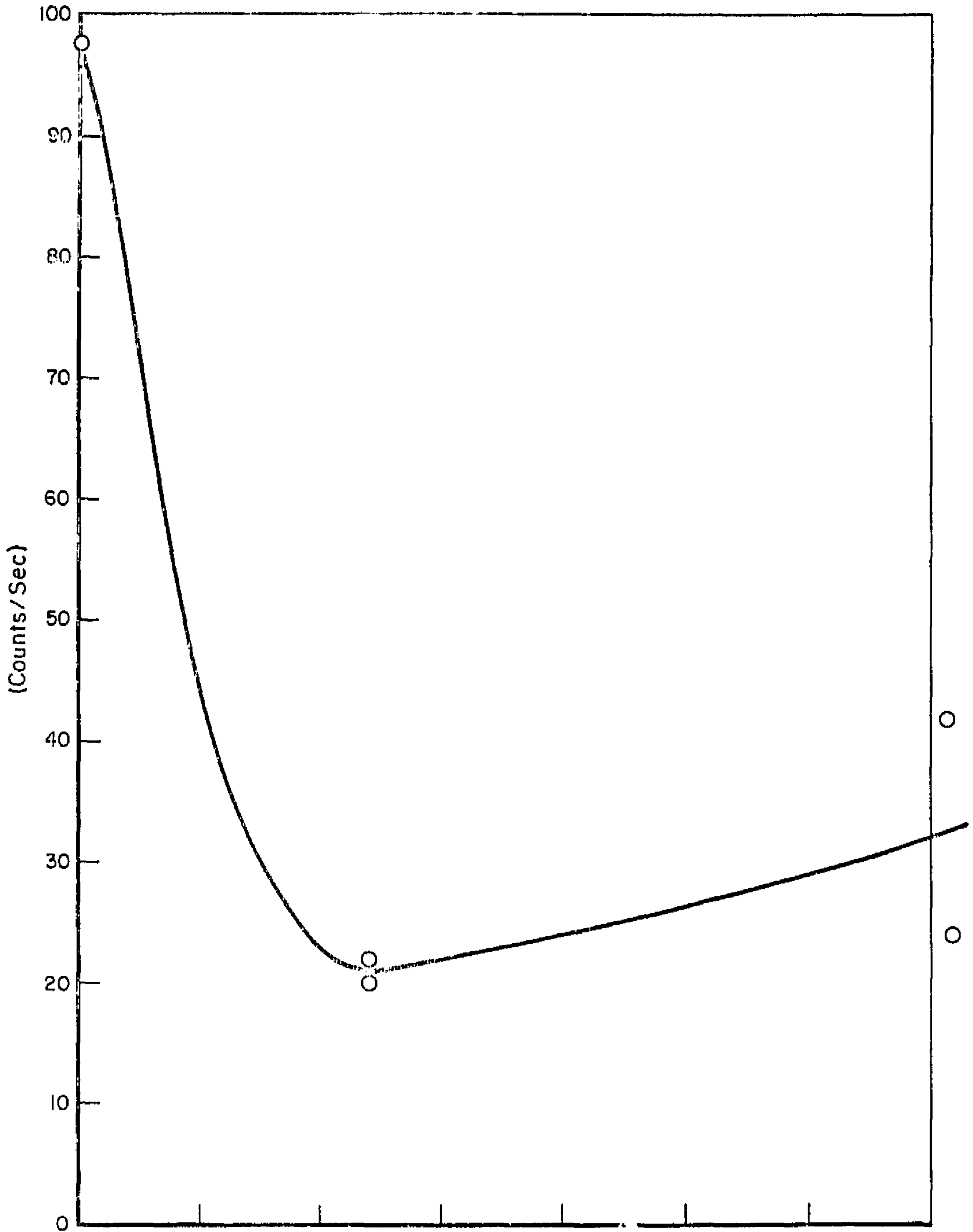


FIGURE 31. CHEMILUMINESCENCE FROM CIS-POLYBUTADIENE 1203 IN OXYGEN AT 100 C (212 F) AS A FUNCTION OF AGING AT 100 C (212 F)

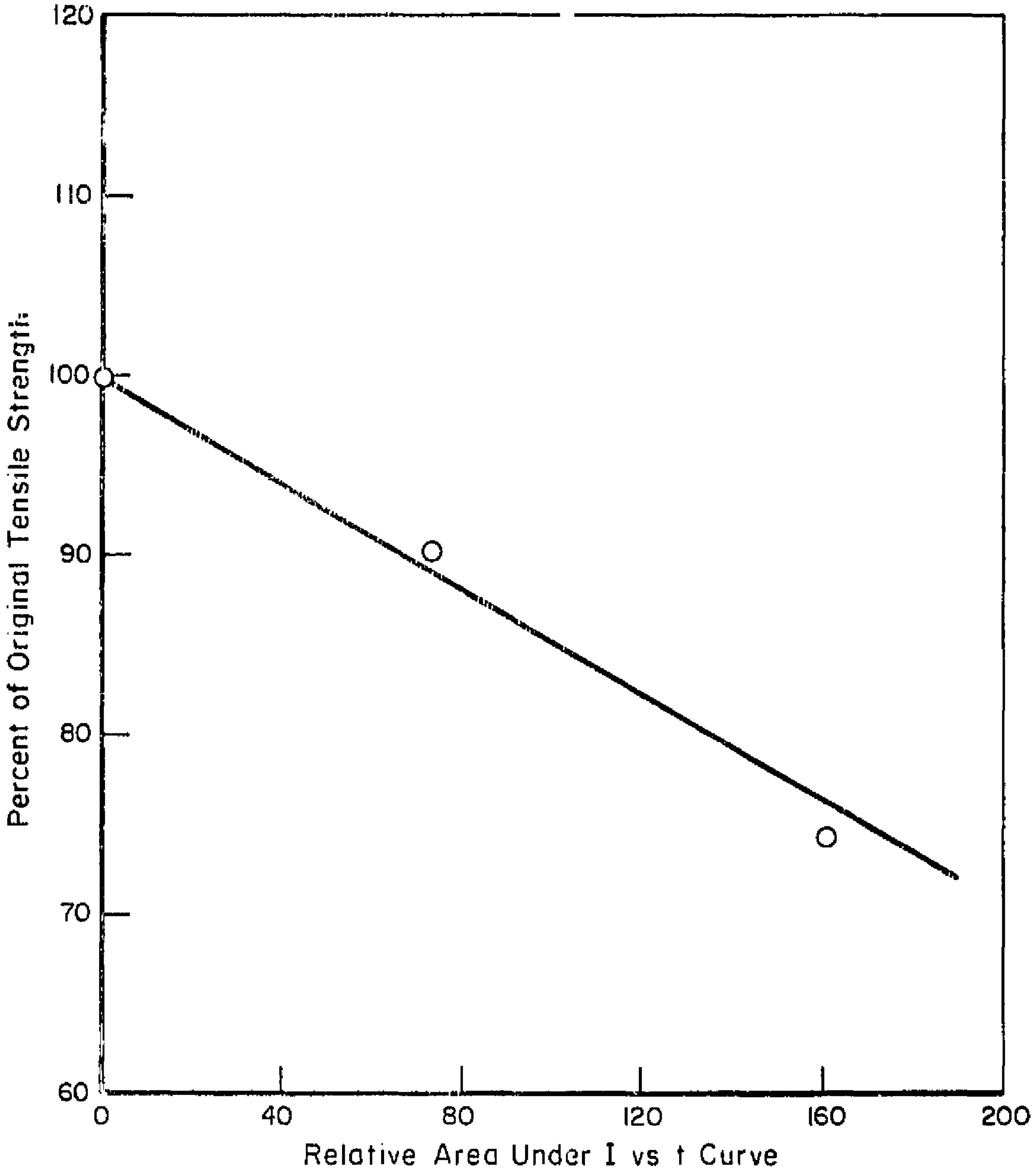


FIGURE 32. LOSS OF TENSILE STRENGTH OF CIS-BR 1203 AS A FUNCTION OF TOTAL LIGHT EMISSION AT 100 C (212 F)

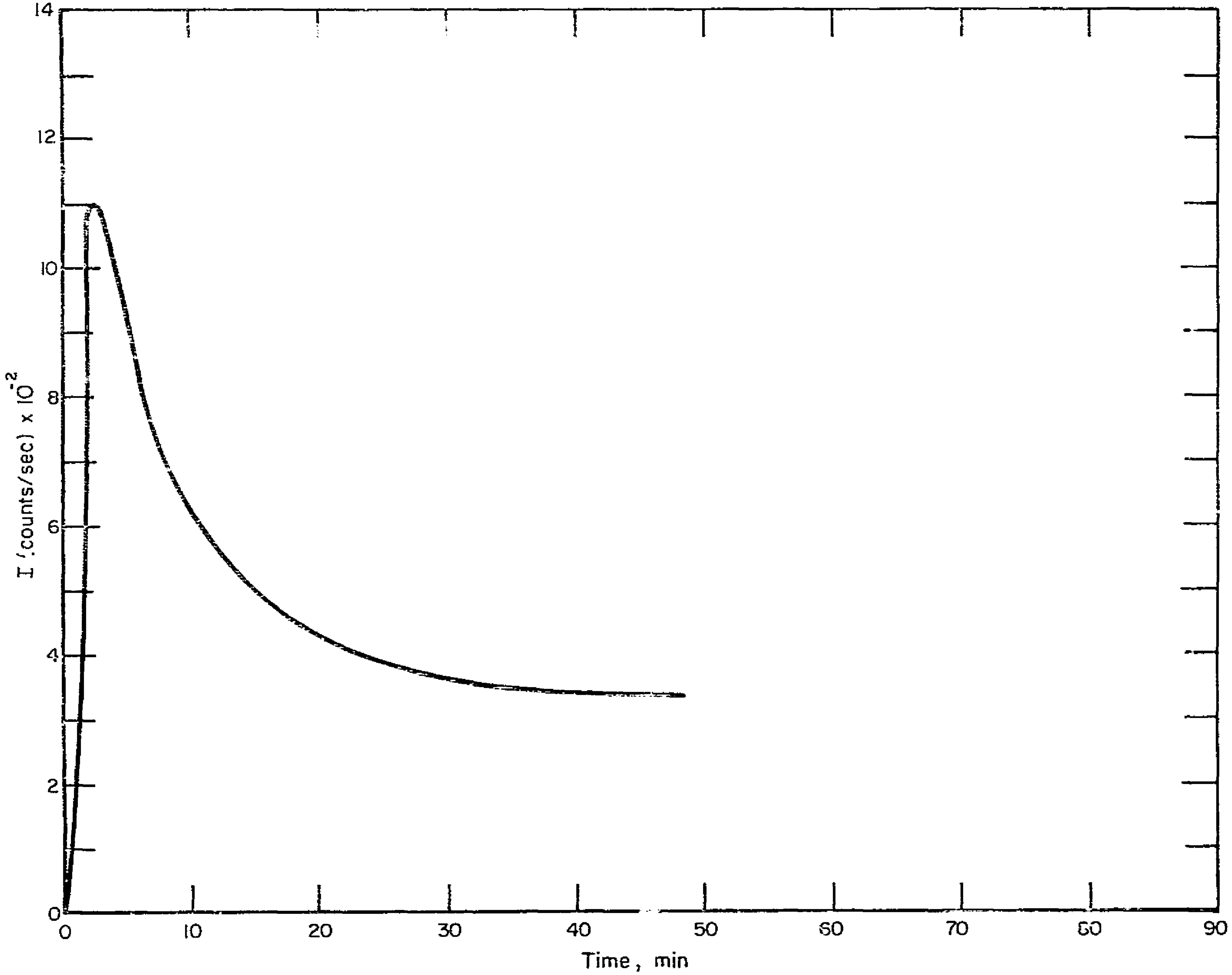


FIGURE 33. CHEMILUMINESCENCE FROM SILICONE W-96 GUM AT 193 C (379 F) IN OXYGEN. RUN 42

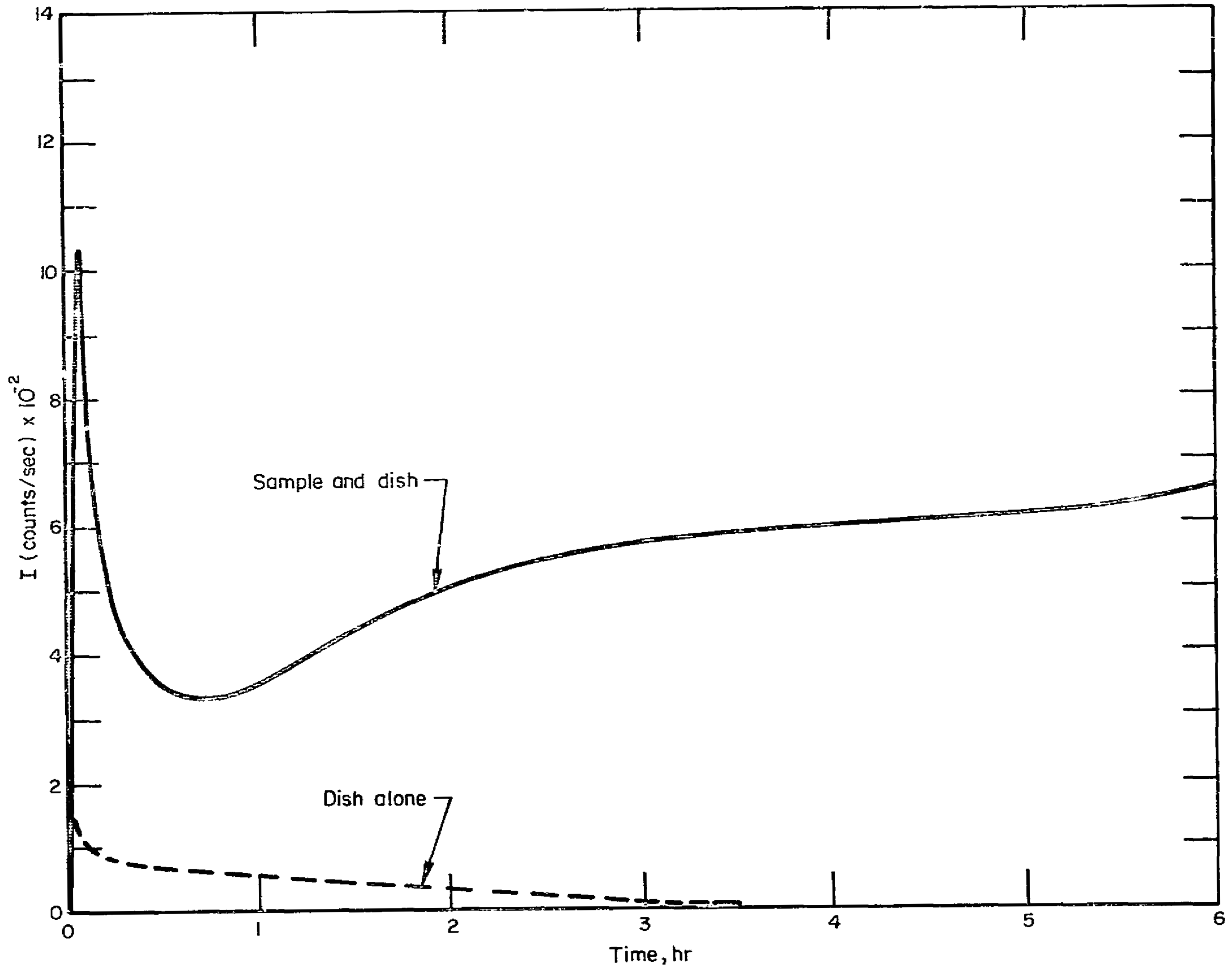


FIGURE 34. CHEMILUMINESCENCE FROM SILICONE W-96 GUM AT 193 C (379 F) IN OXYGEN. RUN 41

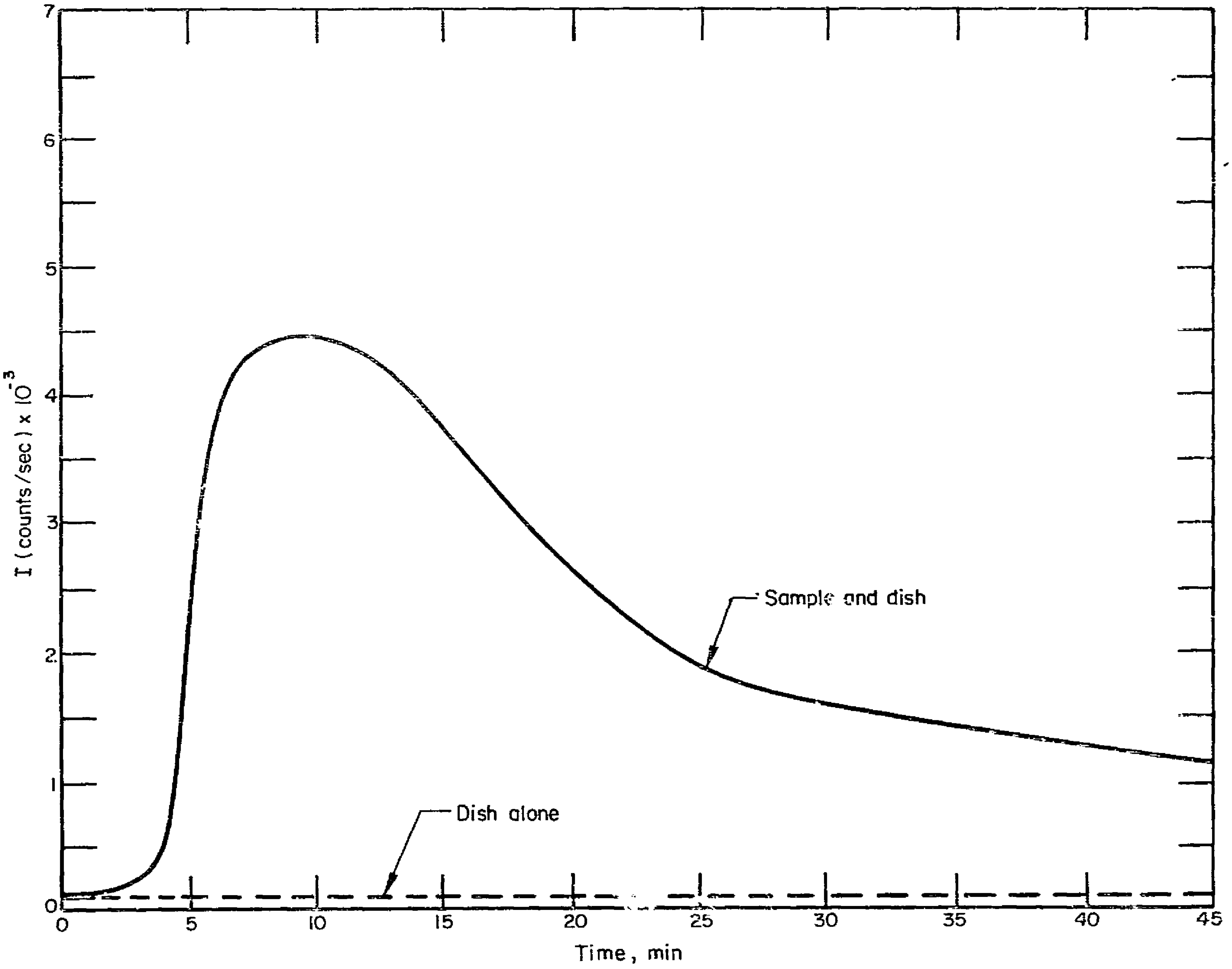


FIGURE 35. CHEMILUMINESCENCE FROM SILICONE W-96 GUM AT 150 C (302 F) IN OXYGEN. RUN 44

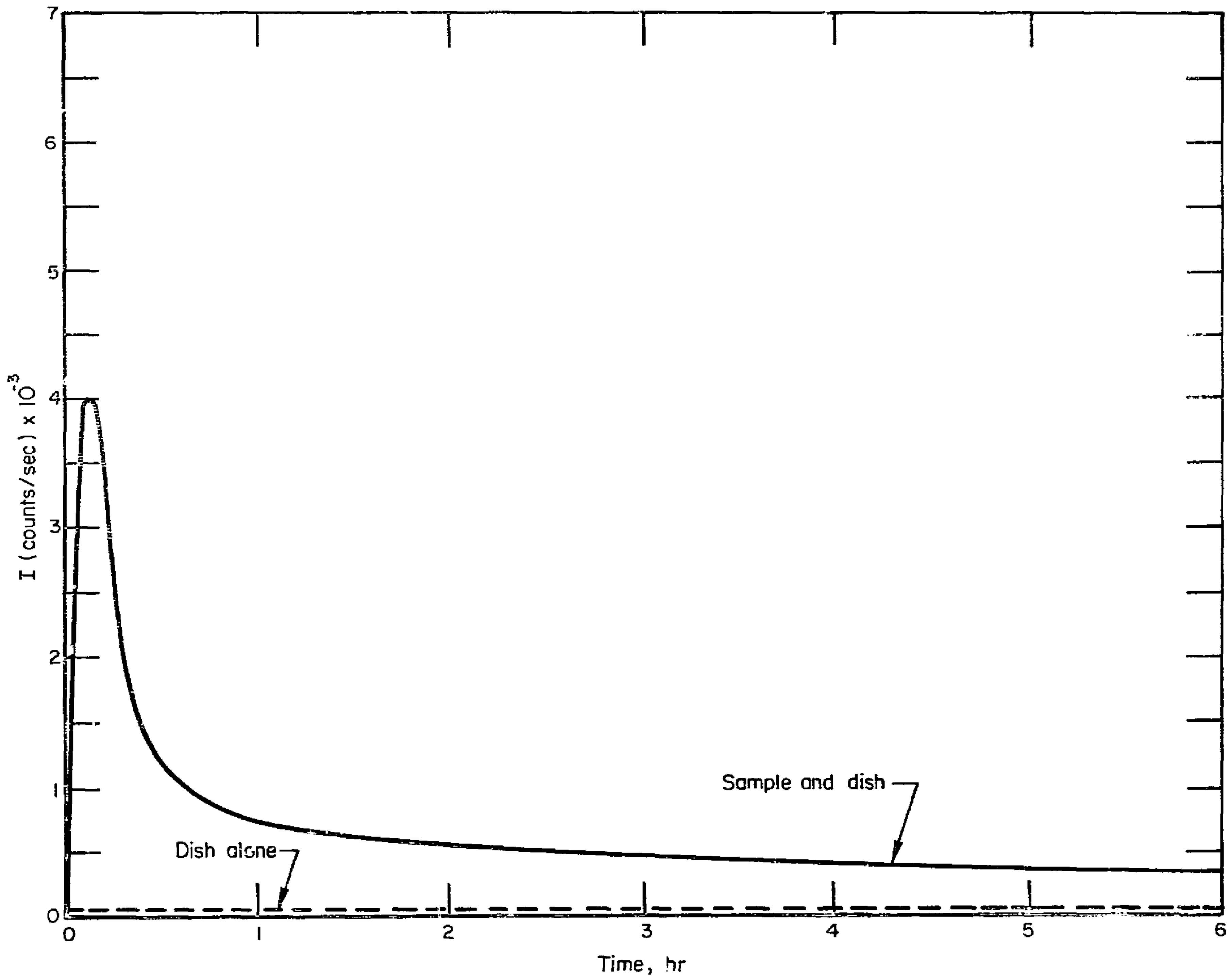


FIGURE 36. CHEMILUMINESCENCE FROM SILICONE W-96 GUM AT 150 C (302 F) IN OXYGEN. RUN 43

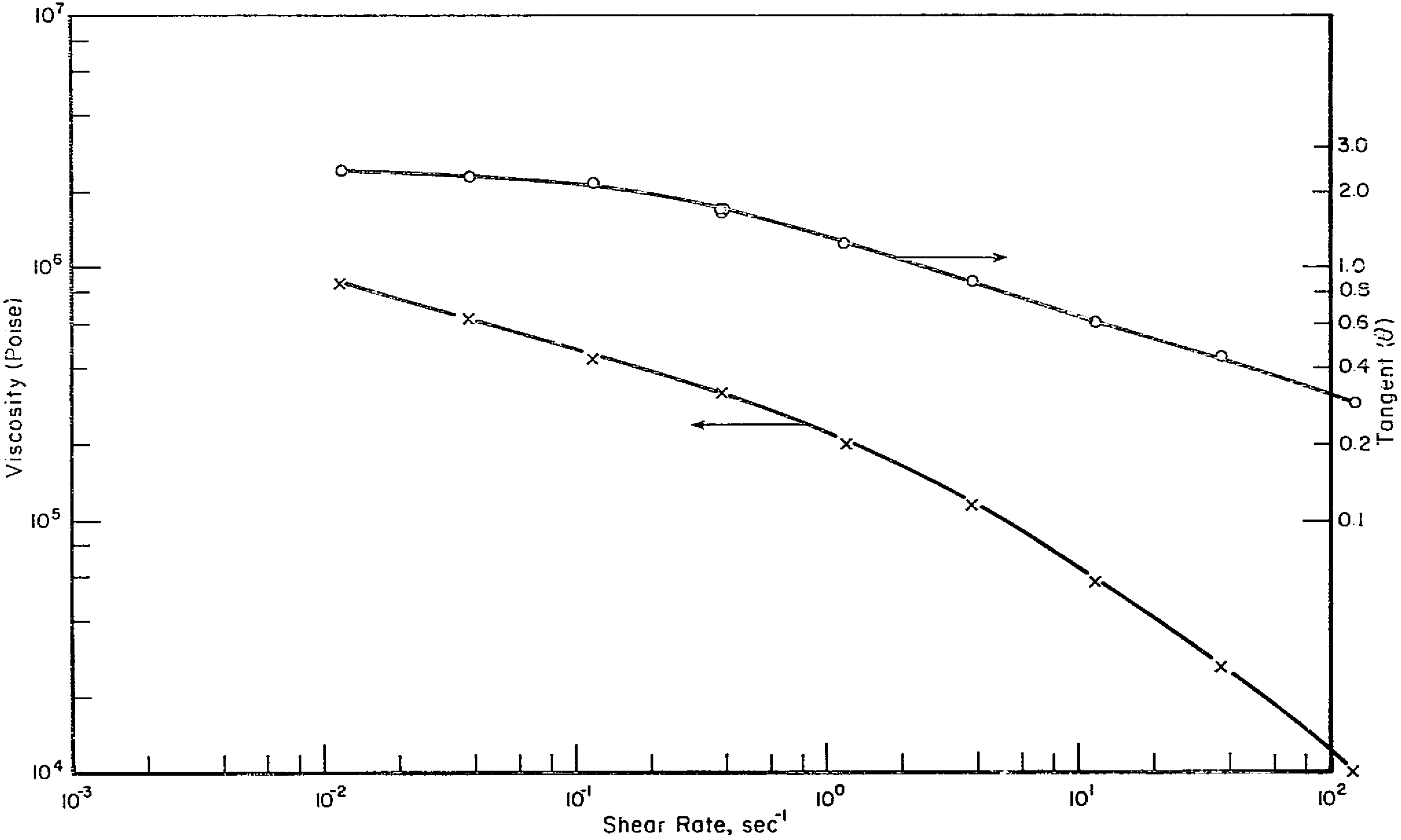


FIGURE 37. SILICONE RUBBER W-96, FIRST PREPARATION. UPPER CURVE: TANGENT (θ). LOWER CURVE: COMPLEX VISCOSITY.

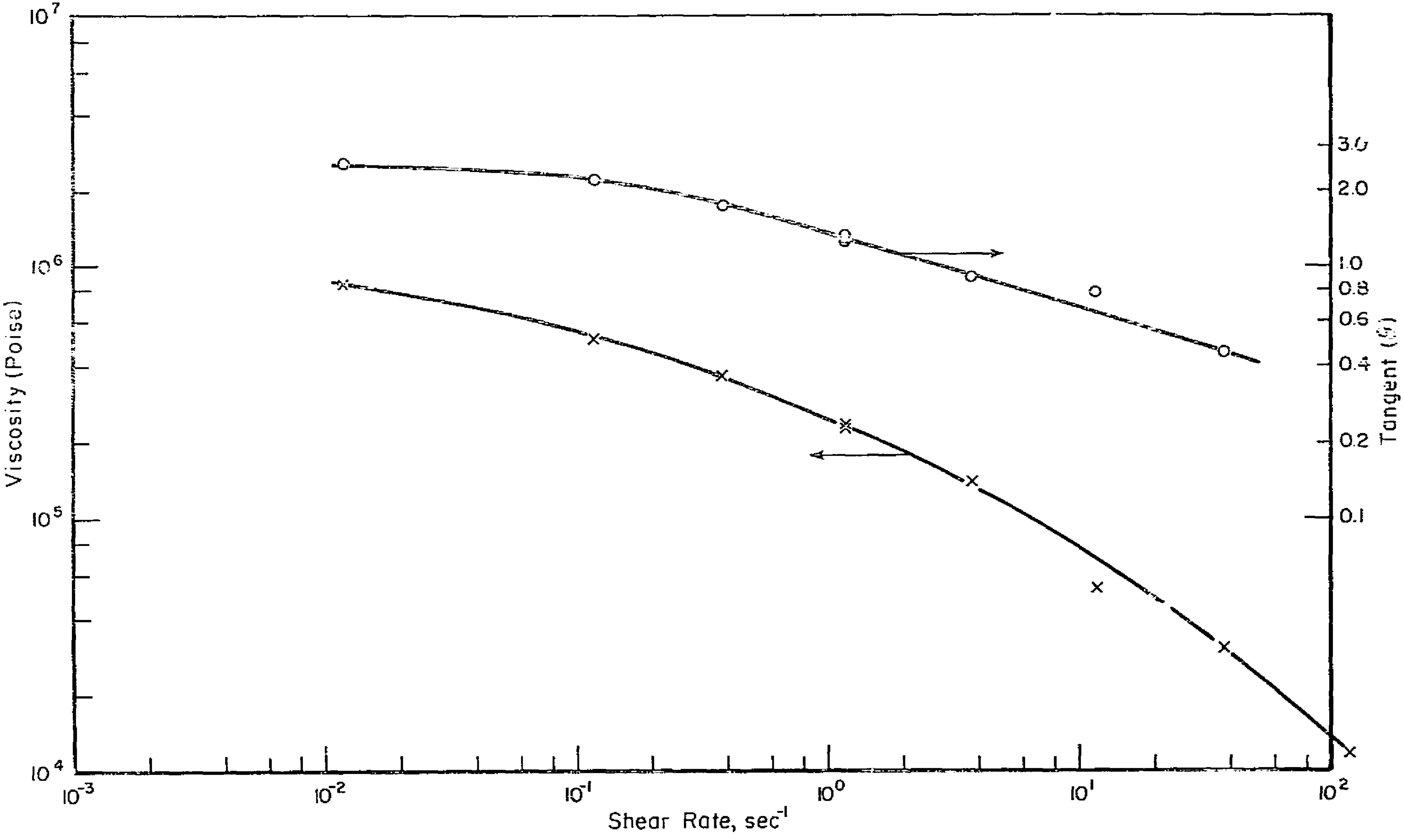


FIGURE 38. SILICONE RUBBER W-96, SECOND PREPARATION. UPPER CURVE: TANGENT (θ). LOWER CURVE: COMPLEX VISCOSITY.

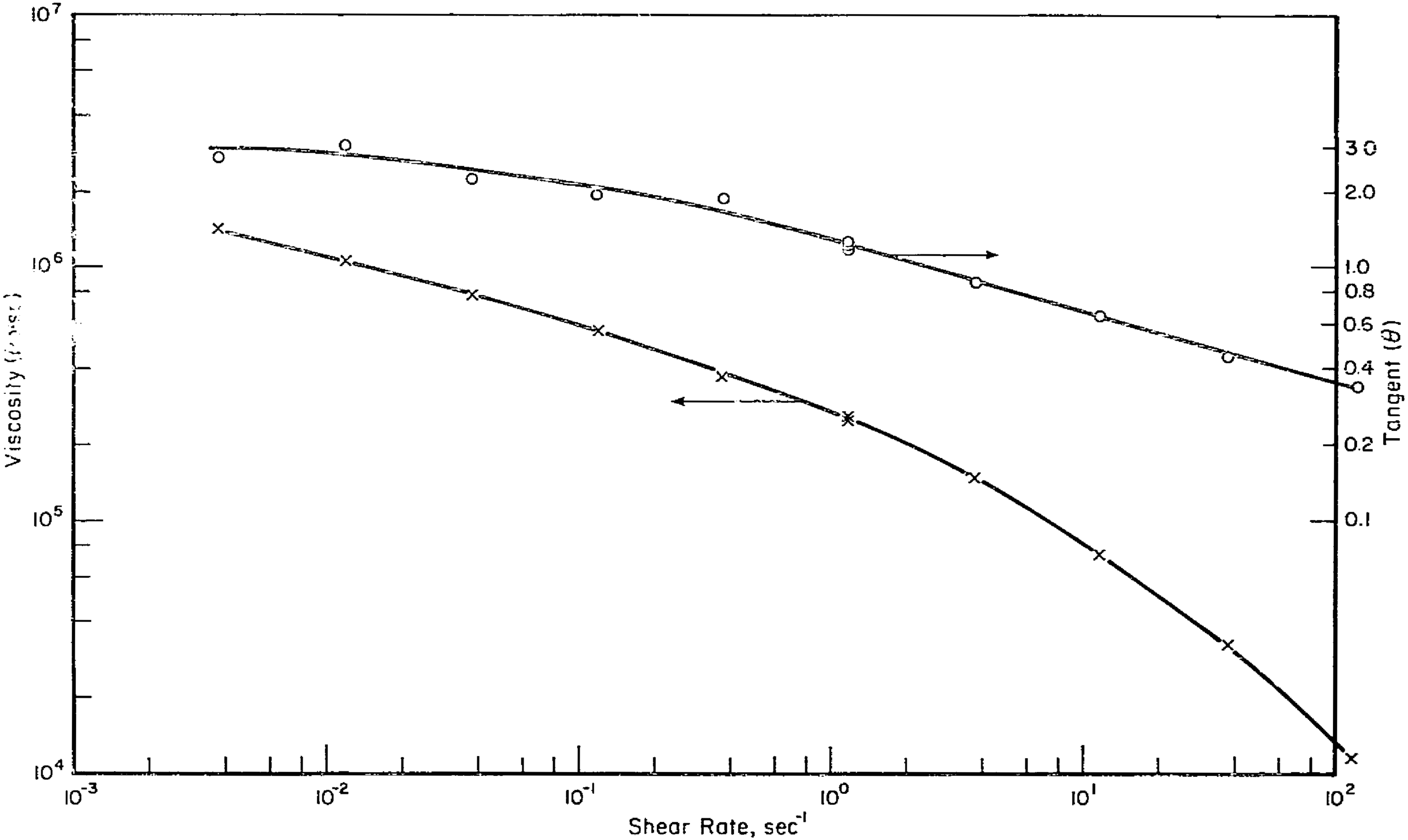


FIGURE 39. SILICONE RUBBER W-96 HEATED 0.75 HR AT 150 C (302 F) IN OXYGEN. UPPER CURVE: TANGENT (θ). LOWER CURVE: COMPLEX VISCOSITY. RUN 44.

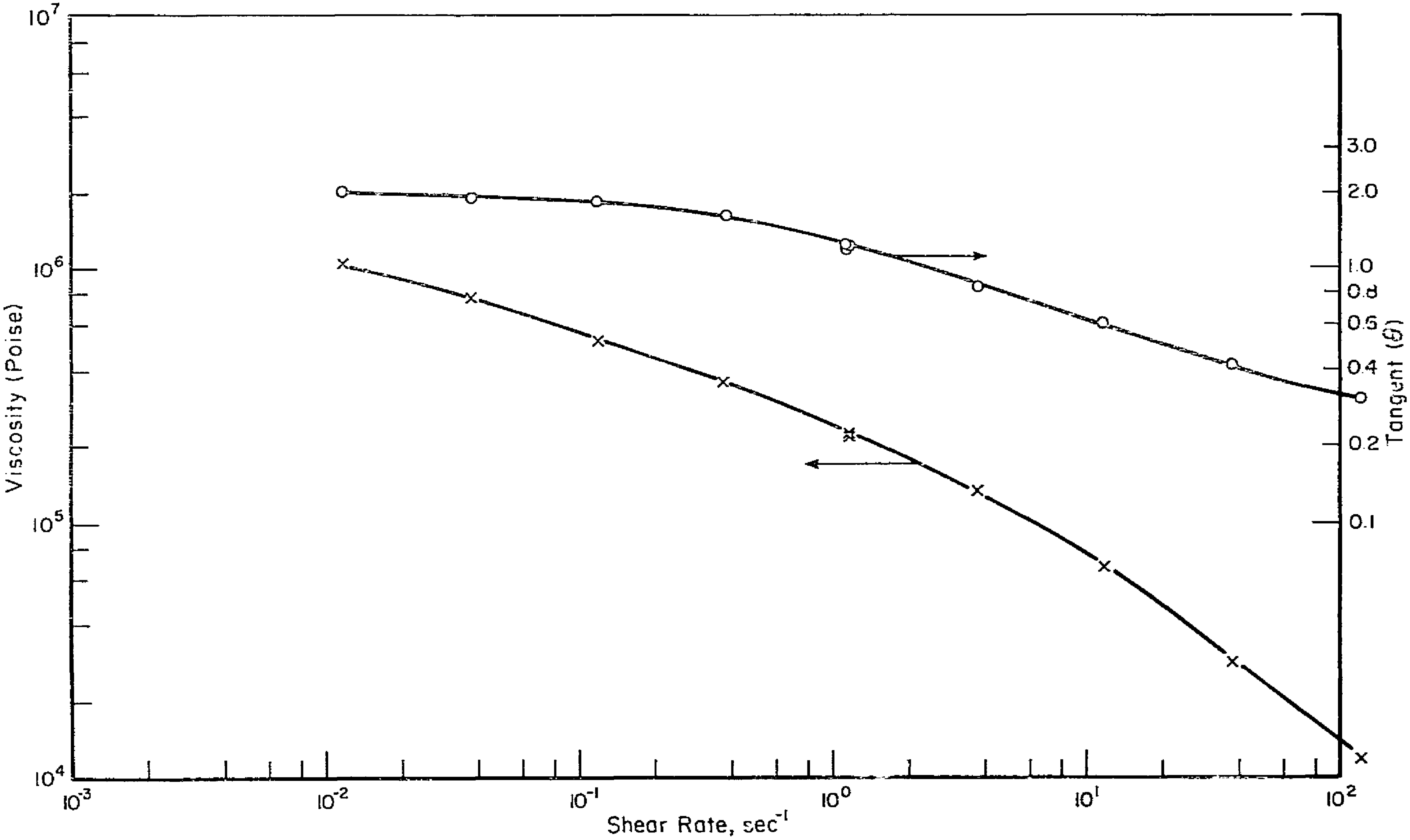


FIGURE 40. SILICONE RUBBER W-96 HEATED 6.3 HR AT 150 C (302 F) IN OXYGEN. UPPER CURVE: TANGENT (θ). LOWER CURVE: COMPLEX VISCOSITY. RUN 43.

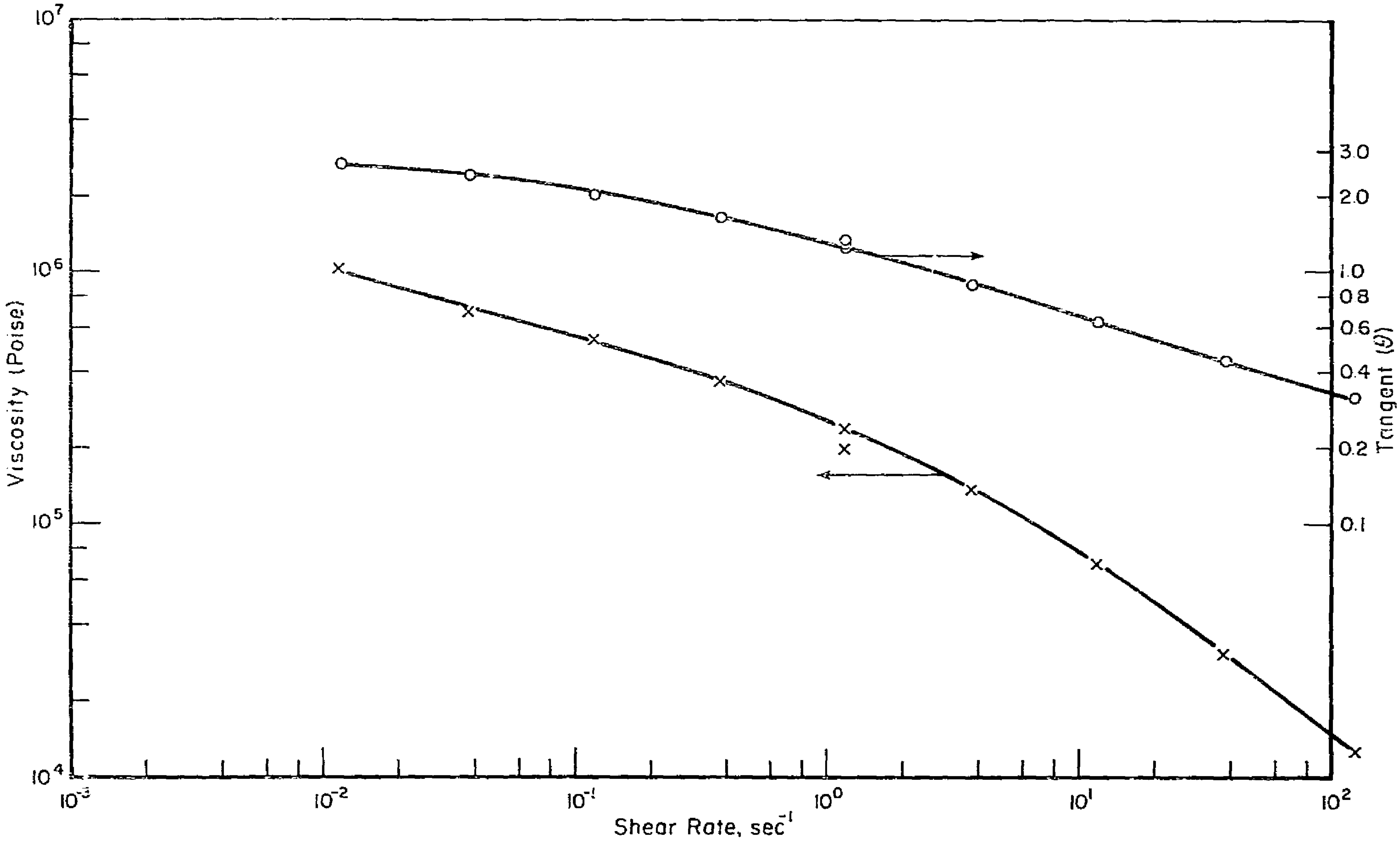


FIGURE 41. SILICONE RUBBER W-96 HEATED 0.75 HR AT 193 C (379 F) IN OXYGEN. UPPER CURVE: TANGENT (δ). LOWER CURVE: COMPLEX VISCOSITY. RUN 42.

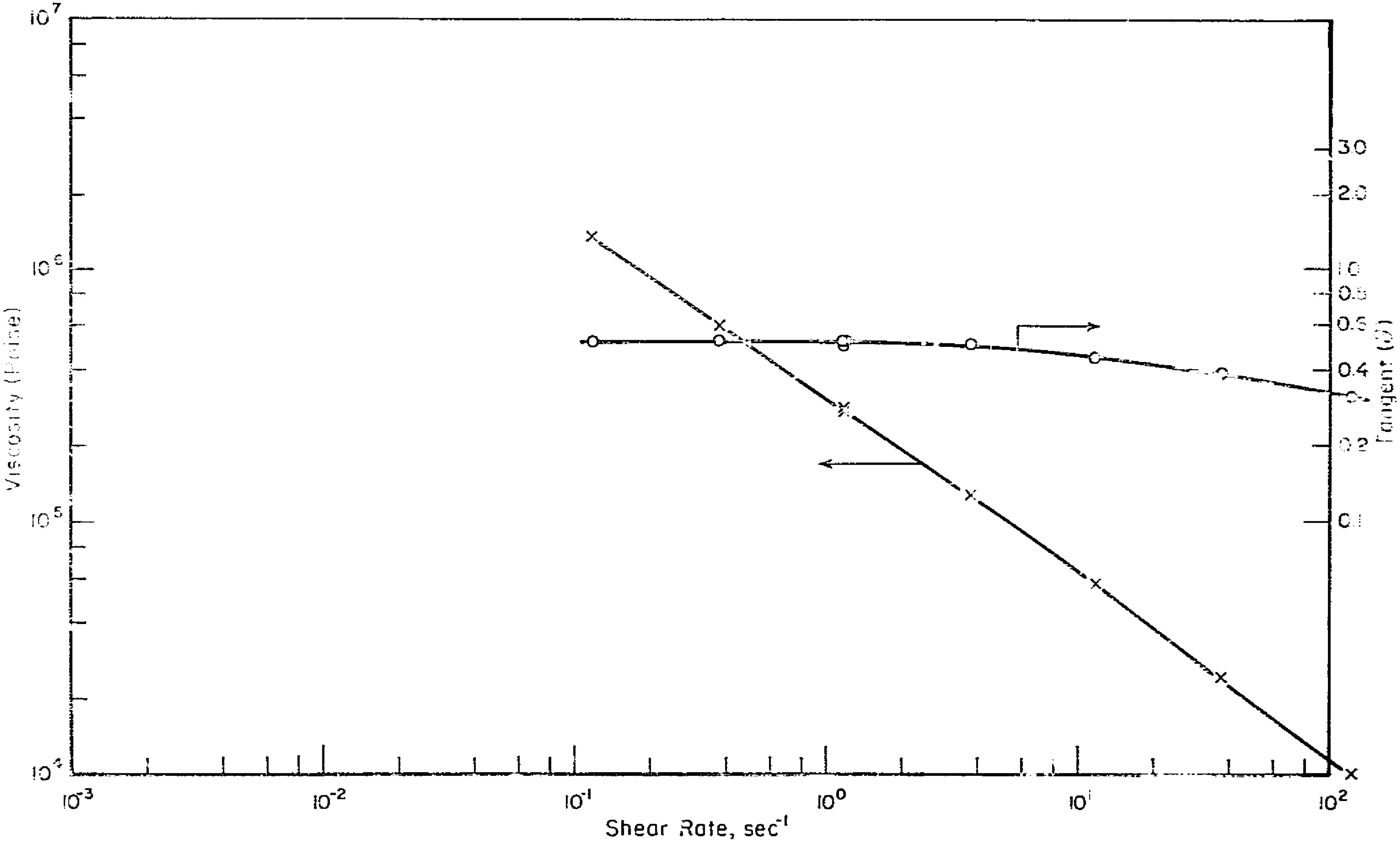


FIGURE 42. SILICONE RUBBER W-96 HEATED 6 HR AT 193 C (379 F) IN OXYGEN. UPPER CURVE: COMPLEX VISCOSITY. LOWER CURVE (CIRCLES): TANGENT (θ). RUN 4.

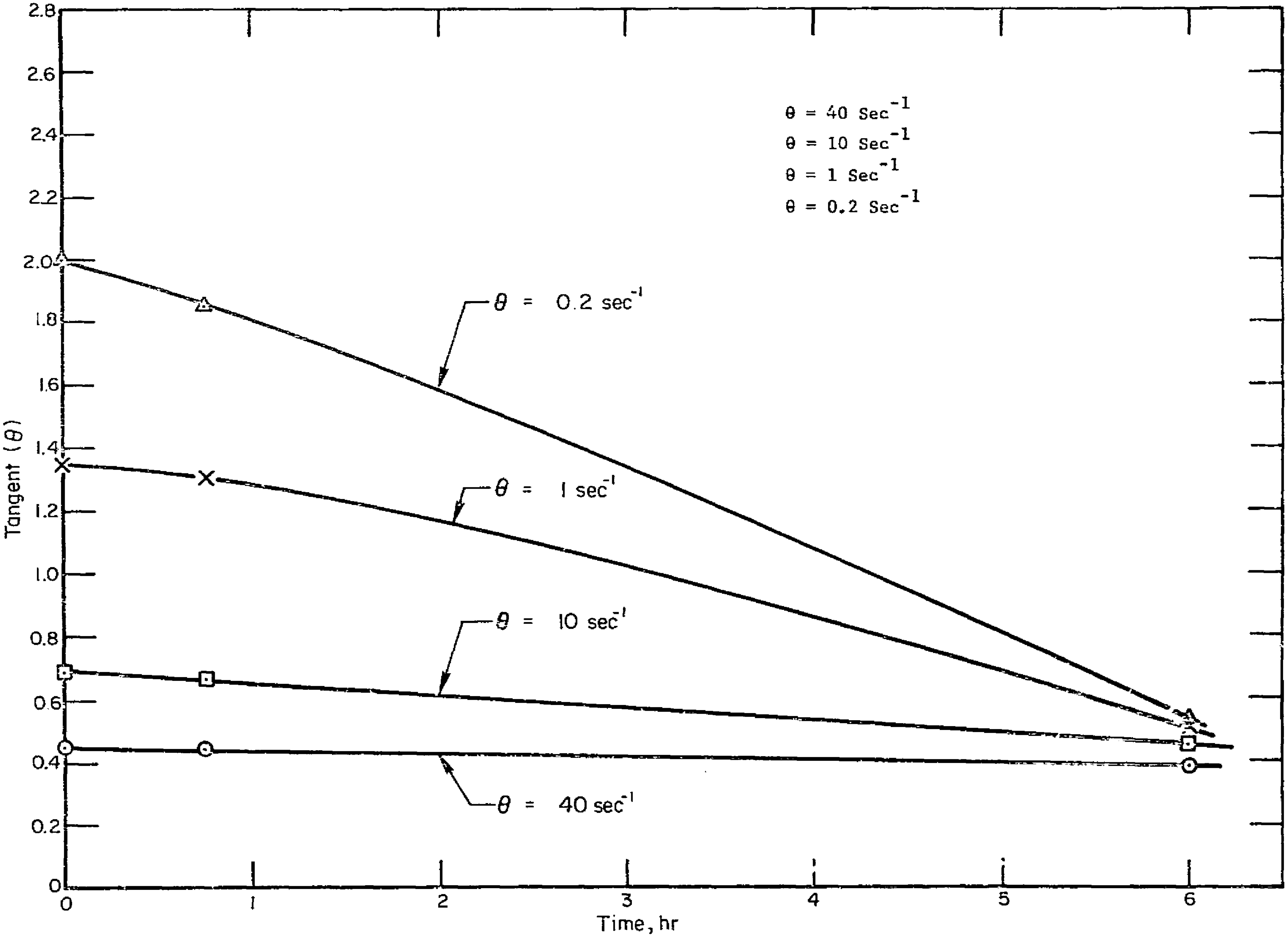


FIGURE 43. TANGENT θ VS AGING TIME OF SILICONE GUM W-96 IN OXYGEN AT 193 C (379 F)

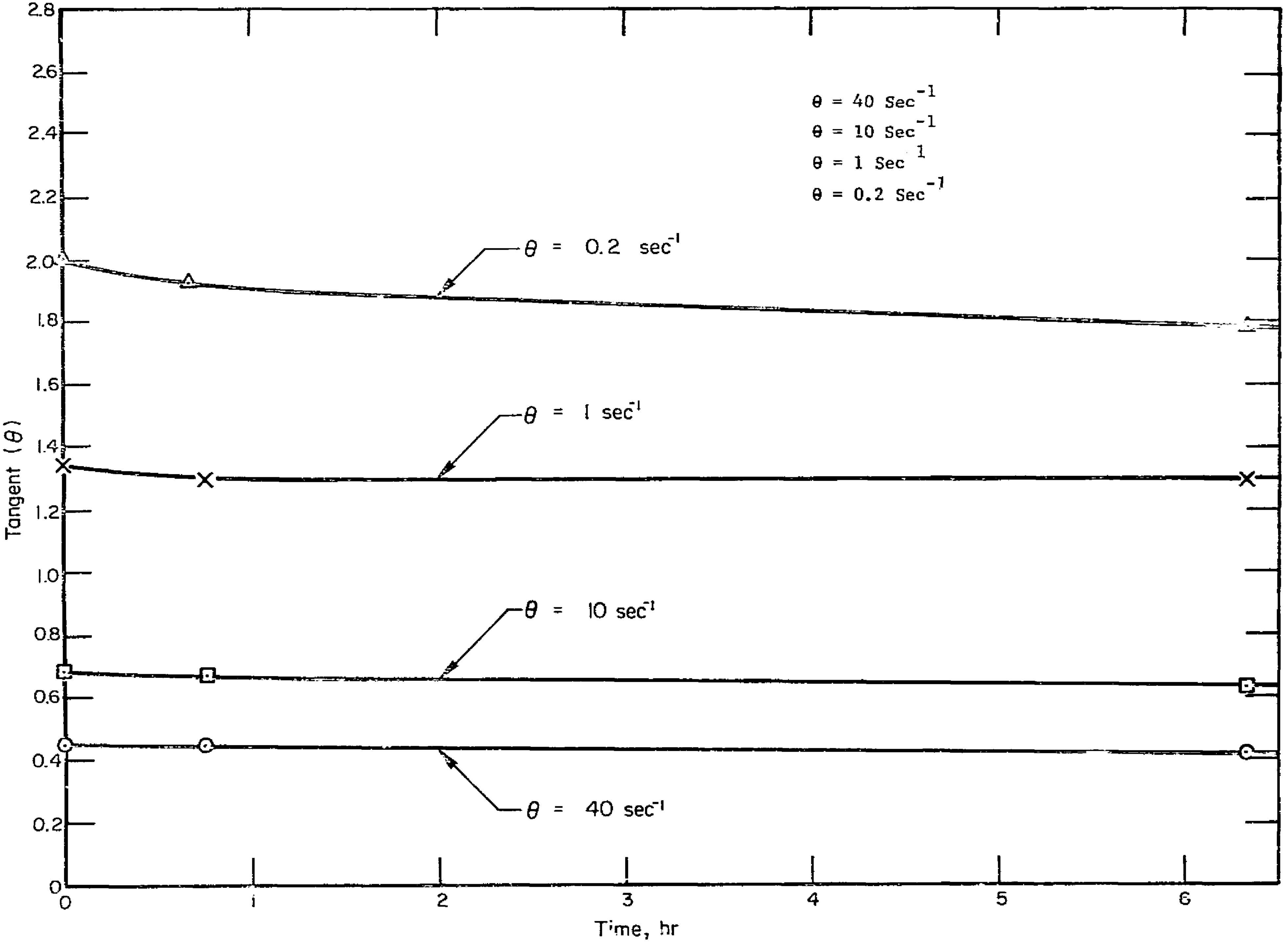


FIGURE 44. TANGENT (θ) VS AGING TIME OF SILICONE GUM W-96 IN OXYGEN AT 150 C (302 F)

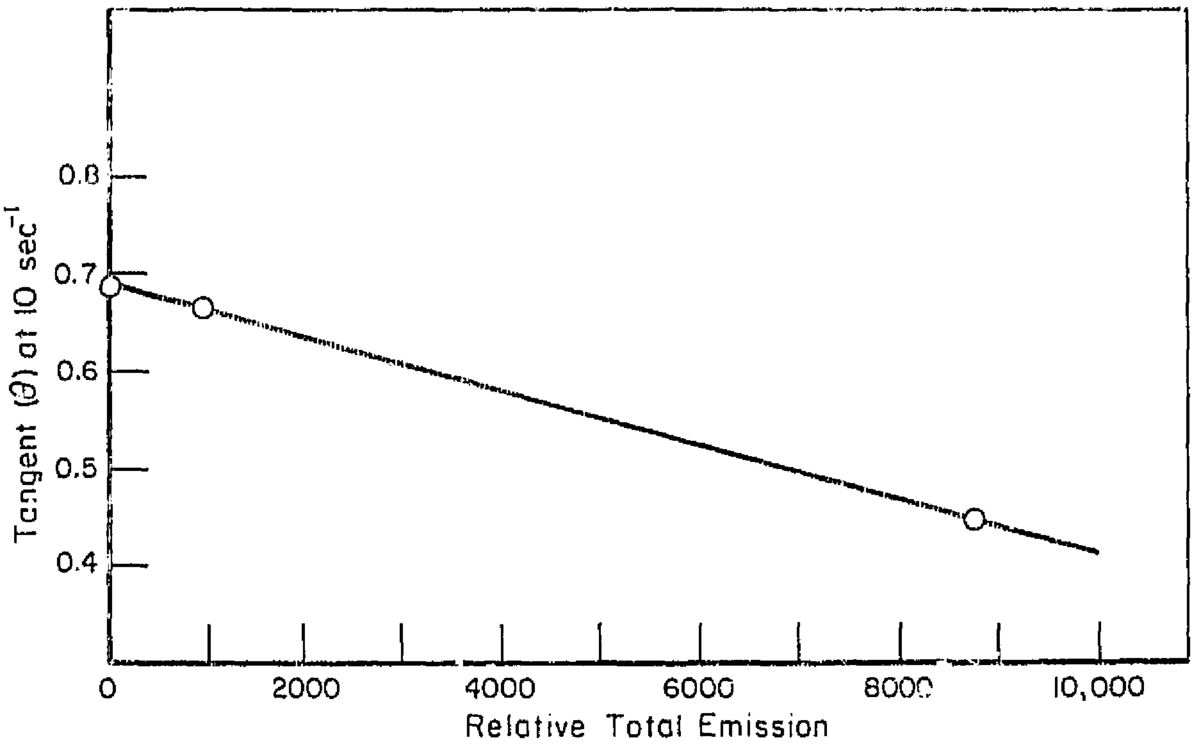


FIGURE 45. TOTAL RELATIVE EMISSION FROM SILICONE W-96 GUM VS. TANGENT (θ) AT 10 SEC^{-1}. CHEMILUMINESCENCE FROM SAMPLE AT 193 C (379 F) IN OXYGEN.

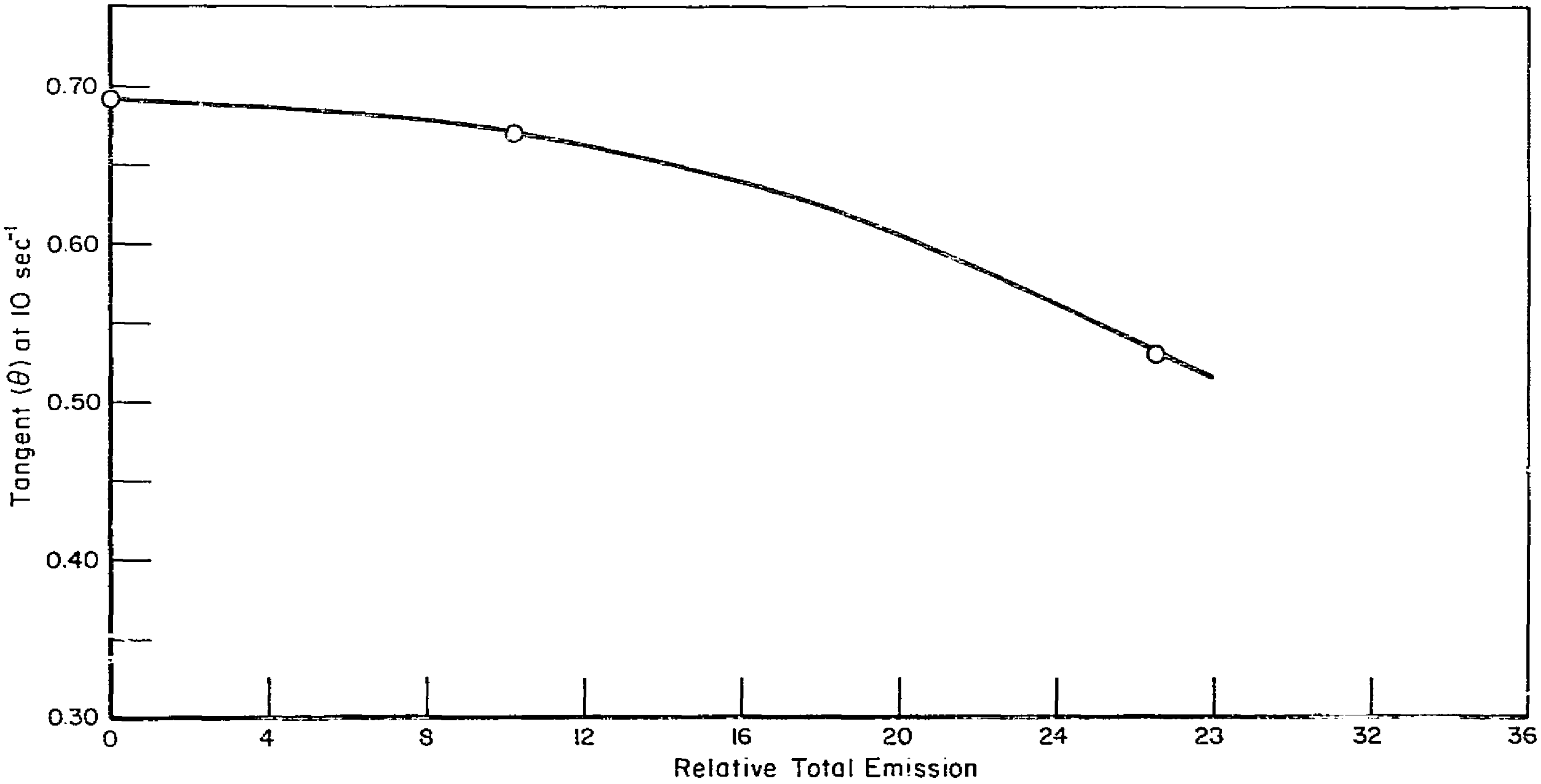


FIGURE 46. TOTAL RELATIVE EMISSION FROM SILICONE W-96 GUM VS. TANGENT (θ) AT 10 SEC^{-1}. CHEMILUMINESCENCE FROM SAMPLE IN OXYGEN AT 150 C (302 F).

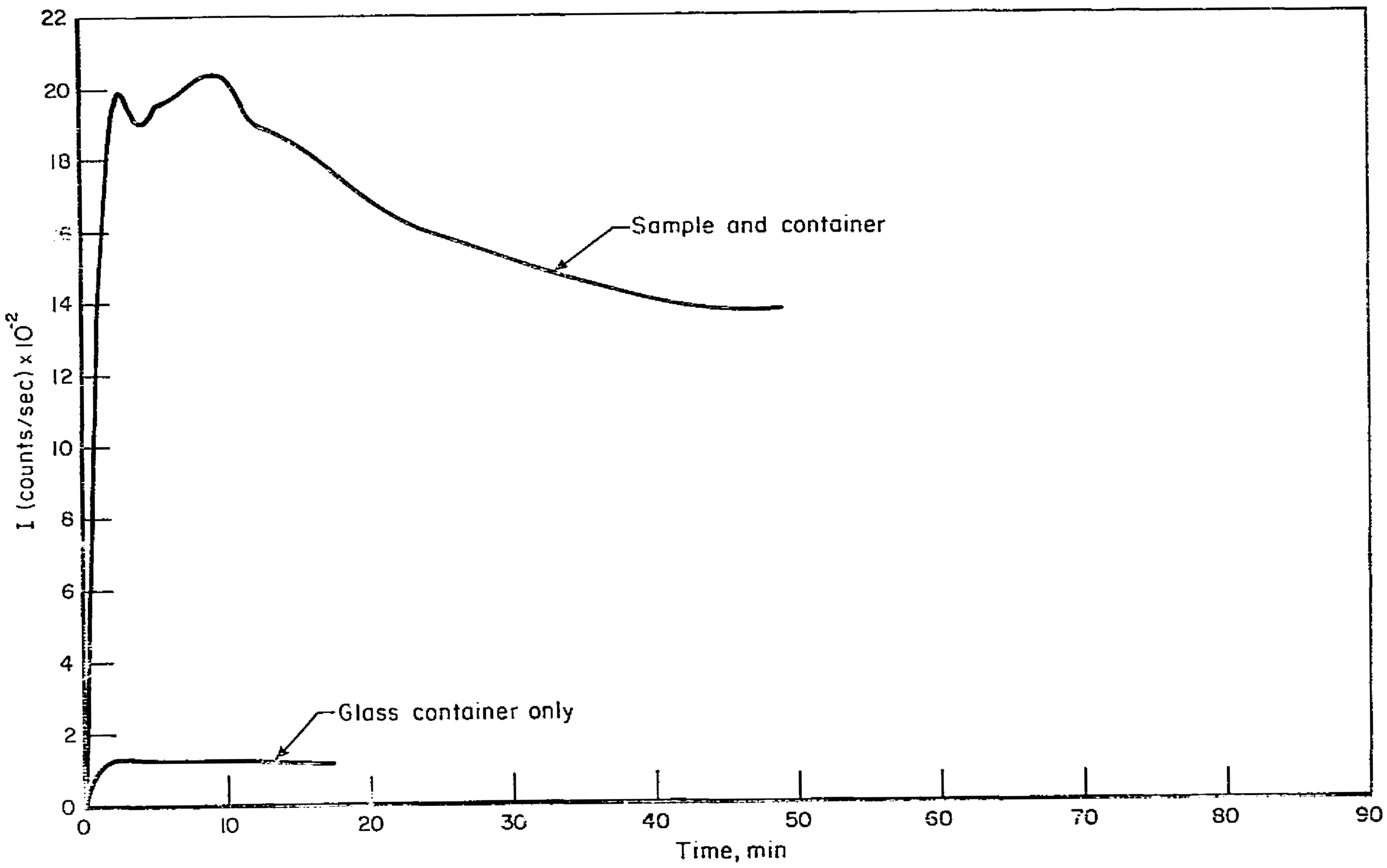


FIGURE 47. CHEMILUMINESCENCE FROM VITON A AT 150 C (302 F) IN OXYGEN. RUN 54.

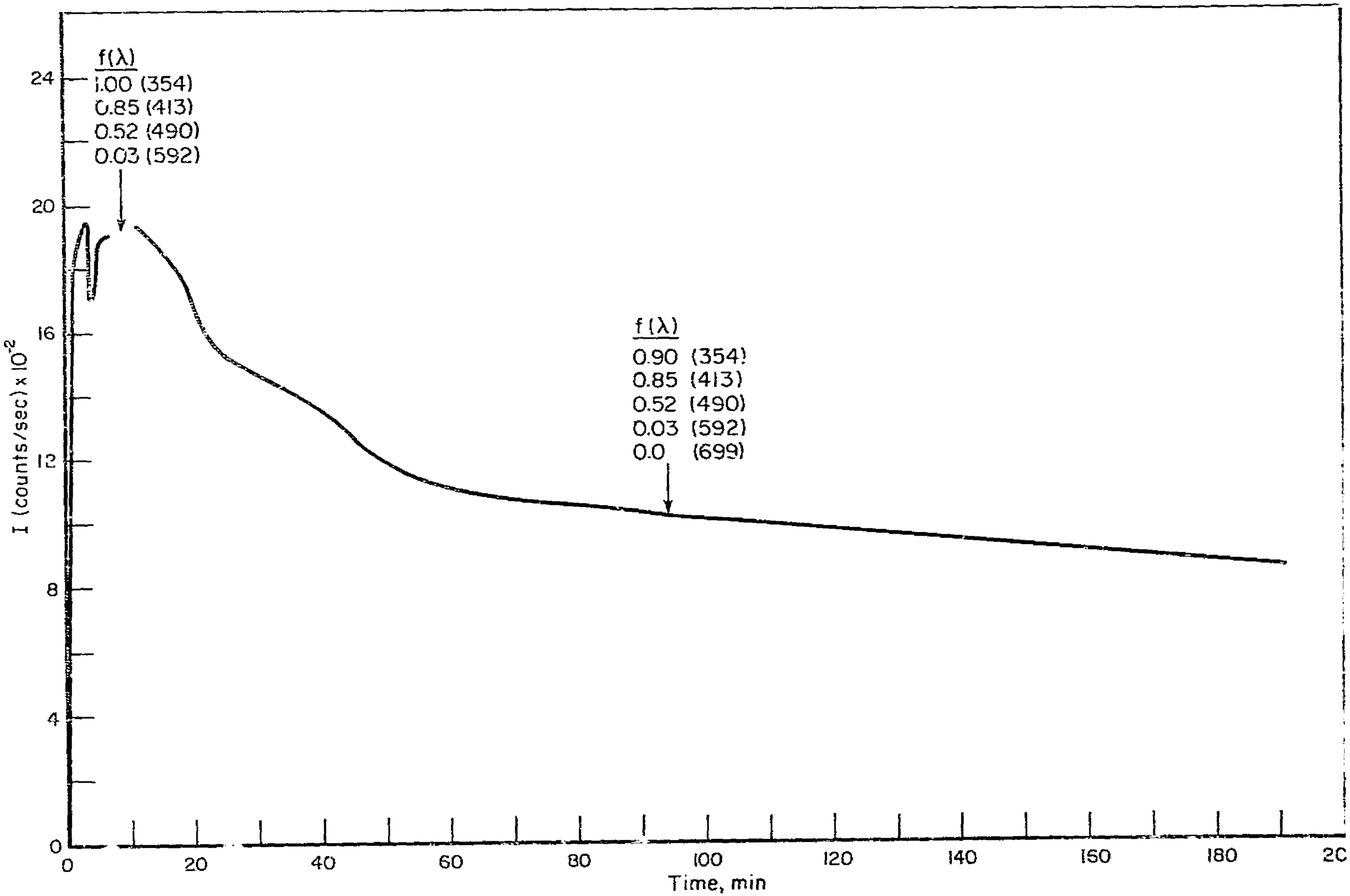


FIGURE 48. CHEMILUMINESCENCE FROM VITON A AT 150 C (302 F) IN OXYGEN. RUN 52.

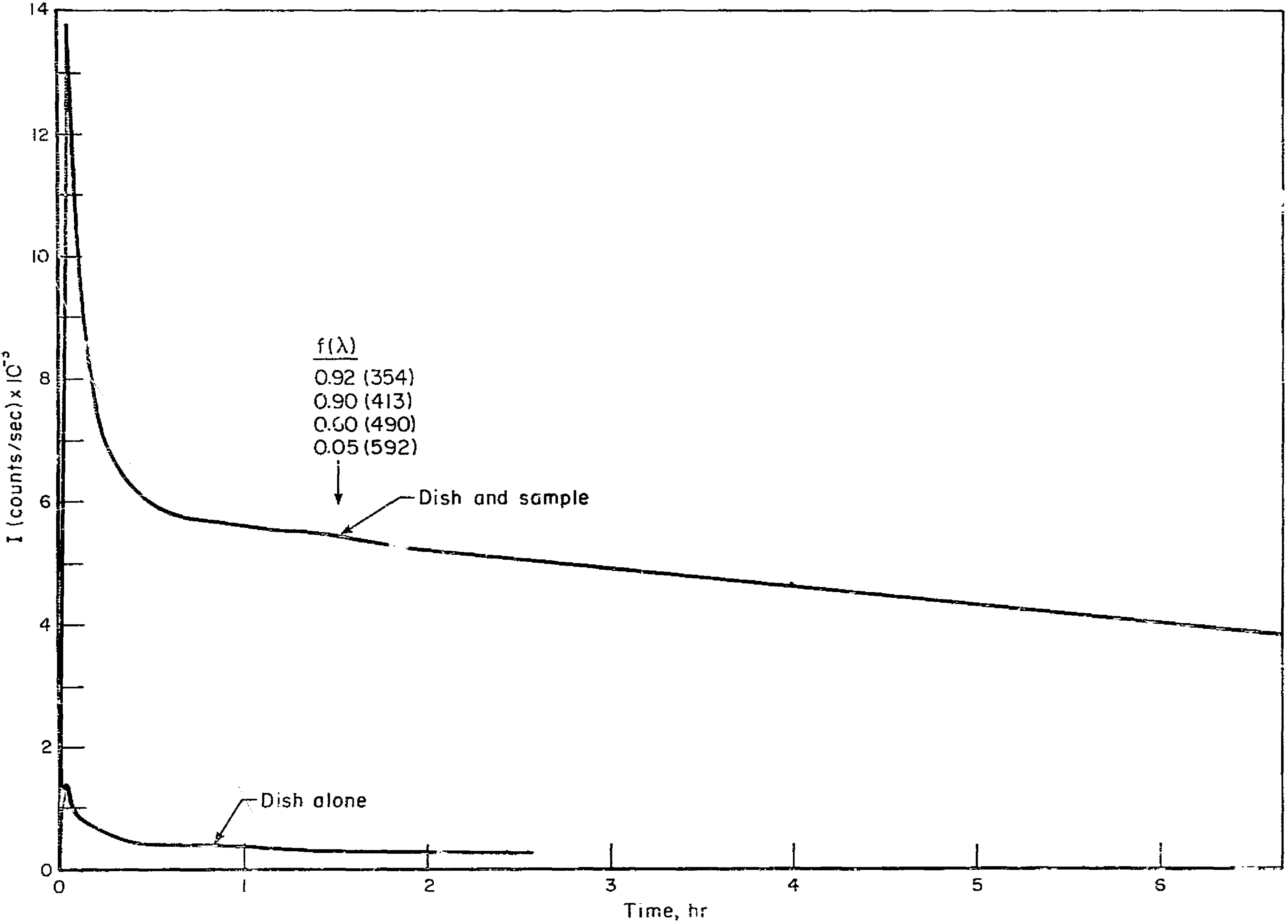


FIGURE 49. CHEMILUMINESCENCE FROM VITON A AT 200 C (392 F) IN OXYGEN. RUN 50.

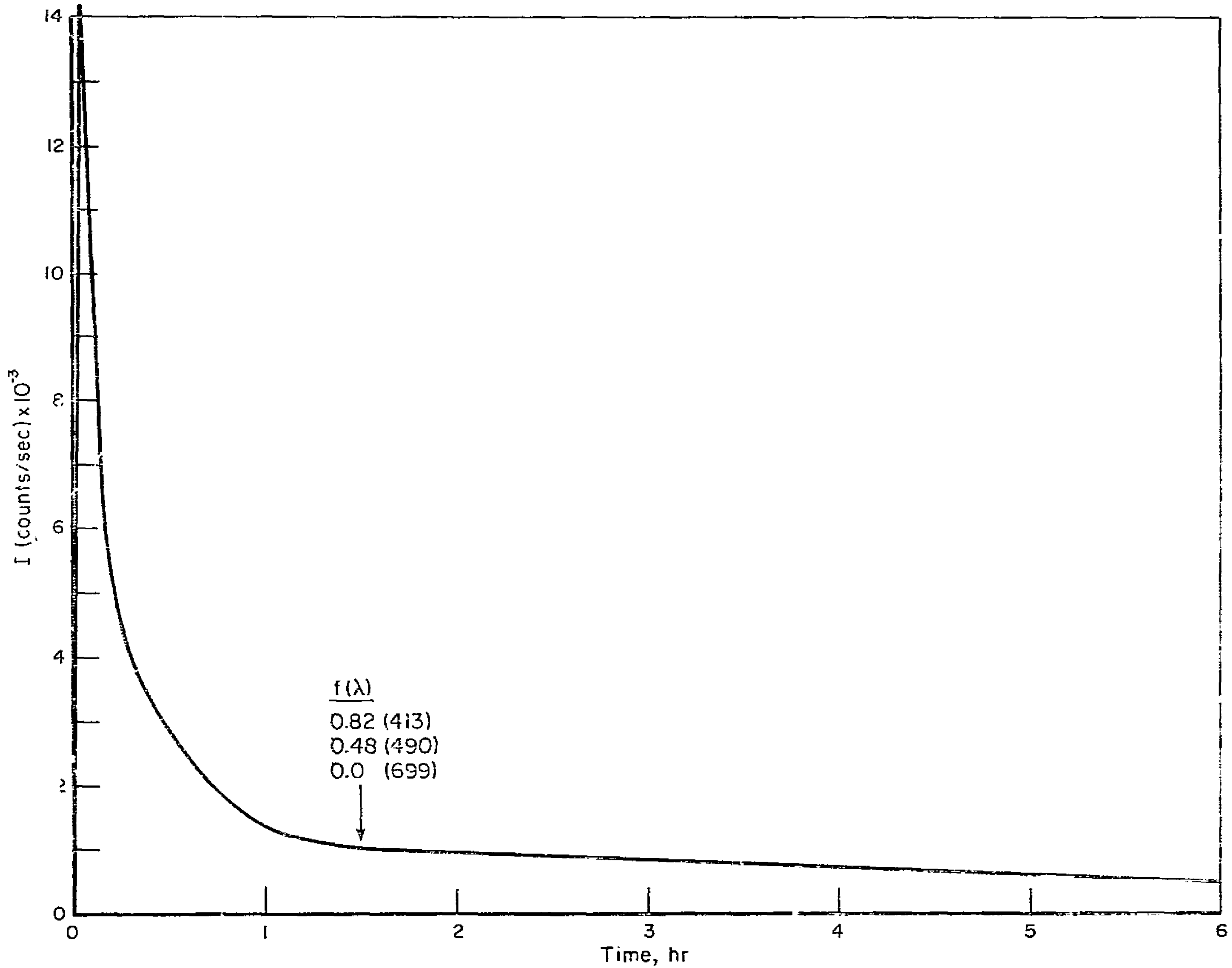


FIGURE 50. CHEMILUMINESCENCE FROM VITON A CONTAINING 0.5% N-PHENYL-2-NAPHTHYLAMINE AT 200 C (391 F) IN OXYGEN. RUN 56-2

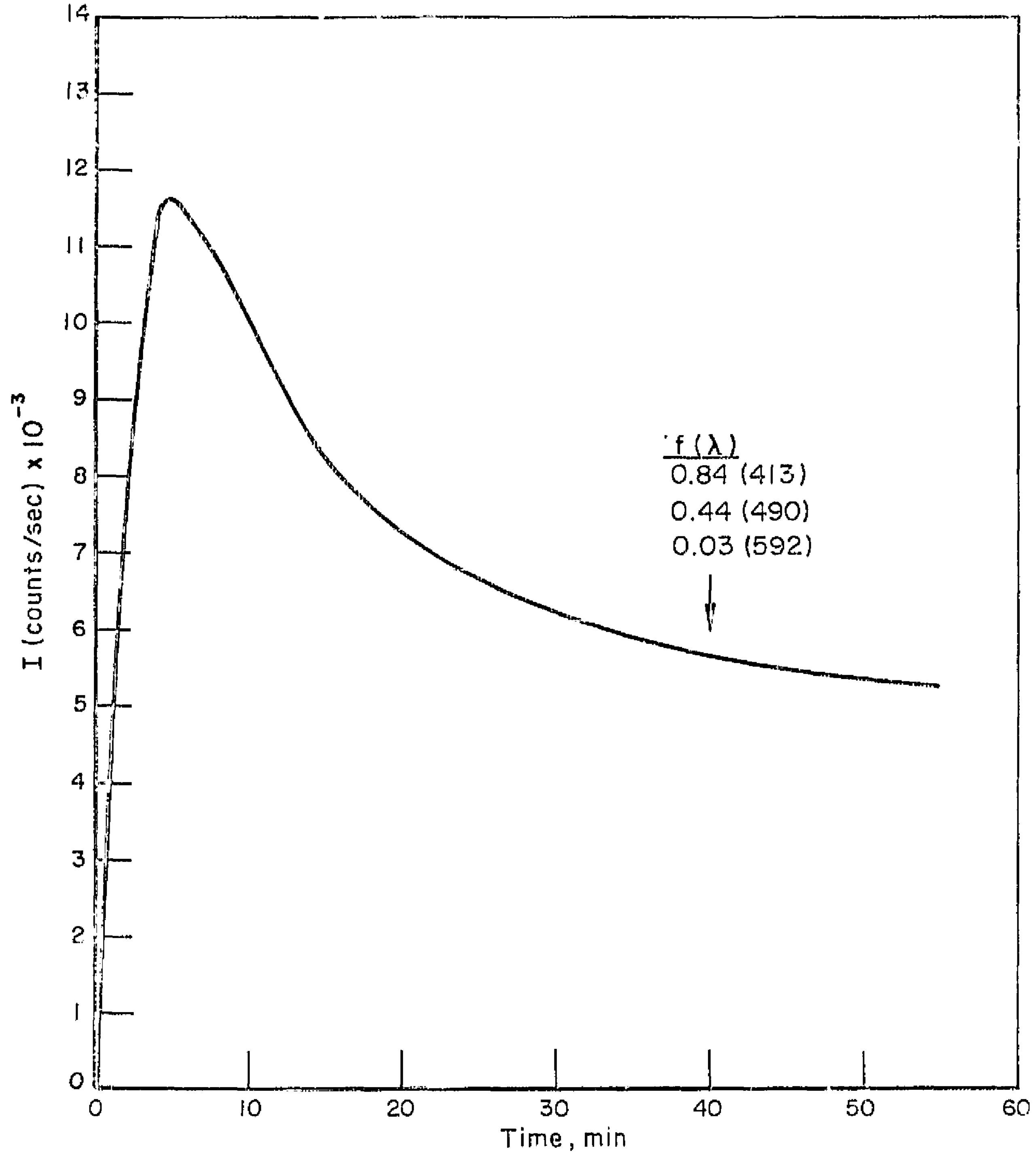


FIGURE 51. CHEMILUMINESCENCE FROM VITON A CONTAINING 0.50 % N-PHENYL-2-NAPHTHYLAMINE IN OXYGEN AT 200 C (392 F). RUN 56-1

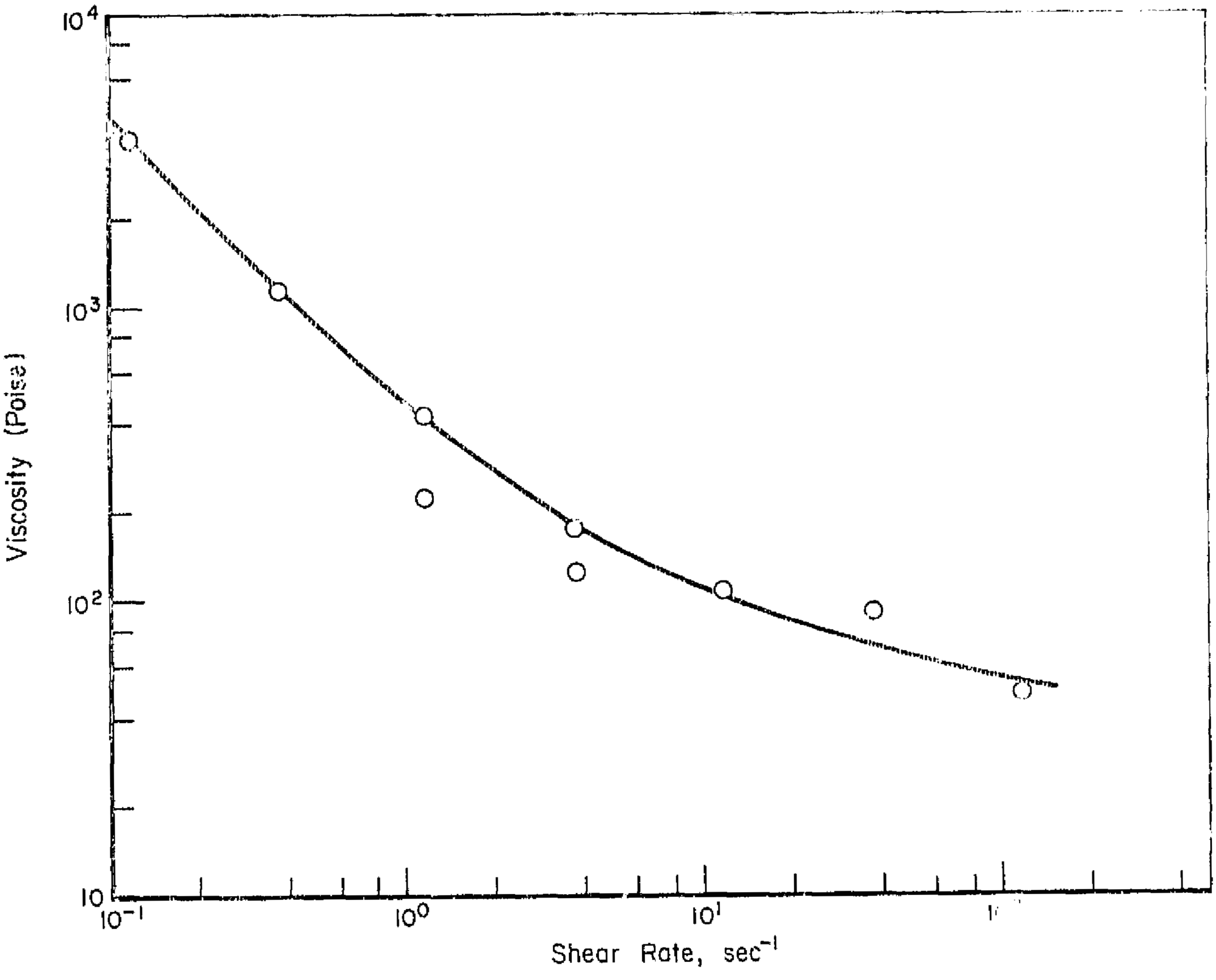


FIGURE 52. VISCOSITY OF UNAGED VITON-A (20% SOLUTION IN ACETONE). RUN 31719-53

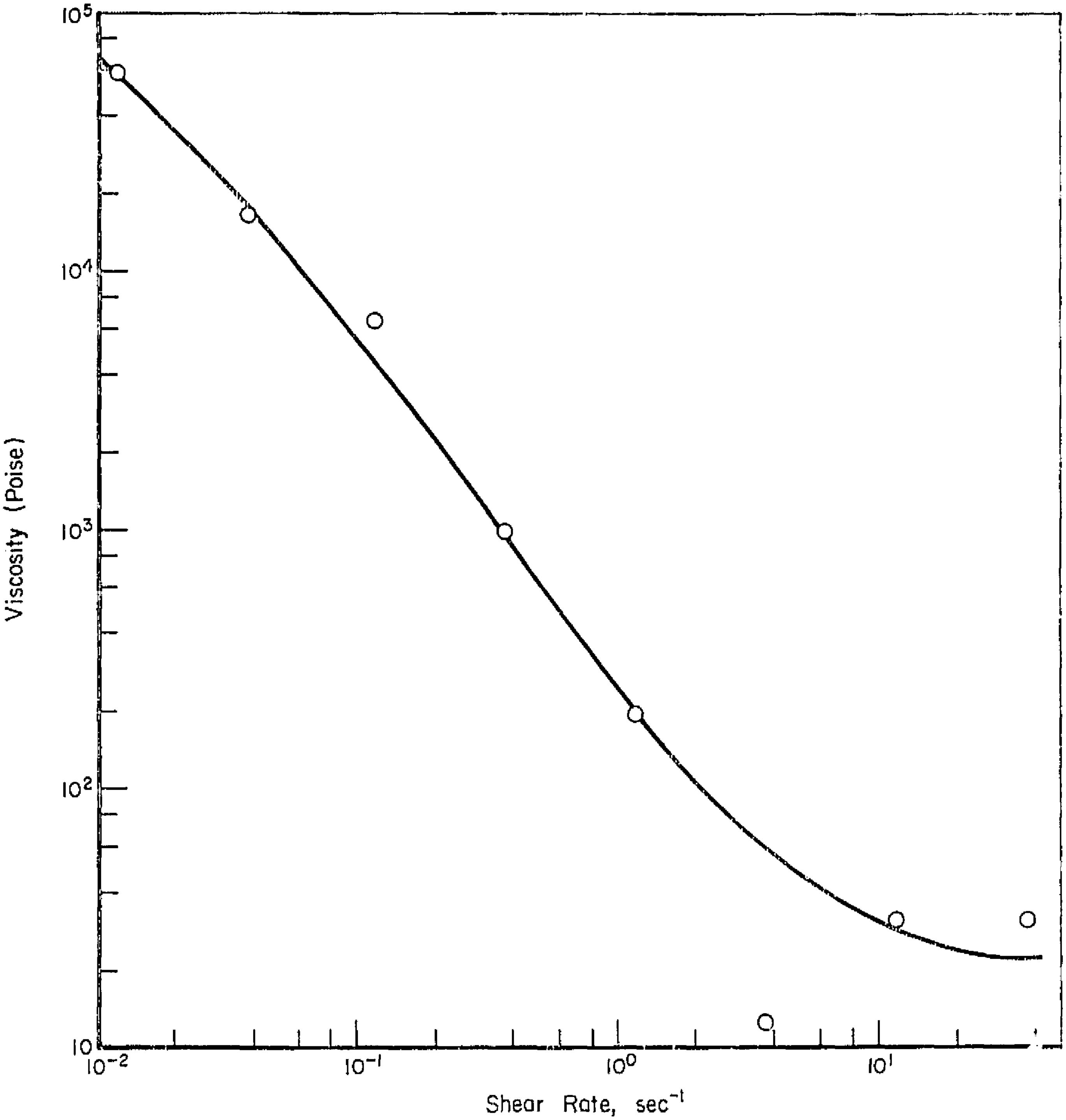


FIGURE 53. VISCOSITY OF VITON-A AGED 48 MINUTES AT 150 C (302 F) (20% SOLUTION IN ACETONE). RUN 31719-54

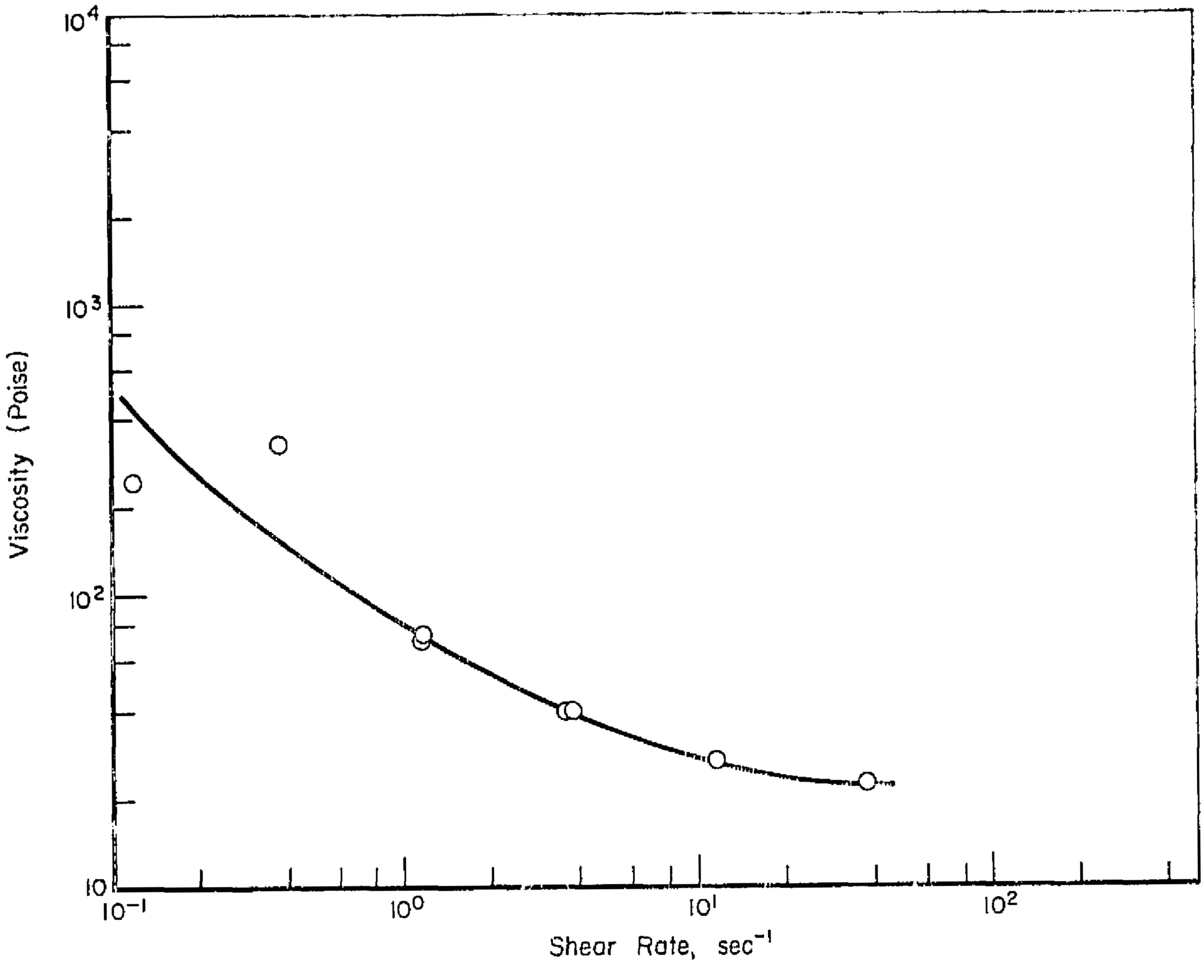


FIGURE 54. VISCOSITY OF VITON-A AGED 196 MINUTES AT 150 C (302 F) (20% SOLUTION IN ACETONE). RUN 31719-52

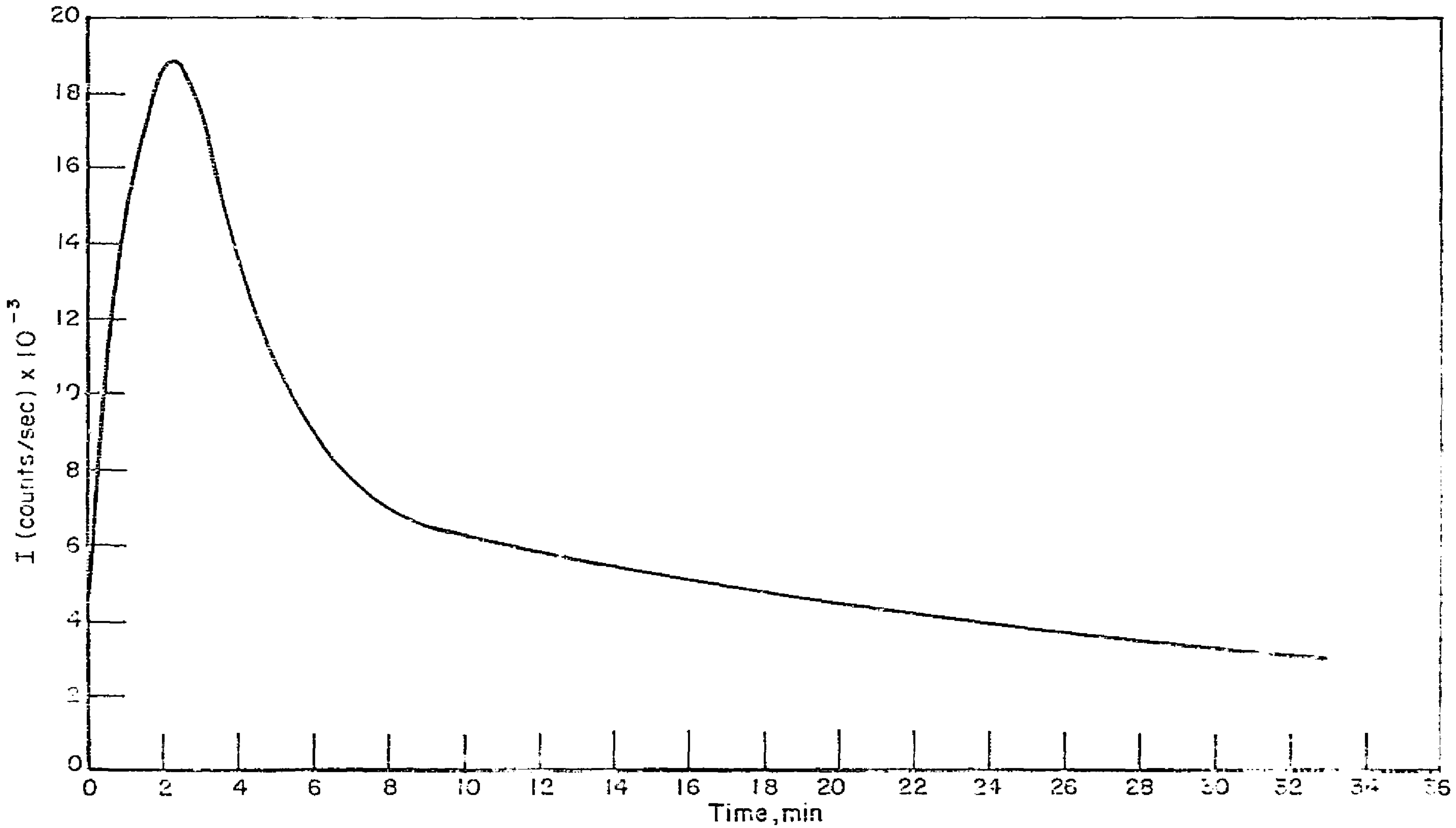


FIGURE 55. CHEMILUMINESCENCE FROM UNPURIFIED ESTANE 5703 IN OXYGEN AT 150 C (302 F). RUN 61-2

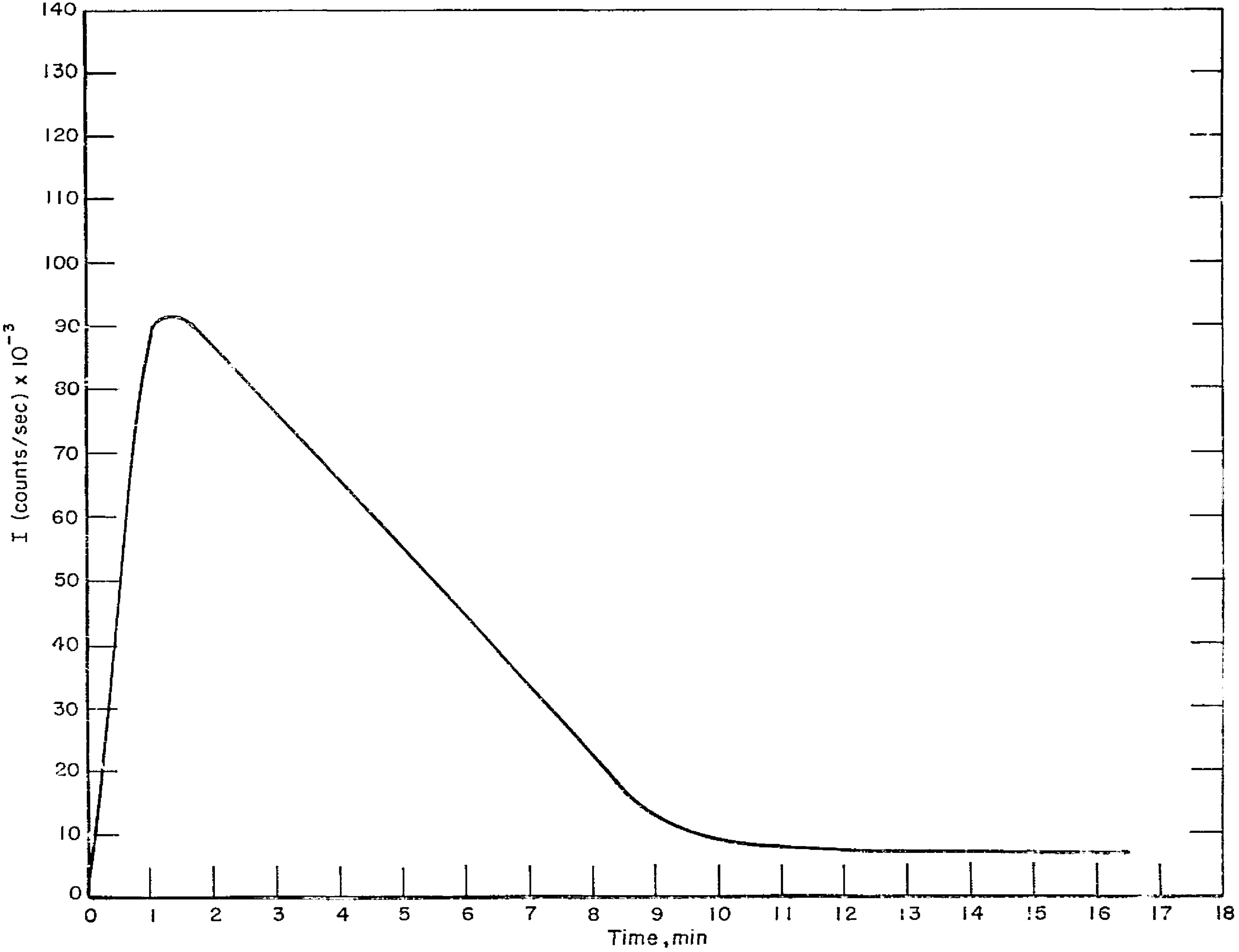


FIGURE 56. CHEMILUMINESCENCE FROM ESTANE 5703 IN OXYGEN AT 150 C (302 F). RUN 59-2

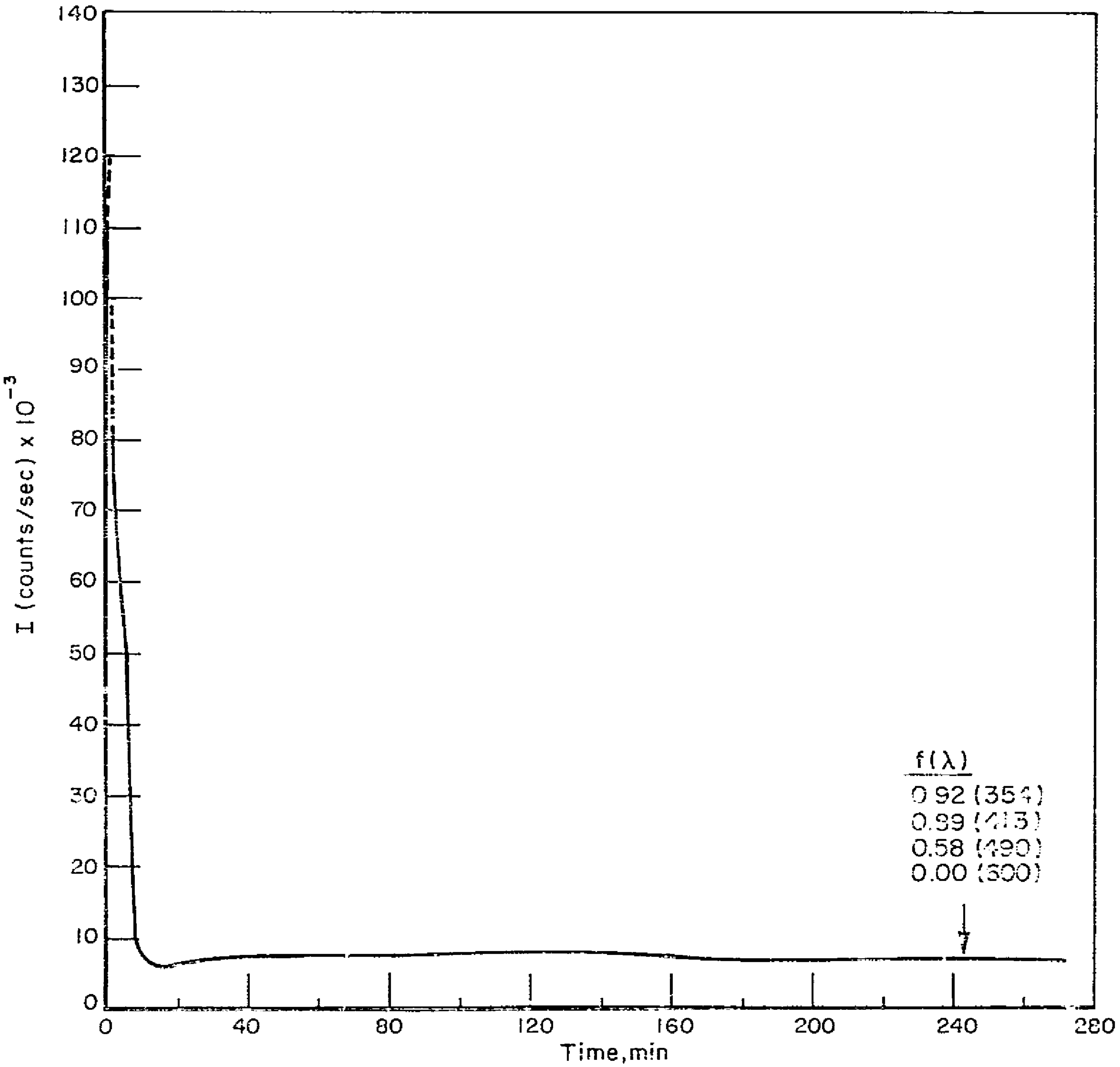


FIGURE 57. CHEMILUMINESCENCE FROM ESTANE 5703 IN OXYGEN AT 150 C (302 F). RUN [illegible]

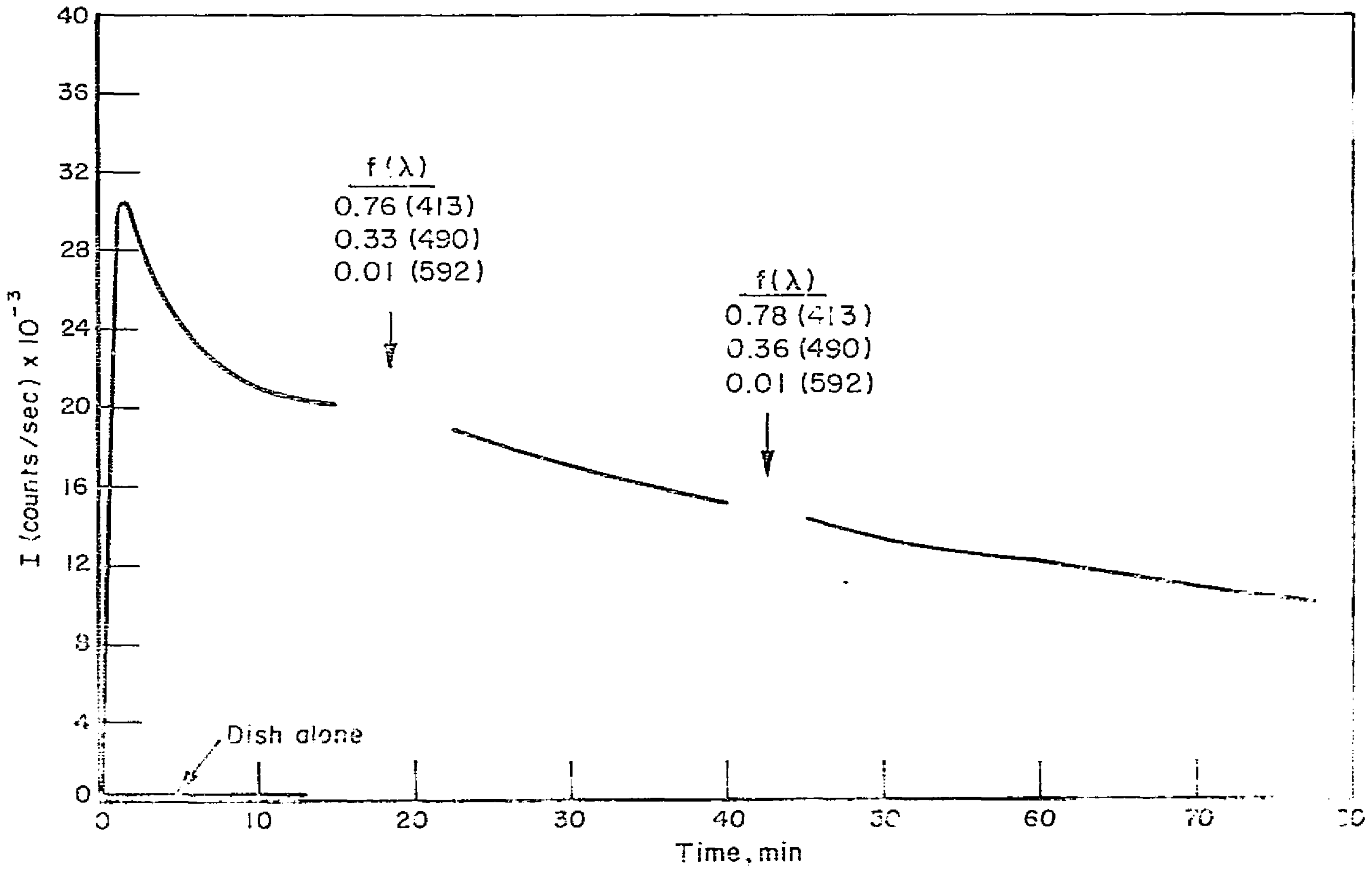


FIGURE 58. CHEMILUMINESCENCE FROM ESTANE 5703 CONTAINING 0.50% N-PHENYL-2-NAPHTHYLAMINE IN OXYGEN AT 150 C (302 F). RUN 60.

TABLE 1. CHEMILUMINESCENCE FROM POLYMERS AT 100 AND 150 C (212 AND 302 F) UNDER ARGON (PROCEDURE A)

Polymer	Chemiluminescence, counts/sec	
	100 C[(a)]	150 C[(b)]
cis-Polybutadiene 1203	4	16
Viton E60-C	7	12
Halon G-80	-	131
SBR-1500	4.3	8.6
Natural Rubber SMR-5	31	113
Silicone TRV-560	3.6	29
PL 731 Adhesive	200	125
SP 296 Composite	124	210
PL 731 and SP 296 on Titanium	85	170
PL 731 on Titanium	120	175

(a) Sample brought to 100 C under oxygen, then flushed with argon.

(b) Sample brought to 150 C under argon.

TABLE 2. APPARENT ACTIVATION ENERGIES FOR CHEMILUMINESCENCE OF POLYMERS IN OXYGEN (METHOD A)

Polymer	Activation Energy ($E_{I_{max}}$, Kcal/mole)
cis-Polybutadiene	12
Viton A	13.6
Halon G-80	17.2
SBR-1500	[12](a)
Natural Rubber SMR-5	18.6
Silicone TRV-560	17.4
PL 731 Adhesive	18.3
SP 296 Composite	19.1
PL 731 and SP 296 on Titanium	18.5
PL 731 on Titanium	18.3

(a) May not be true value. Represents best linear fit of apparently nonlinear data.

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TABLE 3. CHEMILUMINESCENCE FROM NATURAL RUBBER (MALAYA) MEASURED AT 100 C (212 F) IN OXYGEN

Sample	Time of Aging (day)	Counts/sec Initial	Normalized	Final	Normalized	Tensile Strength, (% Loss)[a]	Elongation at Break[a]
1	1	3440	2800	1560	1270	8.5	681 (init. 710)
2	3	2808	2800	1860	1860	14.5	563
3	14	2460	2800	1764	2000	49	564

[a] From literature furnished with sample.

TABLE 4. CHEMILUMINESCENCE OF POLYTETRAFLUOROETHYLENE (HALON) MEASURED IN OXYGEN AT 80 C (176 F)

Sample	Time (min)[a]	Counts/sec[b]
<u>Halon G-10</u>		
1. As received	7.5	54 (max)
	40	48
2. Same	7.5	49 (max)
3. Extracted 24 hours	2	21 (max)
	60	11
	110	11
4. Extracted 48 hours	5	14
	40	4
<u>Halon G-80</u>		
5. As received	8	173 (max)
	100	68
	17 hours	38
6. Same	12.5	150 (max)
	125	45
7. Surface abraded	8	46 (max)

[a] Samples aged in chemiluminescence apparatus.

[b] Unfiltered emission detected.

TABLE 5. CHEMILUMINESCENCE FROM CIS-POLYBUTADIENE MEASURED AT 100 C (212 F) IN OXYGEN

Sample	Time of Aging (hr)	Initial	Normalized	Final	Normalized
1	24	97.9	97.9	20.0	20.0
2	24	80.9	97.9	26.9	22.3
3	72	77.0	97.9	30.6	24.1
4	72	95.7	97.9	43.3	42.3

TABLE 6. AGING DATA FOR CURED *CIS*-BUTADIENE RUBBER (8801-52-15)

Time Aged(a)	Load at Break(b)	% Elong. at Break	Initial Modulus
0	618	500	0.071
	668	450	0.42
	435	350	0.15
	Avg. 574 (123)	433 (76)	0.21 (0.18)
100 min.	378	300	0.15
	722	480	0.15
	512	390	0.15
	Avg. 537 (173)	390 (90)	0.15 (0)
440 min.	570	360	0.18
	544	350	0.17
	362	260	0.20
	Avg. 495 (116)	323 (55)	0.18 (0.02)
1440 min. (24 hr)	588	380	0.20
	407	300	0.25
	Avg. 498 (128)	340 (57)	0.23 (0.04)

(a) At 150 C (302 F) in air.

(b) Standard deviations in parantheses.

TABLE 7. EFFECT OF MECHANICAL WORKING ON CHEMILUMINESCENCE FOR RUBBER SAMPLE 8801-4-25 (FRS 178)

Treatment	Chemiluminescence at 14 C (57 F) in O_2
None	8.7 counts per second
Stretched, relaxed	12.0
Hammered	17.4
New sample	17
Rubbed on Al surface	22

TABLE 8. EFFECT OF MILLING ON CHEMILUMINESCENCE

Polymer	Chemiluminescence, counts/g-sec Before Milling	 After Milling
Halon G-10 (extracted 24 hr)	3.2	9.6
Viton A	0	10
Silicone W-96	3.7	27
Estane 5703	58	76
cis-polybutadiene	24	28

TABLE 9. EFFECT OF COMPOUNDING ON CHEMILUMINESCENCE

Polymer	Chemiluminescence in Oxygen Counts/Sec at 24(68)	 70(158)	 150 C (302 F)
cis-Polybutadiene (highly purified)	-	ca. 800	318,000
cis-Polybutadiene (gum compound)	5	492	-
cis-Polybutadiene (4-1203, standard compound)	1	9	612

TABLE 10. CONDITIONS FOR SAMPLE RUNS (ALL IN OXYGEN AT 80 CC/MIN)

Run	Material	Temperature, C (F)	Sample	Preparation
42	W-96 Silicone	193 (379)	0.7490 g	In pyrex dish
41	W-96 Silicone	193 (379)	0.6542 g	Ditto
44	W-96 Silicone	150 (302)	0.6104 g	"
43	W-96 Silicone	150 (302)	0.5511 g	"
54	Viton A	150 (302)	0.8315 g	In pyrex dish
52	Ditto	150 (302)	0.8972 g	Ditto
50	"	200 (392)	0.8277 g	"
56-2*	"	200 (392)	0.2342 g	"
56-1*	"	200 (392)	0.3440 g	"
61-2+	Estane 5703	150 (302)	0.2622 g	In pyrex dish
59-2	Ditto	Ditto	-	Cold pressed on 0.0076 cm Al foil
59-1	"	"	-	
60*	"	"	0.7202	Concentrated from acetone solution in Al pan

* With 0.50% N-phenyl-2-naphthylamine.

\+ Crude estane containing talc additive.

TABLE 11. WEIGHT CHANGES FOR VITON-A SAMPLES IN OXYGEN

Run	Temperature C	(F)	Time (hr)	Init. Wt. (g)	Final	% Loss
54	150	(302)	0.80	0.8315	0.8124	2.3
52	150	(302)	3.17	0.8972	0.8687	3.2
50	200	(392)	6.75	0.8277	0.7883	4.8
51	200	(392)	0.55	0.9212	0.8989	2.4
56-1*	200	(392)	0.55	0.3440	0.3376	1.9
56-2*	200	(392)	6.	0.2342	0.2300	1.8

With 0.50% antioxidant.

TABLE 12. SOLUBILITY CHANGES IN HEAT-AGED VITON-A

Run	Time (hr)	Temp., C (F)	Acetone-Soluble Product (wt %)	Gelled Product (wt %)	Gel Wt Acetone-Insoluble Wt
51	0.5	200 (392)	100	0	--
50	6.8	200 (392)	14	86	28
56-1*	0.5	200 (392)	100	0	--
56-2*	6.9	200 (392)	28	72	26
54	0.8	150 (302)	100	0	--
52	3.3	150 (302)	100	0	--

* With 0.50% N-phenyl-2-naphthylamine.