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A STUDY OF THE EFFECTS OF NUCLEAR RADIATIONS ON ELASTOMERIC COMPOUNDS AND COMPOUNDING MATERIALS

JOHN W. BORN

THE B. F. GOODRICH COMPANY

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FOREWORD

This report was prepared at the B. F. Goodrich Company Research Center under Supplemental Agreement No. S1(55-1021) to USAF Contract No. MIPR AF33(616)-2308. The contract was initiated under Project No. 1252, "ANPP Development Support Project," Task No. 73023, "Radiation Effects," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Messrs. E. R. Bartholomew and W. W. Jackson acting as project engineers.

This report covers work conducted from January 1955 to January 1956.

Mr. A. Hawthorne made the studies with the infrared spectrophotometer. Mr. E. H. Rowe analyzed the volatile products of irradiation with the mass spectrometer. Mr. R. A. Mathes assisted in the selection of special antioxidants and antiozonants as potential Anti-Rads. Dr. R. G. Bauman contributed to the glass dosimetry study with the design of the plate holder and calibration of the dosimeter glass. Their contributions along with those of Messrs. R. H. Shearer, P. E. Brenneman, and W. H. Showen of the Department of Technical Services Research are gratefully acknowledged. Appreciation extends further to the assistants who participated in the development.

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ABSTRACT

Continuous stress relaxation measurements in air detail the effects of temperatures ranging from 25° through 80°C. on radiation damage to rubber compounds. The order of decreasing resistance to damage is natural rubber, GR-S, Neoprene GN, and Hycar 1002 for gum rubber compounds and GR-S, Hycar 1002, natural rubber, and Neoprene GN among the black compounds. Graphs illustrate these results.

Stress relaxation measurements, volume swell measurements, infrared absorption analyses, and mass spectral analyses provided fundamental information about radiation damage. They showed further that heat and radiation damage differ significantly.

The Anti-Rad screening program and the study of the effect of radiation upon dynamic properties of rubber have reached the physical testing stage. Compounds containing 91 specially-selected potential Anti-Rads have received optimum cures, and samples have undergone gamma irradiation. The purpose of the screening is to provide criteria for the synthesis of specific new Anti-Rads.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

The study of Cobalt 60 gamma radiation effects on rubber compounds continued during 1955 under the first supplemental agreement to the original contract. The research fell into four main categories: namely, a development of radiation damage inhibitors termed Anti-Rads; a measurement of static and dynamic physical properties of eight standard rubber compounds as a function of radiation exposure; a study of the effect of heat on radiation damage to rubber; and an attempt to correlate the changes in molecular structure produced by nuclear radiation with the changes in physical properties which result. New equipment was developed which permitted a 48-fold increase in the number of rubber samples for the measurement of stress relaxation during radiation exposure. Measurements were made of the flux inside the Cobalt 60 Source Number Co-17.

II. EXPERIMENTATION

2.1 Dosimetry

Dosimetry, the measurement of radiation dosage, is essential to the proper evaluation of radiation test results. In the 1954 development at this laboratory the dose rate value which was obtained at Brookhaven National Laboratory for our source-shield assembly was used. This year a check was made of both the absolute dose rate at the center of the radiation chamber and of the variation in dose rate with location in the chamber.

Numerous dosimetry methods are available: namely, calorimetry, glass coloration, and gas evolution among the physical methods and modification of aqueous methylene blue solution, aqueous ferrous sulfate solution, aqueous ferrous sulfate-cupric sulfate solution, aqueous ceric sulfate solution, cellophane-dye systems, and polyvinyl chloride - methyl violet systems among the chemical methods (references 1-11 inclusive).

For the present study a dosimetry method was required which is simple to use, gives reproducible and accurate results, and can serve as a universal method of measurement to permit reliable comparisons of results among independent laboratories. The most suitable system for absolute dosimetry appeared to be the ferrous sulfate dosimeter (7). A survey conducted at Brookhaven National Laboratory showed the reliability of independent measurements using this system. The detailed results are reproduced in Table IX. The principal drawback of the system has been the lack of agreement on the number of ferrous ions oxidized by 100 electron volts of absorbed radiation energy (1, 2, and 6). However, a recent study by Lazo, Dewhurst, and Burton (2) ostensibly resolves the controversy. The most useful system for plotting radiation fields appears to be glass dosimetry. Accordingly, these two systems were used in conjunction.

For the absolute dose rate determination Dr. W. P. Tyler of this laboratory formulated an improved ferrous sulfate dosimetry procedure. Aqueous ferrous sulfate solution was placed in a 25 x 50 mm. glass weighing bottle with a glass stopper. Two such dosimeters were placed in the region of the geometric center of Cobalt 60 Source Number Co-17 housed in Lead Shield Number 10. They were exposed to the gamma radiation for periods ranging from 10 to 15 minutes. The radiation induced oxidation of the ferrous ions to ferric ions in proportion to the cumulative dose. The concentration of ferric ions in both the irradiated and unirradiated dosimeter solution was determined by measuring the optical density at a wave length of 305 $m\mu$ with a spectrometer. The absolute radiation dose rate on 10 November 1955 was $(1.69 \pm 0.02) \times 10^5$ roentgens - equivalent - physical per hour. This value agrees well with the figure obtained at Brookhaven National Laboratory after correction for radioactive decay; namely, 1.71×10^5 reps per hour. The latter two figures were obtained by applying the G value used at Brookhaven National Laboratory; namely, 15.4 micromoles of ferric ion produced per liter of dosimeter solution for each 100 electron volts of radiation energy absorbed. The application of the G value obtained by Burton and co-workers; namely, 15.8 ± 0.3 micromoles per liter per 100 electron volts, would reduce our dose and dose rate figures by 2.5 per cent.

Small rectangular glass dosimeter plates were used in plotting the radiation field. The plates were 10 x 25 x 1 mm. rectangles cut from glass microscope slides. A special brass holder was made, having the same dimensions as a sample cell, for mounting the dosimeter plates in the spectrophotometer (Figure 1). The variation in optical density of the glass with radiation exposure was plotted in order to produce a dose calibration curve (Figure 2).

Dosimeter plates were then attached to a cylindrical wire frame for insertion into the sample canister of the Cobalt 60 source-shield assembly. The frame measured 1.5 inches in diameter and 13 inches in length (Figure 3). The dosimeter plates were cleaned, wrapped in aluminum foil to prevent fading and marring of the surface, and taped to the frame. Sixty-eight plates were used. Twelve plates were arranged along the axis of the frame from top to bottom, designated C1 through C12, respectively (Figure 4). Four plates were arranged tangent at 90° separations to each of 14 circles about the vertical axis. There were two circles with diameters of 1.50 and 0.75 of an inch evenly spaced at seven positions from top to bottom on the frame. The glass plates around the 0.75-inch diameters from top to bottom are 1M1-4 through 7M1-4 from top to bottom, respectively. The glass plates around the 1.50-inch diameters from top to bottom are designated 101-4 through 701-4, respectively. The optical density measurements (Table X) prove that there is no significant variation in the radiation field inside the sample canister within the source from its bottom to a height of ten inches. All 58 plates exposed in this region of the field exhibited the same optical density. Above this region the absorbance at the 5200-Å wave length of the spectrophotometer decreased with distance.

The above two dosimeter systems satisfy our immediate requirements. Although glass dosimeters can be packaged with samples which are irradiated at other facilities such as Brookhaven National Laboratory and used to measure the radiation dose, they have several important drawbacks. First, the glass is inorganic and has a higher specific gravity than rubber compounds. Therefore, the mode and rate of energy dissipation during irradiation must be different in the two cases. Second, the radiation-caused color of the glass plates fades at an appreciable rate which is affected by temperature. Since the time and temperature between irradiation and the determination of optical densities of the dosimeter plates are difficult to control, the dose measurements are open to error when irradiations take place outside our laboratory. Third, the plates are subject to breakage. For these reasons a new dosimeter system is being sought. The ideal dosimeter from our viewpoint should be based on a solid high polymer; namely, an elastomer or a plastic, which will dissipate absorbed radiation energy much as rubber polymers do. It also should not alter its dose-detailing properties during the return shipment of the samples after irradiation. Several potential systems are under consideration. One system involves a plastic and the change in birefringences as a function of radiation dose. A second system involves a plastic whose optical density increases with radiation dose. A third system involves the change in the swelled volume of a standard pure gum rubber sample as a function of dose.

2.2 Stress Relaxation Measurements

The study of the effect of Cobalt 60 gamma radiation on the stress relaxation of vulcanized pure gum natural rubber was completed. The purpose of the study was to gain a fundamental understanding of the effect of nuclear radiation on the molecular structure of this representative rubber. The ultimate goal is to relate these structural changes to undesirable changes in the physical properties of rubber materials and to improve their radiation resistance by inhibiting or avoiding such changes. Two types of stress relaxation were measured in air and in vacuum with a dipsometer, which is a specially-designed instrument and is described in Appendix I.

Intermittent stress relaxation measurements reveal the effect of progressive cross-linking and chain scission on the Young's modulus of rubber samples. Figure 5 shows the intermittent stress relaxation of pure gum natural rubber in a vacuum during irradiation and of an identical control sample without irradiation. The net change in stress is caused by irradiation. The stress increased 18 per cent initially with the maximum at a dose of 10^6 roentgens-equivalent-physical (reps). Thereafter, it decreased to the initial stress at an exposure of 1.1×10^8 reps. Figure 6 shows the effect of irradiation in air on the intermittent stress as compared with a control study without irradiation. The stress decreased to 79 per cent of the original value at an exposure of 1.9×10^7 reps. after which the sample broke.

Continuous stress relaxation, the second type of measurement, details the effect of radiation on the modulus of a sample which is maintained in a stretched condition throughout testing. It shows the effect of chain scission alone on the Young's modulus of rubber under constant elongation. Figure 7 reveals the change in continuous stress of the sample in vacuum both during and without gamma irradiation. The continuous stress during irradiation decreased to 44 per cent of the original value at a radiation dose of 7.4×10^7 reps and appeared to approach an asymptote of 40 per cent. The change in air both during and without irradiation is shown in Figure 8. The stress decreased during irradiation to 4 per cent of the original value at a dose of 5.9×10^7 reps and then broke.

A comparison of the above results leads to several important conclusions. First, radiation damage to rubber involves both cross-linking and chain scission and is the net result of the two processes. Second, the irradiation may initially improve the state of cure of the rubber sample. Third, the radiation damage to rubber is much greater in air than in vacuum. Fourth, the radiation damage in vacuum appears to approach a maximum asymptotically. These conclusions led to the hypothesis that specially-developed radiation damage inhibitors might be added to rubber which would prove highly protective. The study described below under Anti-Rad Development grew directly from the latter hypothesis and the discovery of a number of inhibitors in the 1954 study (13).

Since the dipsometer accommodated only one rubber sample at a time and occupied most of the space in the radiation chamber, relatively few stress relaxation studies could be made during irradiation. Therefore, the Multilaxometer was developed at this laboratory. A detailed description of the instrument appears in Appendix II. The Multilaxometer is designed to hold 48 rubber samples, permit their irradiation either stretched or unstretched, and measure either continuous or intermittent stress relaxation with a minimum disturbance of the rubber samples. There are dual assemblies which permit simultaneous measurements of the irradiated samples and the unirradiated control samples. Whereas only pure gum natural rubber was used in the dipsometer studies, four gum rubber and four black rubber compounds were involved in the Multilaxometer measurements. A.S.T.M. gum and black rubber recipes of natural rubber, GR-S, Neoprene GN, and Hycar 1002 (a nitrile-type elastomer) were used. The recipes appear in Table XI. Six samples of each of the eight compounds were irradiated through radiation doses of approximately 1×10^8 reps, and their continuous stress relaxation at 80 per cent elongation was measured periodically during irradiation. Each sample was 1.25 inches long, 0.25 inches wide, and nominally 0.025 inches thick. This technique was applied to measurements at room temperature and at elevated temperatures.

Figures 9 through 22 give the condensed data from the latter continuous stress relaxation measurements. The figures for the unirradiated and the irradiated samples of any given rubber compound face each other for easy comparison. Each curve represents the average result of six sets of data, among which the agreement was generally good. The first portion of each curve, covering approximately the first 24 hours of stress relaxation, represents the relaxation prior to beginning irradiation. Several general observations can be based on these figures. First, as is well recognized, raising the temperature increases the rate of deterioration of rubber materials. Second, increasing the radiation dose increases the deterioration rate. The data of Table XII, which have been obtained from Figures 9 through 22, indicate no clear-cut difference between the sum of the separate effects of heat and radiation on rubber and the effect of the two factors combined. These data have been corrected to exclude the stress relaxation during the 24 hours prior to irradiation. If the data are not corrected for the relaxation prior to irradiation, the results in Table XIII are obtained. In the majority of the latter cases the deterioration caused by heat and gamma radiation combined exceeds the sum of the deteriorations caused by heat and radiation separately. Third, from an applied research standpoint Figures 23 through 29 show the effect of heat upon the mechanical failure of the rubber compounds during irradiation in air, where the failure is variously defined as a 25, 35, or 50 per cent decrease in equilibrium 80 per cent modulus.

2.3 Anti-Rad Development

The 1954 contract study resulted in the discovery of radiation damage inhibitors which were subsequently termed Anti-Rads. These are organic chemical additives for rubber compounds which inhibit radiation damage of said compounds. The WADC Technical Report 55-58 (13) describes the experiment leading to the discovery. During 1955 a considerable number of potential Anti-Rads were selected for a screening study. The purpose of the study was to correlate chemical structure with inhibiting effectiveness. The resulting criteria are to be used in the synthesis of specific new Anti-Rads.

The program of synthesizing new and more effective Anti-Rads has six phases: first, the selection of potential Anti-Rads from existing chemical supplies; second, the preparation of rubber compounds containing these chemical agents; third, the gamma irradiation of samples from the rubber compounds; fourth, the physical testing of the irradiated samples; fifth, the evaluation and comparison of the numerous agents' effectiveness; and sixth, the selection of specific Anti-Rads based on criteria obtained from the first five phases.

We chose the potential Anti-Rads to include among them the molecular structures and reactive chemical groups which are considered effective. A basic master compound was selected. This was Compound 1GFA7, an A. S. T. M. natural rubber tire tread stock. The 91 potential Anti-Rads were compounded separately into the master recipe. Five parts of Anti-Rad were added per hundred parts of natural rubber in each case to obtain 91 separate compounds. Appendix III lists these rubber compounds according to Anti-Rads. Those in Compounds 1GFA13 through 1GFA47 are commercial rubber chemicals commonly used in rubber manufacture. Compounds 1GFA50 through 1GFA75 contain Anti-Rads which were synthesized for a prior separate study by personnel at the B. F. Goodrich Company Research Center. The potential Anti-Rads in Compounds 1GFA77 through 113 are mostly Commercial chemicals which are not generally used in rubber manufacture.

Optimum cures were determined for the 91 rubber compounds. In a number of cases the additive accelerated cure. In some instances it improved the cure.

Rectangular samples which measured 0.25 inch x 2.75 inches were died from cured sheets nominally 0.025 inch thick for irradiation and testing. The samples were exposed to a series of Cobalt 60 gamma radiation doses of 0.1, 1, 10, 35, 70, and 100 megaroentgens - equivalent - physical (megareps) at Brookhaven National Laboratory under the supervision of Mr. O. A. Kuhl. This series of irradiations was completed in December, 1955. Similar samples are now receiving radiation doses of 500 and 1000 megareps.

The physical tests which have been scheduled for these irradiated samples include measurements of tensile strength, ultimate elongation, and 100 per cent modulus.

The criteria obtained from this screening study will be used in selecting chemical compounds for synthesis as new, specific Anti-Rads. Such synthetic inhibitors will then be evaluated in the same manner as above.

2.4 Dynamic Testing of Irradiated Rubber Compounds

Prior to this stage our study has not included dynamic physical tests of irradiated rubber samples. Because of the need for engineering information about the effect of nuclear radiation on the service properties of rubber products, a dynamic test program was developed.

Eight representative rubber compounds were chosen in the first study. Standard gum and black recipes based on natural rubber, GR-S, Neoprene GN, and Hycar OR-25 were selected from Tentative Methods of Sample Preparation for Physical Testing of Rubber Products, A.S.T.M. Designation: D15-54T, according to the procedures set forth therein. The recipes appear in Table XI.

The test program comprises nine tests which will produce thirteen physical property values for each rubber compound at each radiation dose. The tests include measurements with the Electrographic Stress-Strain Machine, the 100 per cent modulus machine, the Yerzley Oscillograph, the Goodrich Flexometer, the Gehman low temperature modulus machine, the Pico abrader, the Shore A Durometer, the compression set apparatus, and the Beatty belt flex tester. The thirteen physical properties to be measured are tensile strength and ultimate elongation for broad general comparison, 100 per cent modulus, static modulus, dynamic modulus, the load required for a 20 per cent deformation, dynamic resilience, low temperature modulus and brittle point, abrasion resistance, Durometer hardness, compression set, and belt flex resistance.

The required sample specimens were given optimum cures and then underwent Cobalt 60 gamma irradiation at Brookhaven National Laboratory. The irradiation program included a series of doses: namely 0.1, 1, 10, 35, 70, and 100 megaroentgens - equivalent - physical (megareps). These irradiations are still in progress at the close of 1955 and are nearing completion. Thereafter, the physical tests will be run. Radiation doses of 500 and 1000 megareps and similar physical tests are also scheduled.

2.5 Studies of Changes in Molecular Structure

There are two obvious approaches to improving the resistance of rubber compounds to radiation damage. One is to put chemical additives into the rubber compounds which will inhibit such damage. The Anti-Rad development already shows success in this respect and promises further benefits. The other approach involves the synthesis of a new elastomer with superior resistance to radiation damage. Before a synthesis can be conducted with any assurance of success, much must be learned about the fundamental effects of nuclear radiation on the molecular structures of the elastomeric systems and about the relationship of changes in structure to changes in physical properties. Four types of measurements have been made so far to provide initial information.

2.5.1 Measurements of intermittent and continuous stress relaxation of pure gum natural rubber in air versus in vacuum both with and without gamma irradiation were made. They permit evaluation of the change in molecular structure as a function of time and irradiation or of time alone. Specifically, we calculated the change in S, the number of network chains of all kinds per cubic inch of cured pure gum rubber which remain unbroken and unrelaxed at the time of measurement. The equation which was used and the calculated values appear in Appendix IV. Figures 32 through 35 represent the results of these evaluations. Under the conditions of air versus vacuum environment and irradiation versus no irradiation, a greater change in S occurs during continuous stress relaxation than during intermittent relaxation. The change in S is strikingly greater for a sample stressed in air than for one stressed in vacuum. It is also noteworthy that both samples which were irradiated in air broke, whereas those irradiated in vacuum did not break. During irradiation in air the intermittently stressed sample broke after a much shorter radiation exposure than did the continuously stressed sample.

2.5.2 Determining changes in M_c, the number average molecular weight of polymer chain between cross links, by swelling measurements is a second useful approach to understanding molecular changes which occur in rubber during irradiation. To quote Frith and Tuckett (14), ''When an amorphous polymer is vulcanized, it is converted into a stable network structure, insoluble in all solvents; it will, however, still swell freely in many liquids to different equilibrium values.'' ''The situation inside the network is very like that which occurs when a vulcanized polymer is stretched by the external application of a force, and which is discussed fully in Chapter 8.'' With benzene as the swelling agent and irradiated pure gum natural rubber strips as samples, we measured the strip lengths before and after swelling for 16 hours. Then the equation in Appendix V was used to compute the M_c values recorded therein. Measurements of M_c for eight natural rubber gum compounds appear as a function of radiation dose. All eight compounds had been irradiated approximately one year before in Cobalt 60 source. Seven of the compounds contain a different antioxidant in each case, and one compound is the control stock having no antioxidant in it. The eight compounds are based on the same recipe as follows:

Parts by Weight	Pigment
100	Natural Rubber
5	Zinc Oxide
1	Stearic Acid
0.5	Mercaptobenzothiazole
2.5	Sulfur
3	Antioxidant

Compound 1GEA109 is the control compound, having the above recipe without antioxidant. The other seven compounds have the above recipe with the following antioxidants:

Compound 1GEA	Antioxidant
110	p-Methoxyphenol
111	p-Dimethoxybenzene
112	1,3-Naphthalenediol
113	1,5-Naphthalenediol
116	N, N'-Di-beta-naphthyl-p-phenylenediamine
118	2,5-Ditertiarybutylhydroquinone
124	N, N'-Diphenyl-p-phenylenediamine

It is interesting to compare the list of the above seven Anti-Rads in order of decreasing effectiveness obtained by the above method with that obtained by stress-strain measurements a year earlier. Table XIV makes this comparison. The ratings by the two methods disagree in part. The Anti-Rads 2,5-ditertiarybutylhydroquinone and p-methoxyphenol are paired in both lists, as are the two phenylenediamines on the one hand and p-dimethoxybenzene and no Anti-Rad on the other. However, the relative ratings differ. The stress-strain rating of effectiveness appears the more reasonable of the two from the standpoint of chemical structure of the Anti-Rads. The disagreement between stress-strain and swelling ratings may result from changes in the samples which took place during the year which elapsed. A further investigation of post-irradiation effects will be made.

2.5.3 Attempts have been made to determine by infrared analysis what changes in molecular structure result from irradiation of rubber compounds. The results of infrared analysis of thin vulcanized rubber films after irradiation with x-rays in nitrogen gas were given in WADC Technical Report 55-58 (13). The 1955 infrared analysis involved gamma irradiation of similar vulcanized rubber films in air. Five gum rubber compounds were studied; namely, Compounds 1GFA2 through 6 (Table XI), inclusive, based on natural rubber, GR-S, Neoprene GN, Hycar 1002, and butyl rubber, respectively. The radiation exposures ranged from 1 x 10^5 through 1 x 10^8 reps. First, the infrared absorption curves of the unirradiated samples were graphed. The films next were placed in ambient air in the Cobalt 60 Source Number Co-17. A sample film of each rubber was removed after each of seven exposures. The films were kept in a nitrogen atmosphere after irradiation until they were analyzed.

Of the molecular changes which the infrared spectrophotometer detects, oxidation is the main effect of irradiation in air and may obscure other changes. This qualification is important. GR-S and Hycar 1002 rubber compounds show the least effect. That is, the hydroxyl and carbonyl peaks are not as strong in their spectra as in the spectra of irradiated Neoprene GN and natural rubber compounds. No butyl sample survived an exposure greater than 5 x 10^6 reps, being degraded to a low molecular weight gel. Neoprene GN was slightly oxidized prior to irradiation.

In the previous study of X-radiation effects on natural rubber, the cured films were protected from oxidation by flushing the container with a steady flow of nitrogen. Under these conditions the decrease in the height of the infrared absorption peak at a wavelength of 11.9 microns, which characterizes the $-C(CH_3)=CH-$ double bond, indicates that radiation damage to natural rubber involves a decrease in ethylenic unsaturation. At the exposures which previously produced significant changes in unsaturation, oxidation of the film caused such a large increase in absorption that individual peaks in the 11.9 micron region were not resolved. A detailed description of the effects of irradiation in air appears in Appendix VI. This irradiation study will be repeated with the sample films in a nitrogen atmosphere to prevent oxidation.

2.5.4 The mass spectrometer was also used to study structural changes in rubber compounds resulting from gamma irradiation. The vulcanized gum rubber compounds which were used were as follows: 1GFB1 (Neoprene GN), 1GFB2 (Hycar 2001), 1GFB3 (natural rubber), and 1GFB4 (Hycar 1001). The recipes for the latter compounds appear in Appendix VII. Approximately three grams of each compound were cut into small bits and placed in break-seal glass tubes. A measured amount of helium was added as an internal standard. This was done by evacuating sample and tube, introducing the helium, allowing air to enter until atmospheric pressure was reached, and sealing the tubes. All samples were then exposed to a Cobalt 60 gamma ray dose of 1 x 10^8 reps. After the irradiation the sample tubes were attached to the gas sample system of the mass spectrometer, the internal seals were broken, and the volatile irradiation products were cooled to liquid nitrogen temperature. The uncondensed fraction was analyzed quantitatively for hydrogen, helium, carbon monoxide, and methane. The helium analysis permitted relating the other results to the sample weight. The experimental values appear in Table XV.

The oxygen was quite effectively removed from the sample atmosphere by oxidation of the elastomers. No oxides of nitrogen were detected. No hydrogen chloride was detected from the Neoprene GN, but experience in the pyrolysis of chlorinated polymers suggests that the HCl is strongly absorbed on the glass interior surface of the mass spectrometer sample system.

A comparison of these analytical results indicates that Neoprene GN is the most resistant of the four elastomers to cross-linking, as shown by the low hydrogen liberation. Natural rubber is the most resistant to chain scission, as shown by the low methane production. Hycar 2001 (a butadiene-styrene copolymer with a high styrene ratio) appears to be the most resistant to oxidation. This latter conclusion is made more evident if the carbon monoxide content of each sample is corrected for the different oxygen contents in the sample tubes before irradiation. Table XVI illustrates this point. It is interesting to note that the Hycar 2001, which has the highest aromatic group content, has the best all-round resistance to radiation damage.

The fraction of the gaseous product condensable at liquid nitrogen temperature and volatile at room temperature was examined also. No quantitative analyses were made on this portion, but all samples were mainly carbon dioxide. This shows again that oxidation is the principal radiation damage detected by the spectral analyses.

A comparison of the volatile products of pyrolysis with those of gamma irradiation showed important differences. Only irradiation produces hydrogen and methane. Both processes promote oxidation. Irradiation produces more hydrocarbons than does the heat treatment. This information supports the belief that an effective age resistor or antioxidant is not necessarily effective as an Anti-Rad.

III. SUMMARY AND CONCLUSIONS

The second year's research on the effects of nuclear radiation on rubber compounds and compounding ingredients fell into four main categories: first, the development of specific new Anti-Rads (radiation damage inhibitors); second, the study of radiation effects on the static and dynamic physical properties of rubber compounds; third, a study of the correlations between changes in the molecular structure and changes in physical properties of rubber compounds as a result of irradiation; and fourth, the effect of heat upon the rate and extent of radiation damage to rubber. Also, the radiation flux of the Cobalt 60 Source Number 17 - Lead Shield Number 10 assembly was determined absolutely, and the radiation field inside the source was plotted.

Ferrous sulfate dosimetry gave an absolute radiation dose rate of $(1.69 \pm 0.02) \times 10^5$ reps per hour on 10 November 1955 in very close agreement with the Brookhaven National Laboratory figure of 1.71×10^5 reps per hour after correction for radioactive decay. It was concluded from these results and the comparison of the other independent results in Table I that the ferrous sulfate dosimeter is highly reliable for the measurement of Cobalt 60 radiation doses.

The 70 per cent modulus of pure gum natural rubber increased 18 per cent during irradiation in vacuum, reaching a maximum at 10^6 reps, and then decreased to the original value at a dose of 10^8 reps. The 70 per cent modulus decreased to 79 per cent of the original value at a dose of 1.9×10^7 reps in air, and the sample broke. The latter values were obtained from intermittent stress relaxation measurements. From them we conclude that radiation vulcanization was the net effect of the initial 10^6-rep dose in vacuum and that subsequently chain scission caused progressive failure. It is important to note, however, that even after the 10^8 rep dose in vacuum the modulus was equal to the original value. The presence of oxygen during irradiation promotes chain scission, speeding the sample failure.

In continuous stress relaxation the failure of the rubber at 70 per cent elongation was more rapid and pronounced. The continuous stress during irradiation in vacuum decreased to 44 per cent of the original value at a dose of 7.4×10^7 reps and appeared to approach an asymptote of 40 per cent thereafter. The stress decreased during irradiation in air to 4 per cent of the original value at a dose of 5.9×10^7 roentgens, and the sample broke. The conclusion is that the presence of oxygen or ozone or both contributes significantly to radiation damage of rubber but is not solely responsible. The question of the extent of damage caused by dissolved oxygen in the rubber during irradiation remains to be answered. Enveloping a rubber product in an inert atmosphere such as helium or nitrogen would reduce the radiation damage rate. The latter two studies gave engineering information about the gross and net radiation - induced changes in 70 per cent modulus of pure gum natural rubber under both intermittent and continuous stress.

The Multilaxometer, a 48-sample apparatus for measuring stress relaxation during irradiation, was designed and built. It provided continuous stress data for four gum and four black rubber compounds during irradiations at 25°, 40°, 50°, 65°, and 80° C. in air. The order of decreasing resistance to damage is natural rubber, GR-S, Neoprene GN, and Hycar 1002 for gum rubber compounds and GR-S, Hycar 1002, natural rubber, and Neoprene GN among the black compounds. The radiation damage rate increased with temperature. A change in the slope of the damage rate-versus-temperature curve and hence in the activation constant of the damage reaction indicated a change in the reaction mechanism with increasing temperature. It was concluded further that the sum of the separate effects of heat and radiation equals the combined effect; there is no synergism.

The Anti-Rad screening program is aimed at the discovery of the most effective chemical structures in the inhibition of radiation damage. Ninety-one potential Anti-Rads representing nine classes of organic chemicals and possessing various combinations of the structures considered effective were chosen for evaluation. At present the compounding, curing, and irradiation have been completed. The physical testing has begun. This program has taken longer than expected. The screening results should appear in the next progress report. Criteria will be drawn from said data to guide the synthesis of new specific Anti-Rads.

The determination of static and dynamic physical properties of standard gum and black compounds of natural rubber, Neoprene GN, GR-S, and Hycar 1002 reached the physical testing stage. The measurement of thirteen physical properties of the irradiated samples is ready to begin. In both of the latter studies the Cobalt 60 gamma radiation doses ranged from 10^5 through 10^8 reps.

The changes in molecular structure of rubber polymers during irradiation were studied in four ways: by stress relaxation measurements, by volume swell measurements, by infrared absorption analysis, and by mass analysis of the volatile products. Stress relaxation curves showed that cross-linking and chain scission occur concurrently to give net radiation damage, the damage rate is much faster in air than in vacuum, the extent of damage is greater in air than in vacuum, and the samples break in air while remaining unbroken in vacuum during irradiation. Volume swell measurements of seven Anti-Rad protected pure gum natural rubber compounds one year after irradiation and stress-strain testing gave a different rating of the Anti-Rads. The discrepancy may be due to post-irradiation effects. A more detailed study of such effects is scheduled. Of the changes detected by infrared absorption analysis the major change in gum natural rubber during irradiation by x-rays in nitrogen was a decrease in unsaturation. The major change during gamma irradiation in air which was detected was oxidation. Comparisons of the latter oxidation effects are given for gum and black compounds of natural rubber, Neoprene GN, GR-S, Hycar 1002, and butyl rubber. Neoprene GN underwent oxidation immediately during irradiation. The other four rubbers showed no apparent effect through a dose of 1×10^6 reps. At 5×10^6 reps natural rubber exhibited slight oxidation. At 1×10^7 reps the Hycar 1002 film was cracked and split but showed no change in the infrared spectrum. The butyl rubber film broke, but the partial spectrum obtained before breakage showed oxidation effects. At 3.5×10^7 reps the GR-S film was cracked and split but showed no other change. At a dose of 7×10^7 roentgens the first oxidation peaks appeared in the GR-S and Hycar 1002 spectra. Although interesting oxidation data were obtained, the oxidation peaks obscured peaks which are characteristic of other molecular changes which may have occurred. Like studies will next be made in a nitrogen atmosphere to detect non-oxidative molecular changes. The volatile irradiation products from pure gum compounds of Neoprene GN, Hycar 2001, natural rubber, and Hycar 1001 were analyzed with the mass spectrometer. The oxygen was completely removed from the sample atmospheres by oxidation of the elastomers. The results show that Neoprene GN is the most resistant to cross-linking, natural rubber is the most resistant to chain scission, and Hycar 2001 is the most resistant to oxidation. The Hycar 2001, which has the largest aromatic group content, has the best all-round resistance to radiation damage. Both pyrolysis and gamma irradiation of rubber compounds promote oxidation. Only radiation produces hydrogen and methane. Radiation produces more hydrocarbons than does the heat treatment. This information supports the belief that an effective age resistor or antioxidant is not necessarily effective as an Anti-Rad.

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APPENDIX I

The Design and Operation of the Dipsometer

The dipsometer is a compact machine which measures the continuous or intermittent stress relaxation of a rubber strip. It permitted the measurement of stress in any chosen atmosphere during gamma irradiation. Figure 30 is a schematic drawing of a dipsometer. This instrument was developed by Mr. M. L. Dannis and Mr. R. C. Brainard of this laboratory for use in other research.

The dipsometer consists of four main parts; namely, a hinged weight and jaw assembly, a sliding weight and jaw assembly, a fixed permanent magnet, and a frame. The two pairs of jaws clamp the ends of the sample strip to permit its elongation for stress measurement. The sliding weight elongates the sample at any time chosen by the operator to the pre-selected elongation. The operator can elongate the sample once for continuous stress or repeatedly for intermittent stress relaxation. The elongation can take place even after the sample and dipsometer have been sealed inside an evacuated glass tube. The hinged weight is designed to counter-balance the retractive force in the stretched rubber sample when the axis of the dipsometer is rotated away from a vertical position. The stress of the sample is proportional to the sine of the net angle of rotation. The fixed permanent magnet keeps the sample elongated during continuous stress relaxation.

APPENDIX II

The Design and Operation of the Multilaxometer

The Multilaxometer is an apparatus for the measurement of either continuous or intermittent stress relaxation of rubber strips. Whereas the dipsometer (Appendix I) permits the irradiation and measurement of only one sample at a time, the Multilaxometer holds 48 samples during irradiation and testing.

Figures 31 through 34 show in detail the design and function of the parts of the apparatus. Photograph 31 shows the entire apparatus. From bottom to top it includes the Safety Lablift, which raises or lowers the samples for attachment to the balance; the square fixed base of the reader apparatus; the cylindrical rotating base, which holds and positions the stress relaxation rack; one of the six stress relaxation racks of the assembly, each of which holds eight sample strips; the hook and connecting rod between sample jaws and triple-beam balance; the switch panel, contact signal light, and battery assembly; and the triple beam balance, which measures the sample stress. The balance, connecting rod, panel assembly, rotating base, fixed base, and Lablift comprise the Stress Relaxation Reader Apparatus.

Photograph 32 details the Stress Relaxation Rack Assembly. A rack assembly consists of a rack holder, which has an inverted-T cross section; the six racks, each of which has two parts and holds eight sample strips at 85 per cent elongation; the 48 sample strips, each clamped between two pairs of jaws with identification numbers stamped in the metal; and the six spacers which prevent the sample jaws and sample arrangement from being disturbed. In the foreground of Figure 32 from left to right are an assembled stress relaxation rack, a spacer, a disassembled rack, another spacer, and a rack ready for sample loading. In the center foreground is the form in which we align a sample in its jaws for clamping. The sample strip and a pair of jaws are in the form. In the background are one stress relaxation rack assembly lacking only samples and sample jaws and a partial rack assembly showing one stretched sample in a rack.

Figures 33 and 34 show the rotating base, a rack, and the connecting rod with its hook in clearer detail. The connecting rod hooks under the screw holding the two top jaws together. The positioning pin in the rotating base insures proper positioning of the rack. The tool to the left in Figure 33 is an Allen wrench for the center bolt which locks the rack in place. As shown in Figures 31 and 33 a storage battery is connected in circuit through the rack-and-reader apparatus with a neon light. The circuit is so arranged that when the top pair of jaws no longer touches the top of the rack the light goes out. This occurs when the slider weights on the balance beam just balance the retractive force, or stress, in the sample strip.

The rack assembly fits inside the canister of the Cobalt 60 source, permitting irradiation of the rubber sample strips without disturbing them during the entire irradiation period. The rack assembly is removed from the source only long enough to measure sample stresses and is then returned. There is a duplicate rack assembly for unirradiated control purposes.

APPENDIX III

The Rubber Compounds Used in Screening the Potential Anti-Rads

All rubber compounds listed below comprise Compound 1GFA7 plus 5 parts of the potential Anti-rad in question per 100 parts of natural rubber. That is, each screening compound has the same general recipe:

Parts by Weight	Pigment
100	Natural Rubber
3	Stearic Acid
5	Zinc Oxide
3	Sulfur
1	Benzothiazyl Disulfide
1	Phenyl-Beta-Naphthylamine
50	EPC Carbon Black
5	Potential Anti-Rad

Compound 1GFA	Potential Anti-Rad
13	p, p'-Dimethoxydiphenyl amine
14	Dioctyldiphenyl amine
15	p-(p-Tolylsulfenylamido)-diphenylamine
16	Phenyl-alpha-naphthyl amine
17	Diphenylamine-acetone product
18	Acetone-anilline product
19	Butyraldehyde-aniline product
20	Phenyl-beta-naphthyl amine
21	Phenyl-beta- naphthylamine-acetone product
22	Aldol-alpha-naphthylamine product
23	Diphenylamine-di-isobutylene
24	N-phenyl-N-o-tolylethylene diamine
25	Di-o-tolylethylene diamine
26	N, N'-cyclohexylphenyl-p-phenylene diamine
27	N, N'-diphenyl-p-phenylene diamine
28	N-p-tolyl-N-p-toluenesulfonyl-p-phenylene diamine
32	o-Phenylphenol
33	p-Benzyloxyphenol
34	2, 2'-Methylene-bis-(4-methyl-6-t -butyl-phenol)
35	Coumarone-indene resin
36	N, N'-di-sec-butyl-p-phenylene diamine
37	2, 6-Di-t-butyl-p-cresol
38	Nickel dibutyl dithiocarbamate
39	Copper inhibitor X-872-L
40	UOP-88

Compound IGFA	Potential Anti-Rad
42	Nonox WSL
43	Aromatic hydrocarbon resin
45	Iron-, copper-, and manganese-inhibitor
46	Mercaptobenzothiazole
47	2, 5-Di-t-butyl-p-quinone
50	3 CD 810
51	3 CD 777
52	8 FE 99
53	8 FE 78AII
54	3 CD 769
55	6 FE 301
56	Age-rite Resin D
57	20 CC 59A
58	20 CC 11C
59	3 CF 163
60	3 CE 16
61	20 CC 130
62	3 CF 167
63	3 CD 221
64	3 CF 615
65	3 CE 251
66	3 CE 52
67	3 CF 159
68	3 CD 804
69	3 CE 250B
70	3 CF 162
71	3 CE 214
72	3 CE 237
73	3 CE 39
74	3 CE 242
75	15 CC 74A
77	Beta-naphthylamine
78	Diphenyl amine
79	Diphenylethylene diamine
80	p-Phenylene diamine
81	Quinoline
82	8-Hydroxyquinoline
83	p-Quninone
84	1, 4-Naphthoquinone
86	Quinhydrone
87	Benzophenone
88	Acridone
89	Hydroquinone
90	2, 5-Di-t-butyl-hydroquinone

Compound 1GFA	Potential Anti-Rad
91	Phenylhydroquinone
92	Hydroquinone monobenzyl ether
93	Hydroquinone dibenzyl ether
94	Naphthalene
95	Anthracene
96	Chrysene
97	Acridine
98	Phenothiazine
99	Pyrrole
100	p-Cresol
101	p-Aminophenol
102	p-Methoxyphenol
103	p-Dimethoxybenzene
104	p-Benzylphenol
105	Beta-naphthol
106	4, 4'-Dihydroxybenzophenone
108	Pyrogallol
109	1, 5-Dihydroxynaphthalene
110	2, 7-Dihydroxynaphthalene
111	Anthraquinone
112	2-Hydroxyquinoline
113	Akroflex C

APPENDIX IV

The Effect of Gamma Radiation on the Number of Intact Original Network Chains per Cubic Inch in Natural Rubber Gum Stock

Tobolsky and Andrews (15) state the following equation, which relates the equilibrium modulus of cured pure gum rubber at moderately low extensions to the number of remaining ''intact'' original network chains:

'' $$f = SkT\left[\frac{l}{l_u} - \left(\frac{l}{l_u}\right)^2\right] \quad , \qquad \text{where}$$

l_u represents unstretched length, l the equilibrium length at tension f, and S represents the number of network chains of all kinds per cc that remain unbroken and unrelaxed at the time of measurement.'' The symbol k represents Boltzmann's constant; and T is the absolute temperature.

The substitution of numerical values for k and T and a partial conversion from metric to English units give the following equation:

$$f/A = 1.66 \times 10^{-17}\ S\left[\frac{l}{l_u} - \left(\frac{l}{l_u}\right)^2\right] \quad \text{grams per square inch.}$$

The symbols in the latter equation have the same significance apart from units as in the former case. The temperature T equals 298°K.; S has the units of ''intact'' original network chains per cubic inch; and A is the original cross-sectional area in square inches. The data tabulated below are derived from the measurements of the stress relaxation of vulcanized pure gum natural rubber during gamma irradiation in air at room temperature as described on page 7. It should be noted clearly that the above equations apply strictly only to cases in which f is the <u>equilibrium</u> tension and l is the <u>equilibrium</u> length of the sample. Figures 35 through 38 permit at least an approximate correction for any departure from equilibrium values. These figures are useful as they stand from a qualitative standpoint at least in understanding the fundamental changes in network structure of the rubber sample during irradiation.

TABLE I

The Change in S during Intermittent Stress Relaxation during Irradiation in Vacuum

Thickness = 0.028 in.; Area = 0.0070 sq. in.; $1/1_u = 1.62$; $S = 6.96 \times 10^{18} f$

Radiation Dose (Megareps)	Retractive Force (Grams)	S (x 10^{-18})
0	220	1530
0.19	240	1670
0.41	235	1635
0.90	238	1655
1.87	254	1765
4.59	242	1680
5.40	246	1710
9.18	242	1680
12.2	232	1610
29.0	228	1585
33.4	232	1610
38.3	228	1585
44.2	228	1585
49.1	222	1545
63.6	220	1530
73.4	218	1515
83.0	217	1510
111.	213	1480

TABLE II

The Change in S during Continuous Stress Relaxation During Irradiation in Vacuum

Thickness = 0.026 in.; Area = 0.0065 sq. in.; $1/1_u = 1.76$; $S = 6.45 \times 10^{18} f$

Radiation Dose (Megareps)	Retractive Force (Grams)	S $(\times 10^{-18})$
0	261.5	1695
0.22	253.2	1630
0.41	250.1	1610
0.69	247.2	1595
1.03	244.2	1580
1.35	240.1	1550
4.75	211.4	1370
6.25	202.0	1305
9.60	186.2	1200
11.2	177.9	1150
14.5	170.6	1100
21.0	156.8	1010
34.3	138.5	895
44.5	133.1	860
55.5	124.5	805
74.4	115.9	750

TABLE III

The Change in S During Intermittent Stress Relaxation in Vacuum without Irradiation

Thickness = 0.026 in.; Area = 0.0065 sq. in.; $1/l_u = 1.72$; $S = 6.74 \times 10^{18}$ f

Relaxation Time (Hours)	Retractive Force (Grams)	S ($\times 10^{-18}$)
0	242	1630
1.22	242	1630
3.17	242	1630
3.92	242	1630
4.88	242	1630
30.13	242	1630
51.55	242	1630
78.13	242	1630
103.13	238	1600
125.55	240	1620
148.23	242	1630
172.53	238	1600
177.87	238	1600
218.95	236	1590
290.38	240	1620
459.28	238	1600
484.53	238	1600

TABLE IV

The Change in S during Continuous Stress Relaxation in Vacuum without Irradiation

Thickness = 0.0254 in; Area = 0.0064 sq. in.; $1/l_u = 1.64$; $S = 7.42 \times 10^{18} f$

Relaxation Time (Hours)	Retractive Force (Grams)	S ($\times 10^{-18}$)
0	193	1430
8.7	192	1425
240.7	187	1390
346.0	185	1370
458.0	185	1370
603.3	184	1365

TABLE V

The Change in S during Intermittent Stress Relaxation during Irradiation in Air

Thickness = 0.0268 in.; Area = 0.0067 sq. in.; $1/1_u = 1.80$; $S = 6.05 \times 10^{18}f$

Radiation Dose (Megareps)	Retractive Force (Grams)	S (x 10^{-18})
0	284	1720
0.05	284	1720
0.10	281	1700
0.20	274	1660
0.38	281	1700
0.78	277	1675
1.17	277	1675
4.35	267	1615
5.76	267	1615
9.09	253	1530
10.4	248	1500
14.3	237	1435
18.6	225	1360
33.7	(Sample Broke)	-

TABLE VI

The Change in S during Continuous Stress Relaxation during Irradiation in Air

Thickness = 0.0240 in.; Area = 0.0060 sq. in.; $1/1_u = 1.71$; $S = 7.35 \times 10^{18} f$

Radiation Dose (Megareps)	Retractive Force (Grams)	S (x 10^{18})
0	234	1720
0.10	236	1730
0.22	232	1705
0.42	230	1690
0.86	233	1710
1.23	226	1660
1.51	224	1645
2.58	219	1610
4.66	208	1530
5.68	202	1485
6.25	198	1455
19.1	130	955
24.0	105	770
30.2	83	610
39.4	48	350
53.3	9.3	68
58.7	(Sample Broke)	-

TABLE VII

The Change in S during Continuous Stress Relaxation in Air without Irradiation

Thickness = 0.0260 in.; Area = 0.0065 sq. in.; $1/l_u = 1.70$; $S = 6.83 \times 10^{18} f$

Relaxation Time (Hours)	Retractive Force (Grams)	S ($\times 10^{-18}$)
0	242	1655
0.62	242	1655
1.58	242	1655
4.87	241	1650
7.33	240	1640
23.53	238	1625
29.42	236	1610
31.33	236	1610
48.12	234	1600
53.33	233	1590
71.42	232	1585
91.08	231	1580
96.53	230	1570
160.17	227	1550
165.03	226	1545
169.58	225	1540
185.33	224	1530
208.25	224	1530
234.27	222	1520
256.20	221	1510
334.95	217	1480
381.67	216	1475
408.87	213	1455
499.80	211	1440

APPENDIX V

The Determination of the Number Average Molecular Weight of Rubber Polymer Chain between Cross-Links

The number average molecular weight of rubber polymer chain between cross-links can be calculated from solvent swelling measurements with the following equation (14):

$$M_c = -\rho V_1 V_2^{1/3} / \left[\ln \; (1 - V_2) + V_2 + \mu V_2^2 \right], \text{ where}$$

M_c is the number average molecular weight of rubber polymer chain between cross-links,
ρ is the bulk density of the unswelled rubber polymer,
V_1 is the molar volume of the swelling agent,
V_2 is the volume fraction of polymer in the swollen gel, and
μ is the liquid-polymer interaction coefficient.

For the pure gum natural rubber-benzene system $V_1 = 88.86$, $\rho = 0.917$, and $\mu = 0.43$. $V_2 = \alpha^{-3}$, where $\alpha^3 = V_c/(V_o)_c = L_c^3/(L_o)_c^3$, $(L_o)_c$ is the corrected dry sample strip length, L_c is the corrected swollen sample strip length, $(V_o)_c$ is the corrected dry sample strip volume, and V_c is the corrected swollen sample strip volume.

The corrections in sample strip length are made with the following equations:

$(L_o)_c = (\text{volume fraction of polymer})^{1/3} \times L_o$, and
$L_c = \left[(\text{volume fraction of polymer})^{1/3} + 1/2 \; (1 - [\text{volume fraction of polymer}]^{1/3}) \right] \times L$,

where L_o is the uncorrected dry sample strip length, and L is the uncorrected swollen sample strip length.

The latter two lengths require correction because of the non-elastomeric portion in rubber, which does not swell appreciably. The correction term $1/2 \left[1 - (\text{volume fraction of polymer})^{1/3} \right]$ was devised by Mr. A. G. Veith of the Research Center.

The results of M_c calculations with these equations, which are discussed on pages 7 and 8, appear below. The recipes for the rubber compounds are given on page 8.

TABLE VIII

The Effect of Gamma Radiation on the M_c of Natural Rubber

Gum Cmpd. 1GEA	$M_c \times 10^{-4}$ (Radiation Exposure in Megaroentgens) 0	0.1	1.0	10	25	35	55	70
109	1.20	1.12	1.12	1.15	0.74	0.59	0.52	0.37
110	1.04	0.98	0.86	0.85	0.76	0.58	0.55	0.50
111	1.17	1.23	1.15	-	0.94	0.55	0.58	0.48
112	1.26	1.32	1.14	-	0.96	0.95	0.76	0.82
113	1.04	1.03	0.90	0.82	0.71	0.59	0.53	0.50
116	1.15	1.12	1.07	1.00	0.84	0.71	0.66	0.65
118	1.20	1.17	1.12	0.95	0.86	0.74	0.72	0.60
124	1.08	1.08	0.96	0.92	0.82	0.77	0.71	0.66

APPENDIX VI

The Analysis of Radiation Damage by Infrared Absorption

The following is an account of the changes in five different gum rubber compounds during gamma irradiation in air as determined by infrared spectroscopic analysis. It supplements the discussion on page 9 above.

Gamma Ray Dose: 1×10^5 Reps

Natural Rubber : no change in the spectrum

GR-S : no change in the spectrum

Neoprene GN : small increase in the hydroxyl (OH) absorption peak

Hycar 1002 : no change in the spectrum

Butyl Rubber : no change in the spectrum

Gamma Ray Dose: 1×10^6 Reps

Natural Rubber : no change in the spectrum

GR-S : no change in the spectrum

Neoprene GN : approximately a threefold overall increase in hydroxyl (OH) absorption

Hycar 1002 : no change in the spectrum

Butyl Rubber : no change in the spectrum

Gamma Ray Dose: 5×10^6 Reps

Natural Rubber : very small hydroxyl and carbonyl (C = 0) absorption peaks

GR-S : no change in the spectrum

Neoprene GN : approximately a sevenfold overall increase in hydroxyl absorption and a small carbonyl absorption peak

Hycar 1002 : no change in the spectrum

Butyl Rubber : no change in the spectrum

Gamma Ray Dose: 1 x 10^7 Reps

Natural Rubber : slight increases in hydroxyl and carbonyl absorption

GR-S : no change in the spectrum

Neoprene GN : approximately a twelvefold overall increase in hydroxyl absorption and a threefold overall increase in carbonyl absorption

Hycar 1002 : splits and cracks in the sample film, but no change in the spectrum

Butyl Rubber : the film survived this exposure but broke after being placed in the spectrometer; the section of the spectrum scanned showed oxidation effects.

Gamma Ray Dose: 3.5 x 10^7 Reps

Natural Rubber : the hydroxyl absorption is twice that after the last dose, and the carbonyl peak is proportionately higher

GR-S : the sample film split and cracked, and the spectrum shows a general decrease in absorption because of less material in the infrared beam but shows no other change

Neoprene GN : oxidation is now so far advanced that individual peaks are no longer resolved

Hycar 1002 : no change in the spectrum

Butyl Rubber : the sample had become a gum clinging to the support ring

Gamma Ray Dose: 7 x 10^7 Reps

Natural Rubber : the hydroxyl absorption is four times that after 1 x 10^7 reps' dose; the carbonyl absorption increased proportionately; and a general increase in absorption in the 7-9 micron region of the spectrum indicates progressive oxidation

GR-S : oxidation effects have begun to appear: a small hydroxyl peak and a general increase in absorption in the 7-9 micron region of the spectrum

Neoprene GN : individual peaks are no longer resolved

Hycar 1002 : oxidation effects have begun to appear in the spectrum, including a small hydroxyl absorption peak

Butyl Rubber : the sample did not survive the dose

Gamma Ray Dose: 1 x 10^8 Reps

Natural Rubber : the hydroxyl peak is now twelve times as high as after the 1 x 10^7 reps' cose; the carbonyl peak has increased proportionately; and an extreme increase in absorption occurred in the 7-12 micron region of the spectrum so that individual peaks cannot be resolved

GR-S : the hydroxyl peak is ten per cent more intense than after the 7 x 10^7 reps' exposure, and there is a general increase in absorption in the 7-9 micron region of the spectrum, indicating progressive oxidation

Hycar 1002 : the hydroxyl peak is twelve per cent more intense than after the 7 x 10^7 reps' dose, and there is a general increase in absorption in the 7-9 micron region, indicating progressive oxidation; the sample film had cracked.

APPENDIX VII

The Rubber Compounds Used in the Study of Radiation Damage with the Mass Spectrometer

The recipes of the four vulcanized compounds which were used in the mass spectrometer study of the volatile products of irradiation are as follows:

Compound 1GFB1: Neoprene GN Gum Rubber

Parts by Weight	Pigment
100	Neoprene GN (Polychloroprene)
1	Stearic Acid
5	Zinc Oxide
4	Magnesium Oxide
0.5	Permalux
2	Neozone A

Compound 1GFB2: Hycar 2001 Gum Rubber

Parts by Weight	Pigment
100	Hycar 2001 (Butadiene-Styrene Copolymer)
1.5	Stearic Acid
5	Zinc Oxide
2	Sulfur

Compound 1GFB3: Gum Natural Rubber

Parts by Weight	Pigment
100	Natural Rubber
1	Stearic Acid
5	Zinc Oxide
3	Sulfur
1	Phenyl-Beta-Naphthylamine
0.6	Captax

Compound 1GFB4: Hycar 1001 Gum Rubber

Parts by Weight	Pigment
100	Hycar 1001 (Butadiene-Acrylonitrile Copolymer)
5	Zinc Oxide
1.5	Sulfur
1	Benzothiazyl Disulfide

TABLE IX

A Comparison of Ferrous Sulfate Dosimeter Data

Brookhaven National Laboratory conducted a survey on the use of the aqueous ferrous sulfate dosimeter. Mr. Jerome Weiss of the Health Physics Division of BNL has reported the results. Listed below are the names of the laboratories which have replied and their percentage deviation from the dose rate measured at BNL.

Laboratory	Percentage Deviation
Dow Chemical Company Midland, Michigan	0.6
Stanford Research Institute Stanford, California	0
University of Chicago Chicago, Illinois	1.8
Massachusetts Institute of Technology Cambridge, Massachusetts	0.8
Columbia University New York, New York	0.5

TABLE X

Optical Densities of the Glass Dosimeter Squares Used in Plotting the Gamma Radiation Field

Dosimeter Square	Absorbance (5200Å)	Dosimeter Square	Absorbance (5200 Å)	Dosimeter Square	Absorbance (5200 Å)
1M1	0.048	C 1	0.058	101	0.048
1M2	0.053			102	0.052
1M3	0.048	C 2	0.136	103	0.050
1M4	0.058			104	0.056
2M1	0.198			201	0.221
2M2	0.221	C 3	0.217	202	0.203
2M3	0.191			203	0.206
2M4	0.197	C 4	0.215	204	0.231
3M1	0.200			301	0.204
3M2	0.217			302	0.216
3M3	0.198	C 5	0.200	303	0.198
3M4	0.192			304	0.203
4M1	0.200	C 6	0.201	401	0.195
4M2	0.210			402	0.192
4M3	0.195			403	0.202
4M4	0.195	C 7	0.197	404	0.202
5M1	0.203			501	0.215
5M2	0.200	C 8	0.210	502	0.212
5M3	0.215			503	0.200
5M4	0.210			504	0.198
6M1	0.198	C 9	0.203	601	0.196
6M2	0.194			602	0.207
6M3	0.185	C10	0.200	603	0.186
6M4	0.209			604	0.202
7M1	0.207			701	0.207
7M2	0.182	C11	0.214	702	0.195
7M3	0.196			703	0.200
7M4	0.204	C12	0.201	704	0.207

TABLE XI

The Recipes of the A. S. T. M. Rubber Compounds

Pigment	1GFA2	1GFA3	1GFA4	1GFA5	1GFA6
Natural Rubber (Hevea)	100				
GR-S (Fatty Acid Base)		100			
Neoprene GN			100		
Hycar 1002				100	
Butyl Rubber (GR-I 18)					100
Stearic Acid	1		0.5		3
Zinc Oxide	5	5	5	5	5
Sulfur	2.5	2		1.5	2
Benzothiazyl Disulfide	1	1.75		1	
Tetramethylthiuram Disulfide					1
Phenyl-Beta-Naphthylamine	1				
Magnesium Oxide			4		
Specific Gravity	0.98	0.99	1.31	1.03	0.97

Pigment	1GFA7	1GFA8	1GFA9	1GFA10	1GFA11
Natural Rubber (Hevea)	100				
GR-S (Fatty Acid Base)		100			
Neoprene GN			100		
Hycar 1002				100	
Butyl Rubber (GR-I 18)					100
Stearic Acid	3		1		3
Zinc Oxide	5	5	5	5	5
Sulfur	3	2		1.5	2
Benzothiazyl Disulfide	1	1.75		1	0.5
Tetramethylthiuram Disulfide					1
Phenyl-Beta-Naphthylamine	1				
Magnesium Oxide			4		
EPC Black	50	40	35		50
SRF Black				50	
Specific Gravity	1.14	1.13	1.40	1.20	1.13

TABLE XII

The Corrected Effects of Heat and Radiation on Rubber

CMPD. 1GFA-	TEMP. (°C)	TIME (HRS.)	ΔS_{TR} (Corr.)	ΔS_T (Corr.)	ΔS_R (Corr.)	$\Delta S_T + \Delta S_R$ (Corr.)
2	80	150	-0.70	-0.35	-0.25	-0.60
3	40	75	-0.03	-0.02	-0.03	-0.05
4	65	150	-0.59	-0.31	-0.37	-0.68
7	80	150	-0.65	-0.54	-0.18	-0.72
8	65	150	-0.25	-0.04	-0.07	-0.11
9	80	150	-0.53	-0.44	-0.36	-0.80
10	65	150	-0.39	-0.04	-0.28	-0.32

ΔS_{TR} is the change in stress during heating and irradiation combined.

ΔS_T is the change in stress during heating alone.

ΔS_R is the change in stress during irradiation at room temperature (25°C).

TABLE XIII

The Uncorrected Effects of Heat and Radiation on Rubber

CMPD. 1GFA-	TEMP. (°C)	TIME (HRS.)	ΔS_{TR} (Uncorr.)	ΔS_T (Uncorr.)	ΔS_R (Uncorr.)	$\Delta S_T + \Delta S_R$ (Uncorr.)
2	80	150	-0.72	-0.35	-0.23	-0.58
2	65	150	-0.45	-0.06	-0.23	-0.29
3	40	75	+0.06	+0.03	-0.02	+0.01
4	65	150	-0.49	-0.15	-0.34	-0.49
7	80	150	-0.65	-0.54	-0.18	-0.72
7	65	150	-0.44	-0.15	-0.18	-0.33
7	40	75	-0.12	-0.04	-0.07	-0.11
8	65	150	-0.34	-0.04	-0.08	-0.12
8	40	75	-0.07	+0.01	-0.03	-0.02
9	80	150	-0.50	-0.40	-0.36	-0.76
9	40	75	-0.40	-0.09	-0.23	-0.32
10	65	150	-0.31	+0.01	-0.25	-0.24

ΔS_{TR} is the change in stress during heating and irradiation combined.

ΔS_T is the change in stress during heating alone.

ΔS_R is the change in stress during irradiation at room temperature (25°C).

TABLE XIV

A Comparison of the Relative Effectiveness of Anti-Rads by Two Evaluation Methods

Stress-Strain Rating	Anti-Rad	Swelling Rating
1	2, 5-Ditertiarybutylhydroquinone	4
2	p-Methoxyphenol	5
3	1, 3-Naphthalenediol	1
4	1, 5-Naphthalenediol	6
5	N, N'-Di-β-naphthyl-p-phenylene-diamine	3
6	N, N'-Diphenyl-p-phenylenediamine	2
7	p-Dimethoxybenzene	7
8	No Anti-Rad (control stock)	8

TABLE XV

Mass Spectral Analysis of the Low-Temperature Fraction

Volatile Irradiation Product	Moles of Volatile Product per Gram of Sample 1GFB1	 1GFB2	 1GFB3	 1GFB4
Hydrogen	14.8×10^{-7}	23.0×10^{-7}	34.6×10^{-7}	38.5×10^{-7}
Methane	0.27×10^{-7}	0.11×10^{-7}	trace	0.95×10^{-7}
Carbon Monoxide	78.2×10^{-7}	46.1×10^{-7}	69.3×10^{-7}	71.3×10^{-7}

TABLE XVI

Mass Spectral Analysis for Carbon Monoxide Corrected for Equivalent Oxygen Contents

Compound 1GFB-	Carbon Monoxide Content (Moles per Gram of Sample)
1	78.2×10^{-7}
2	31.5×10^{-7}
3	49.7×10^{-7}
4	45.4×10^{-7}

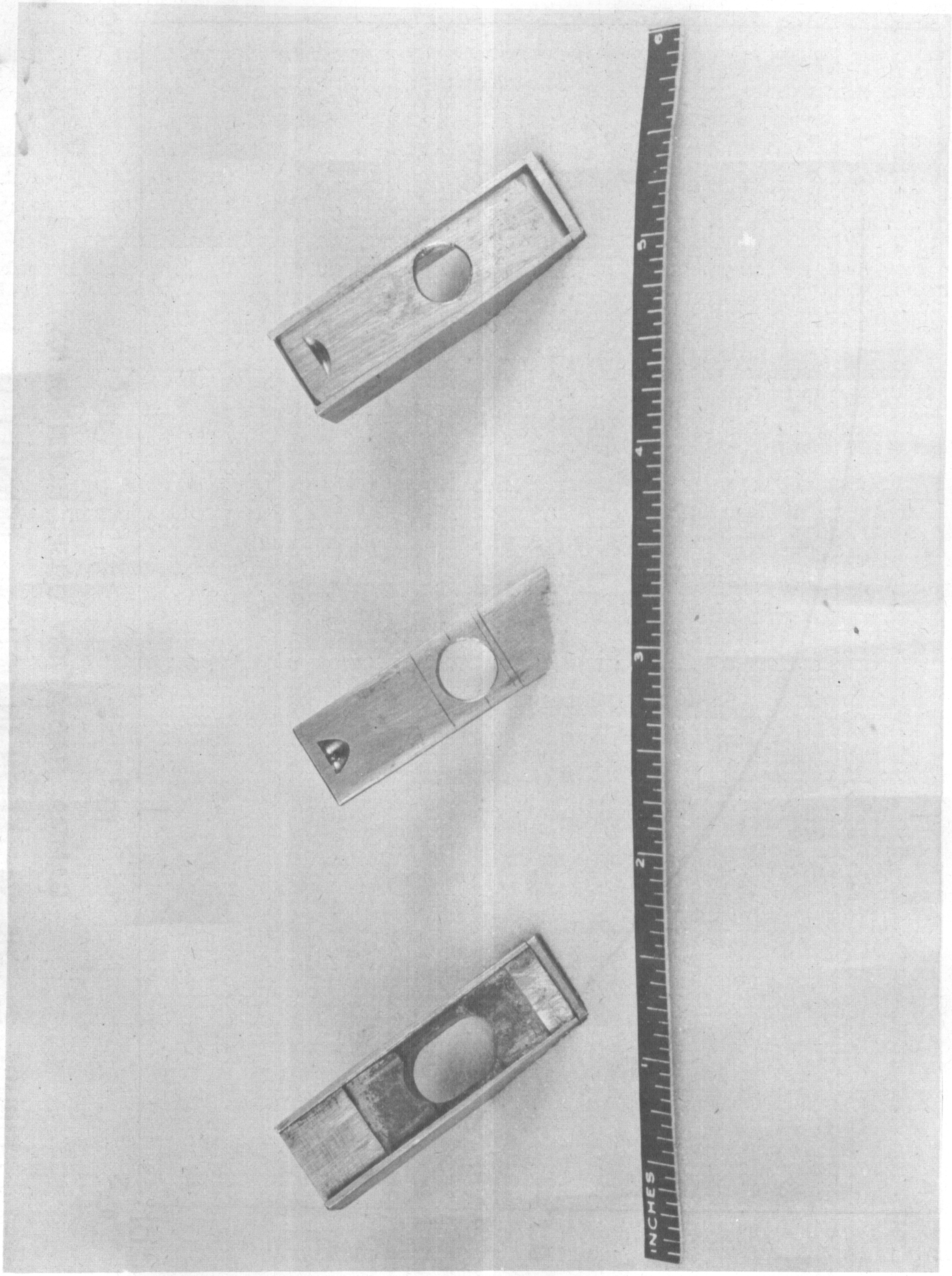

Figure 1. DOSIMETER PLATE HOLDER FOR SPECTROMETRY

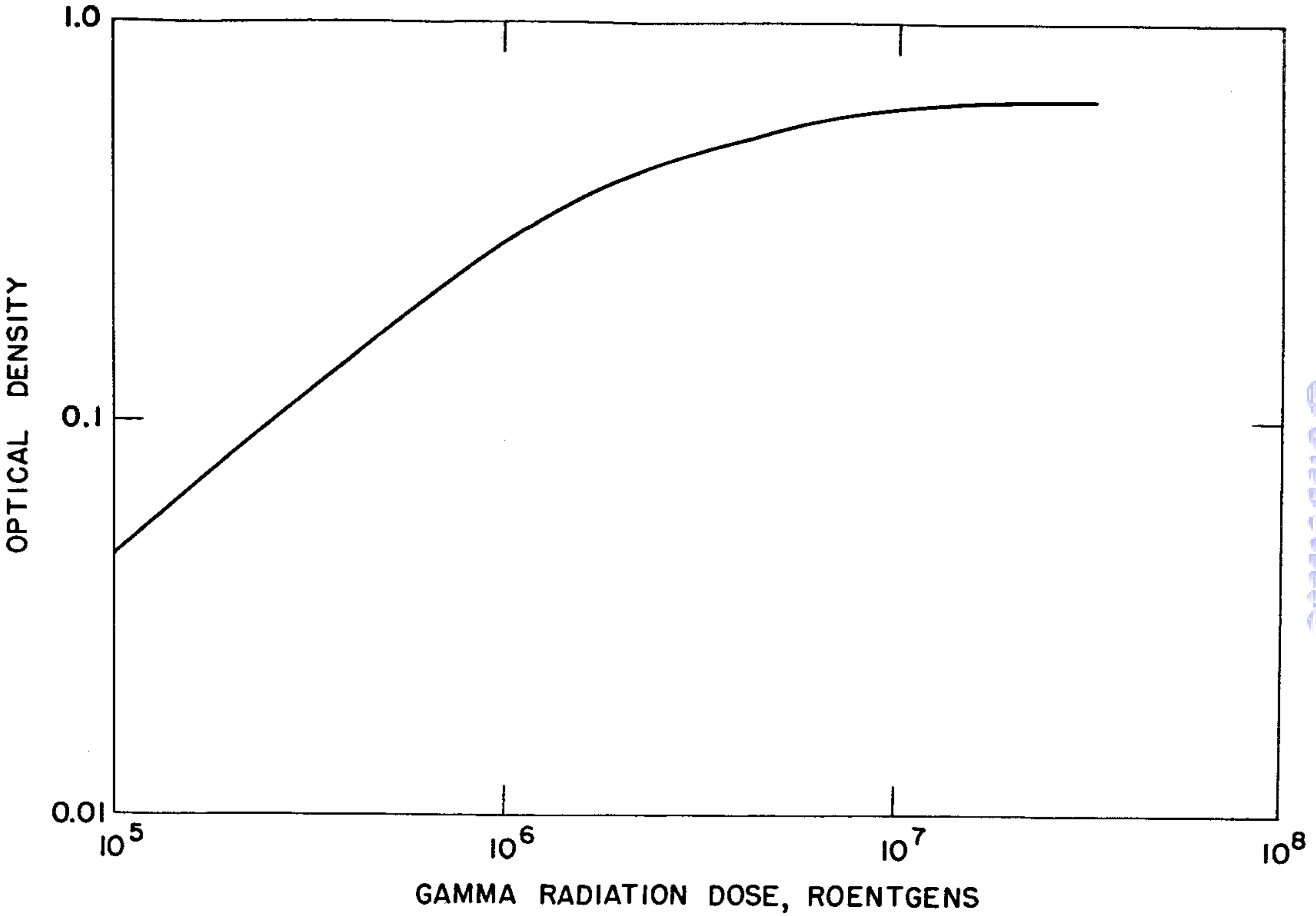

FIGURE 2. THE VARIATION IN OPTICAL DENSITY OF MICROSCOPE SLIDE GLASS WITH GAMMA RAY DOSAGE

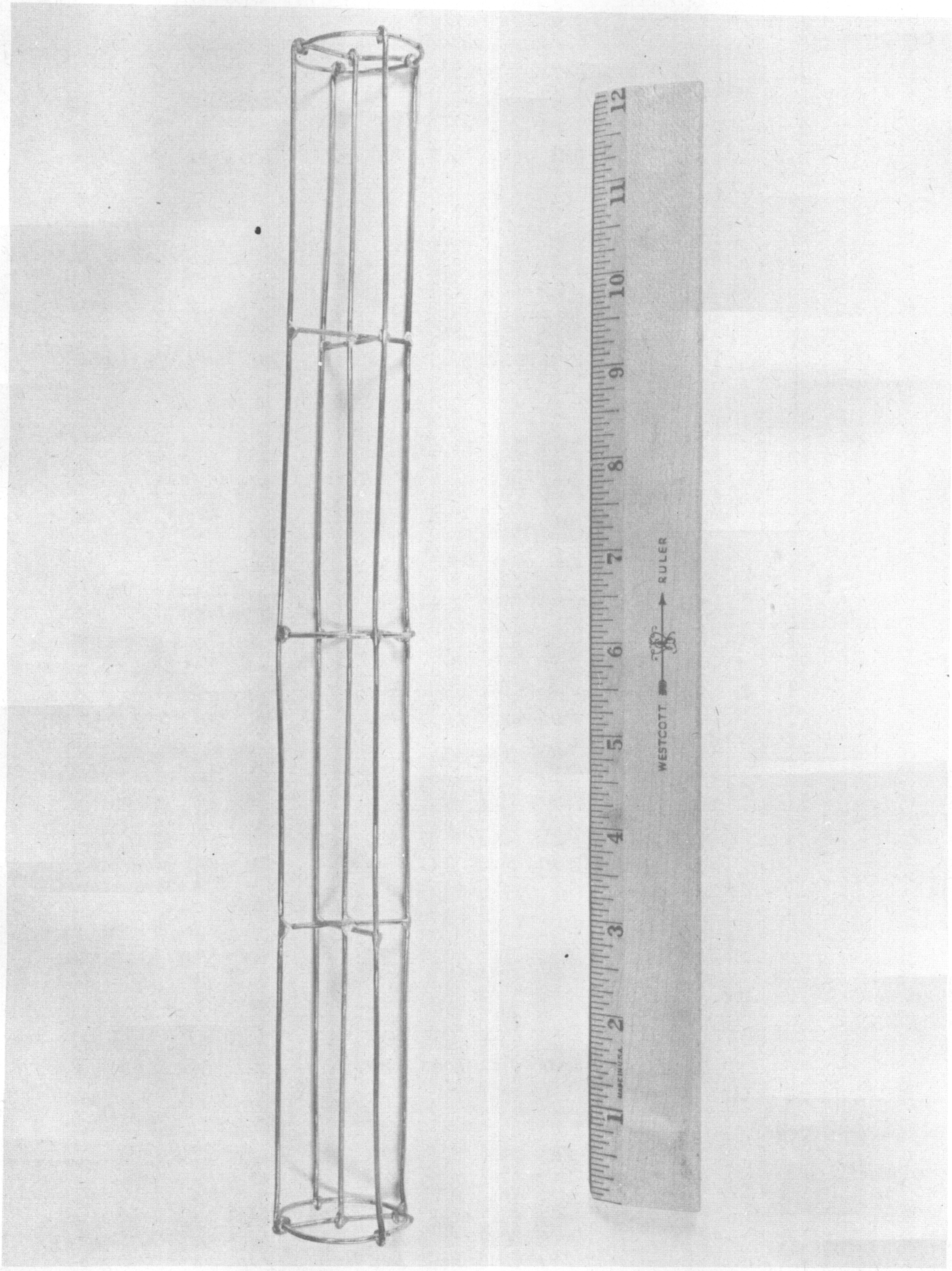

Figure 3. CYLINDRICAL WIRE HOLDER FOR DOSIMETER PLATES DURING IRRADIATION

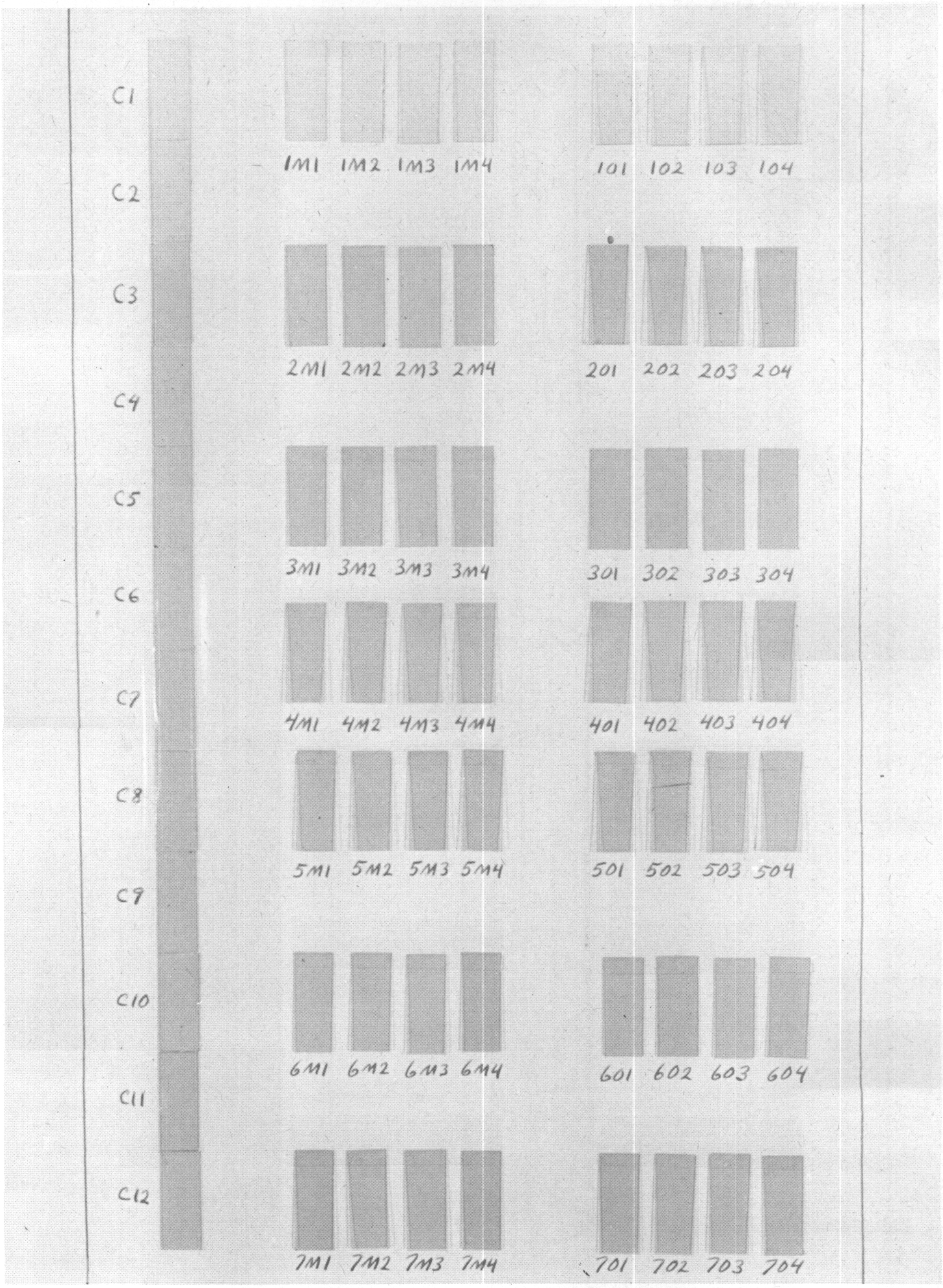

Figure 4. GLASS DOSIMETER PLATES AFTER GAMMA IRRADIATION

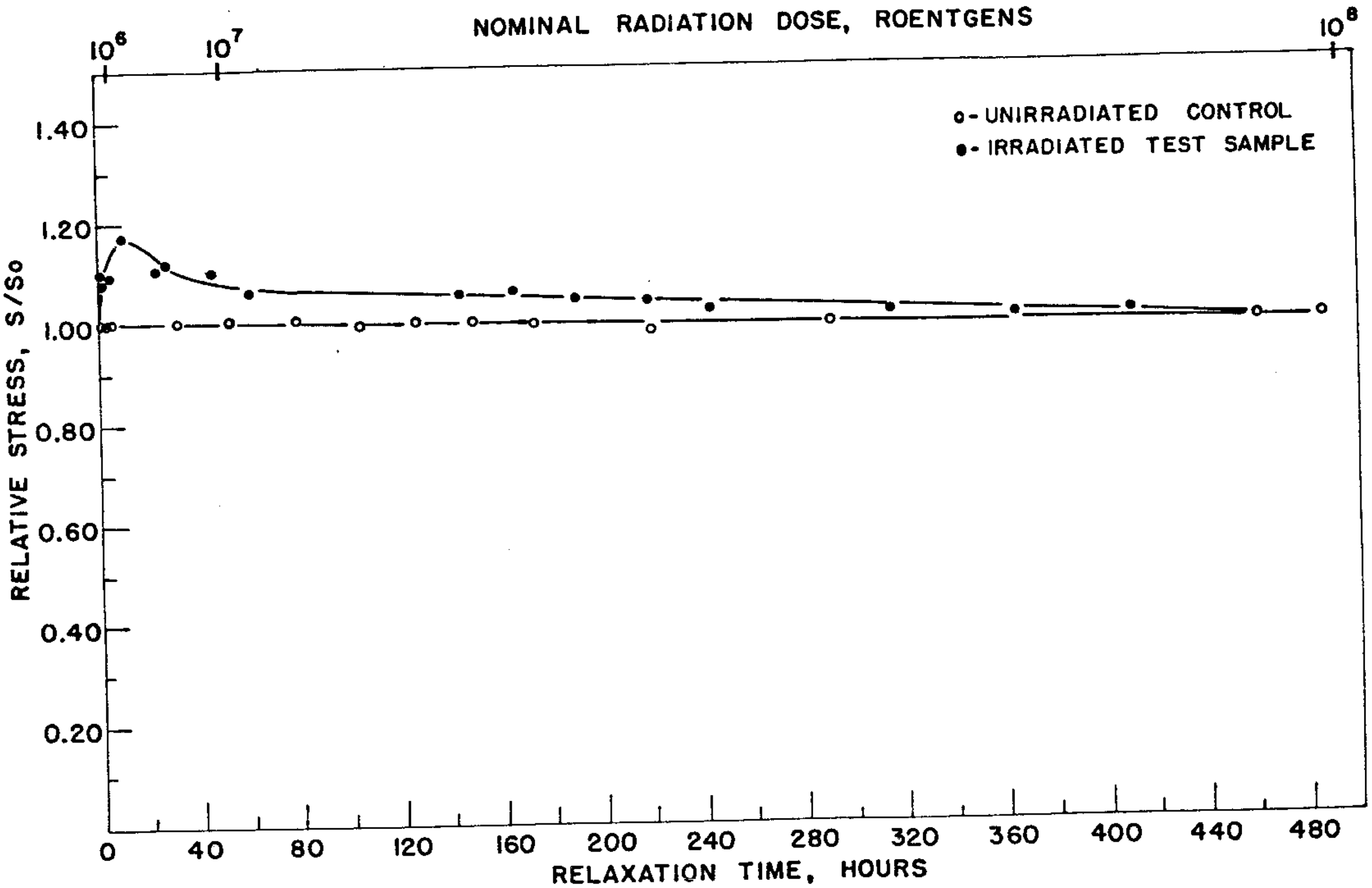

Figure 5. INTERMITTENT STRESS RELAXATION OF RUBBER IN A VACUUM DURING GAMMA IRRADIATION

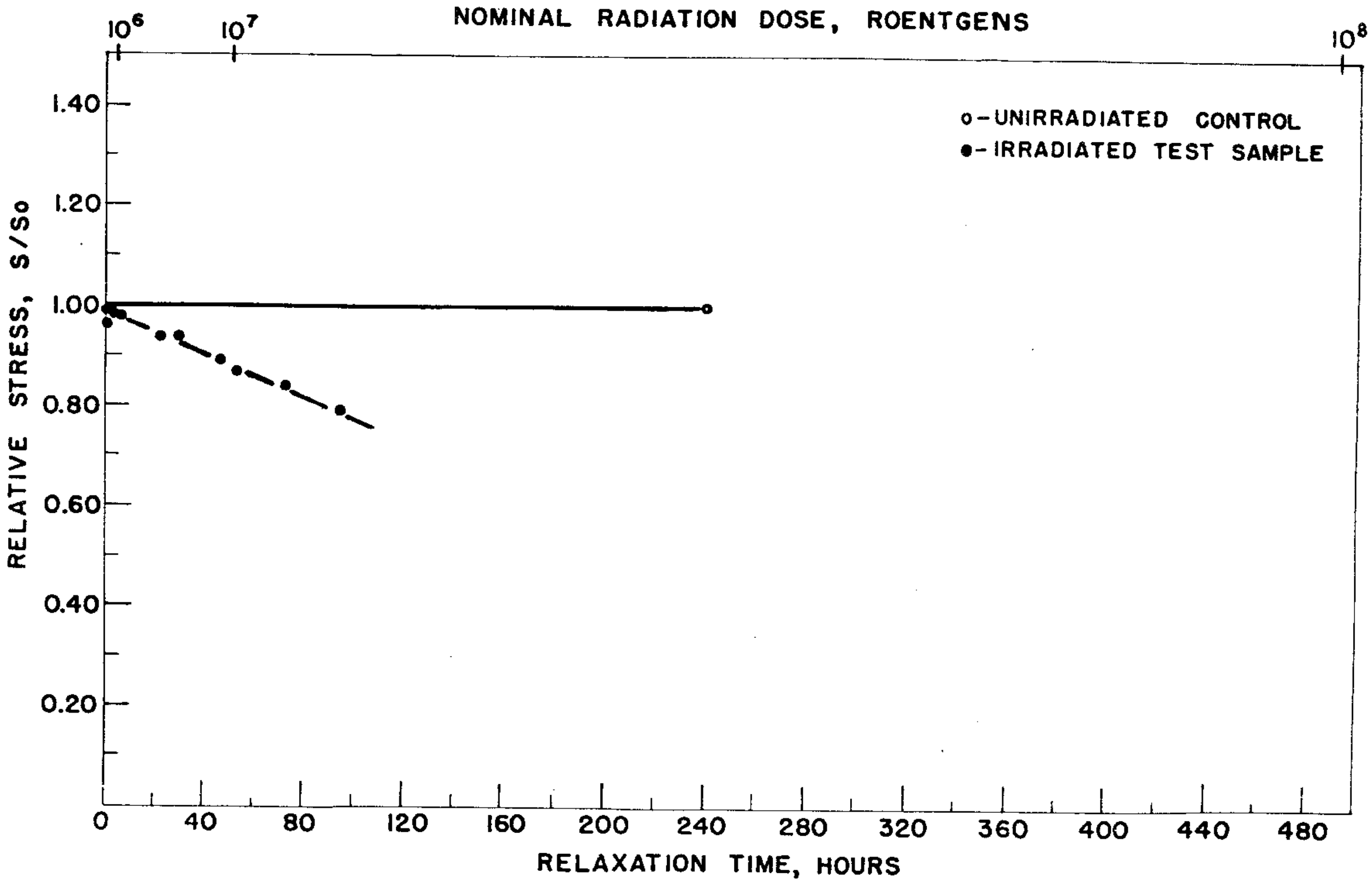

Figure 6. INTERMITTENT STRESS RELAXATION OF RUBBER IN AIR DURING GAMMA IRRADIATION

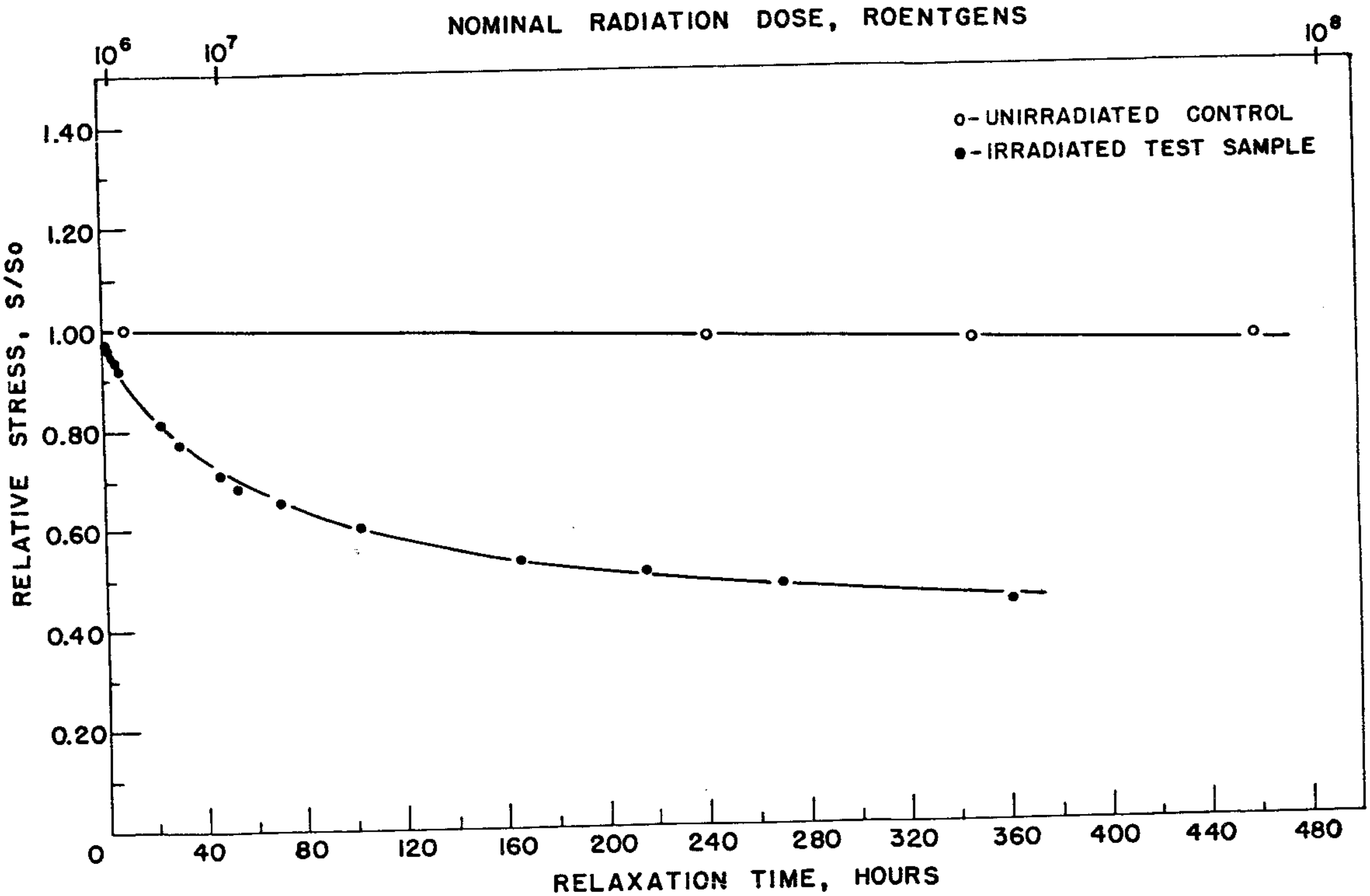

Figure 7. CONTINUOUS STRESS RELAXATION OF RUBBER IN A VACUUM DURING GAMMA IRRADIATION

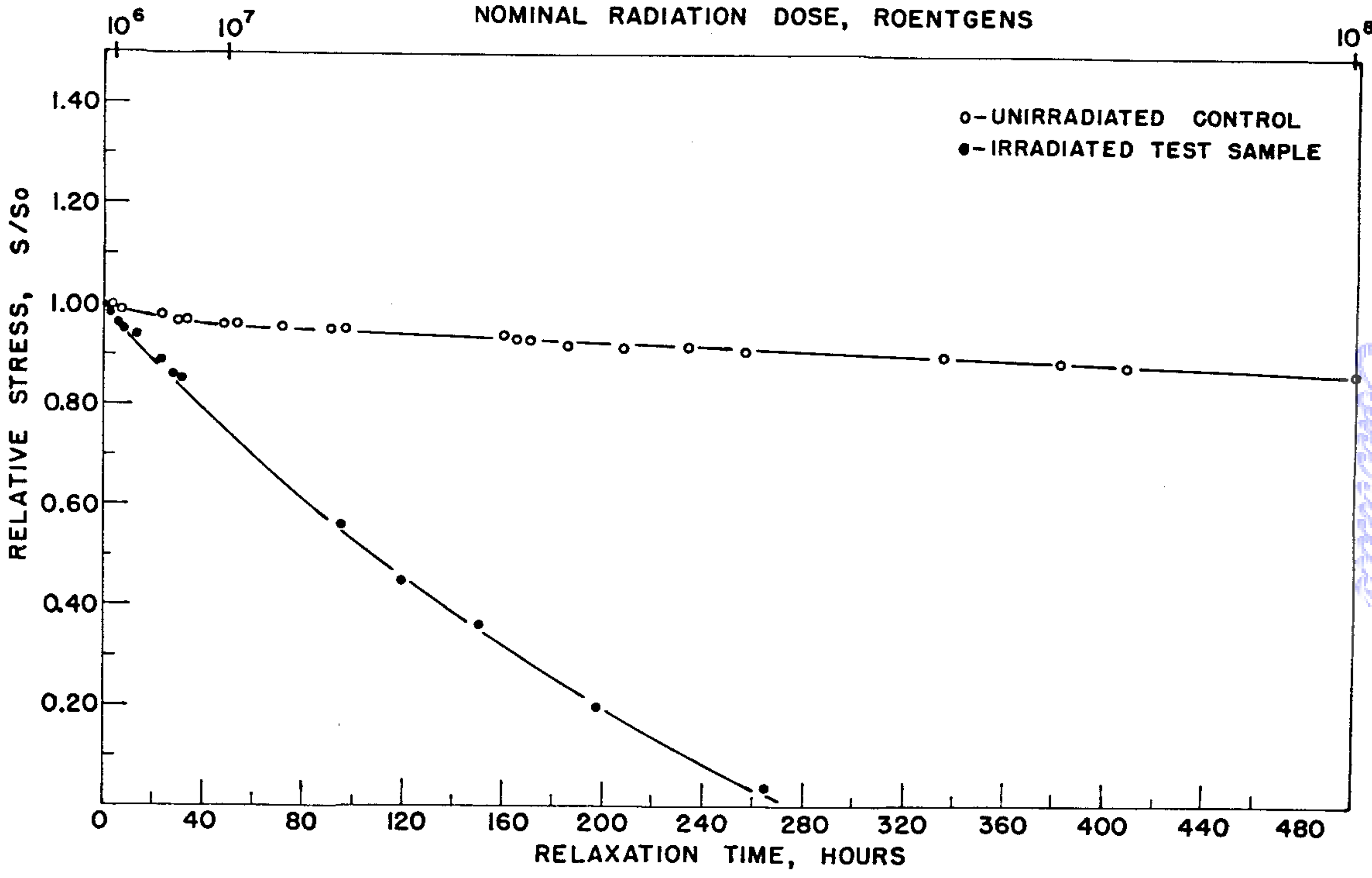

Figure 8. CONTINUOUS STRESS RELAXATION OF RUBBER IN AIR DURING GAMMA IRRADIATION

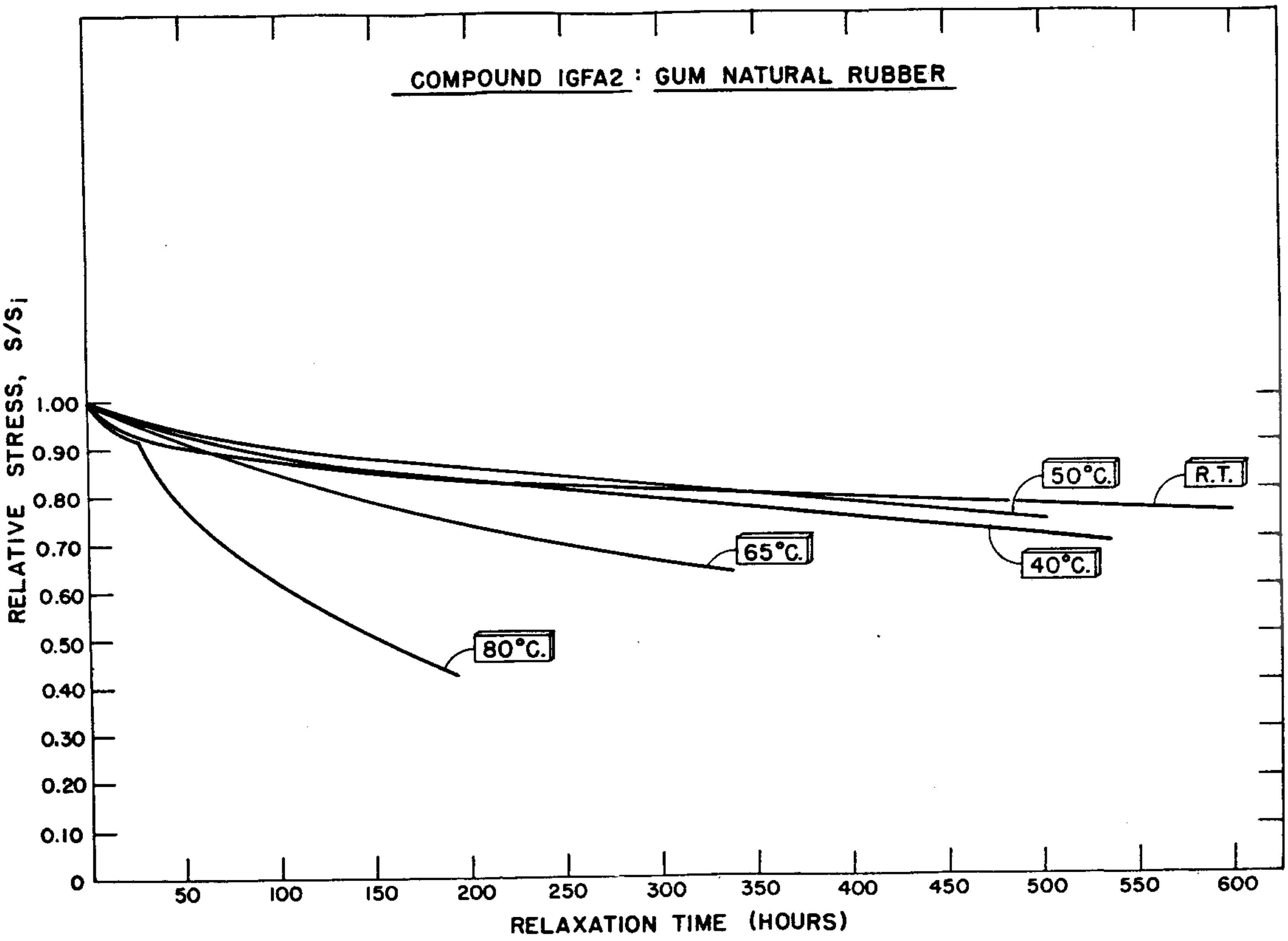

FIGURE 9. CONTINUOUS STRESS RELAXATION OF GUM NATURAL RUBBER DURING HEATING IN AIR

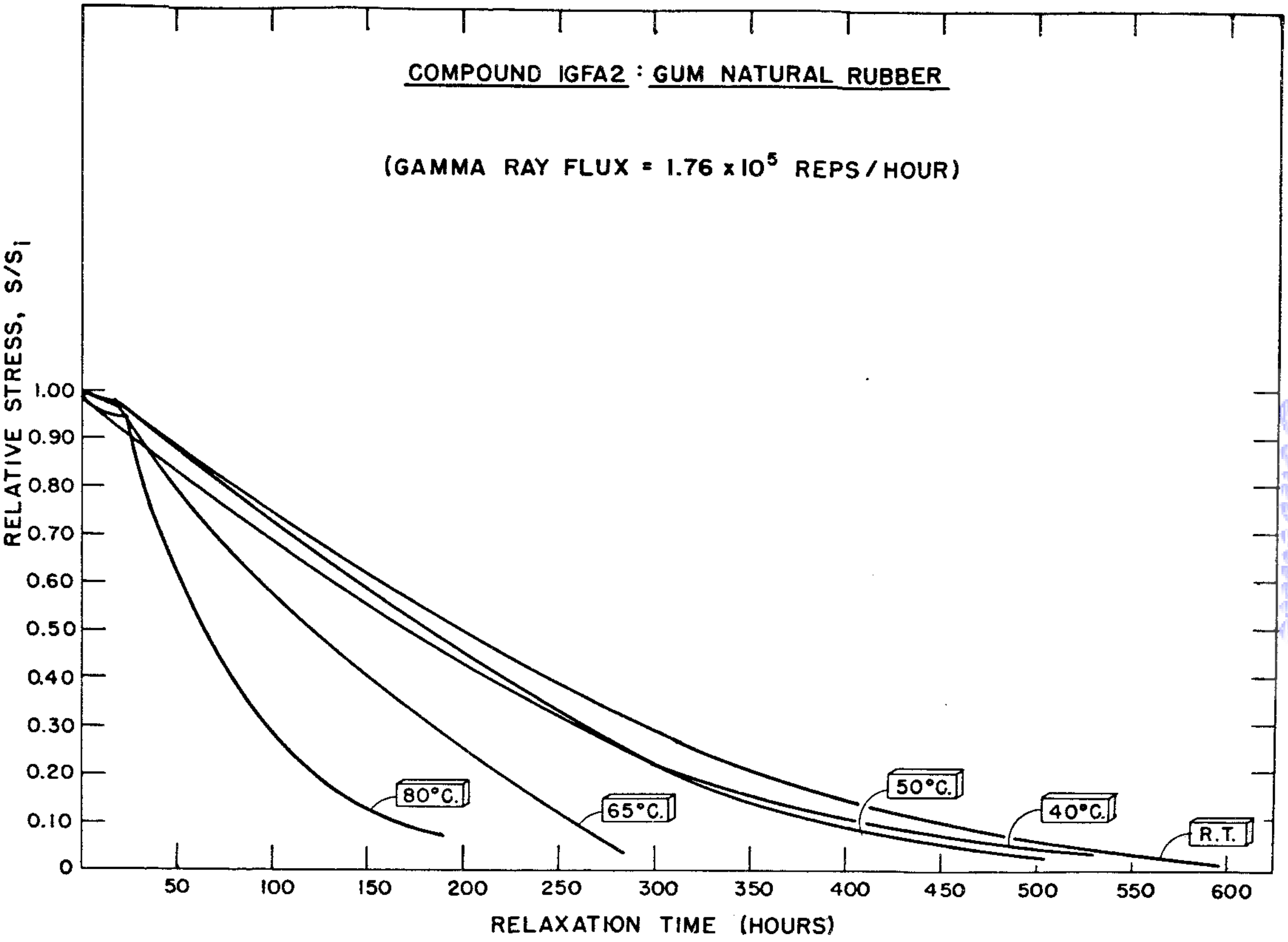

FIGURE 10. CONTINUOUS STRESS RELAXATION OF GUM NATURAL RUBBERS DURING IRRADIATION AND HEATING IN AIR

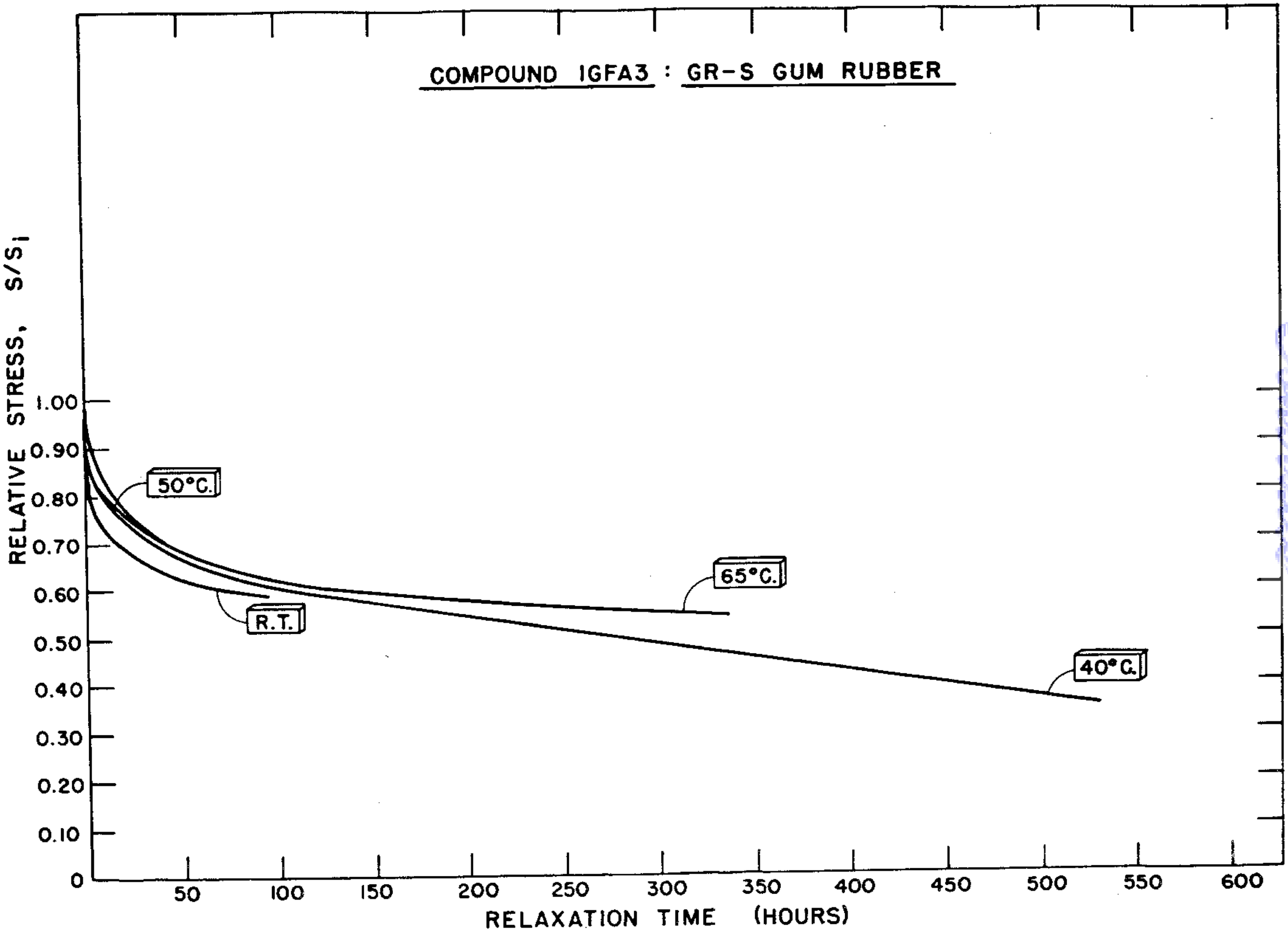

FIGURE II. CONTINUOUS STRESS RELAXATION OF GUM GR-S DURING HEATING IN AIR

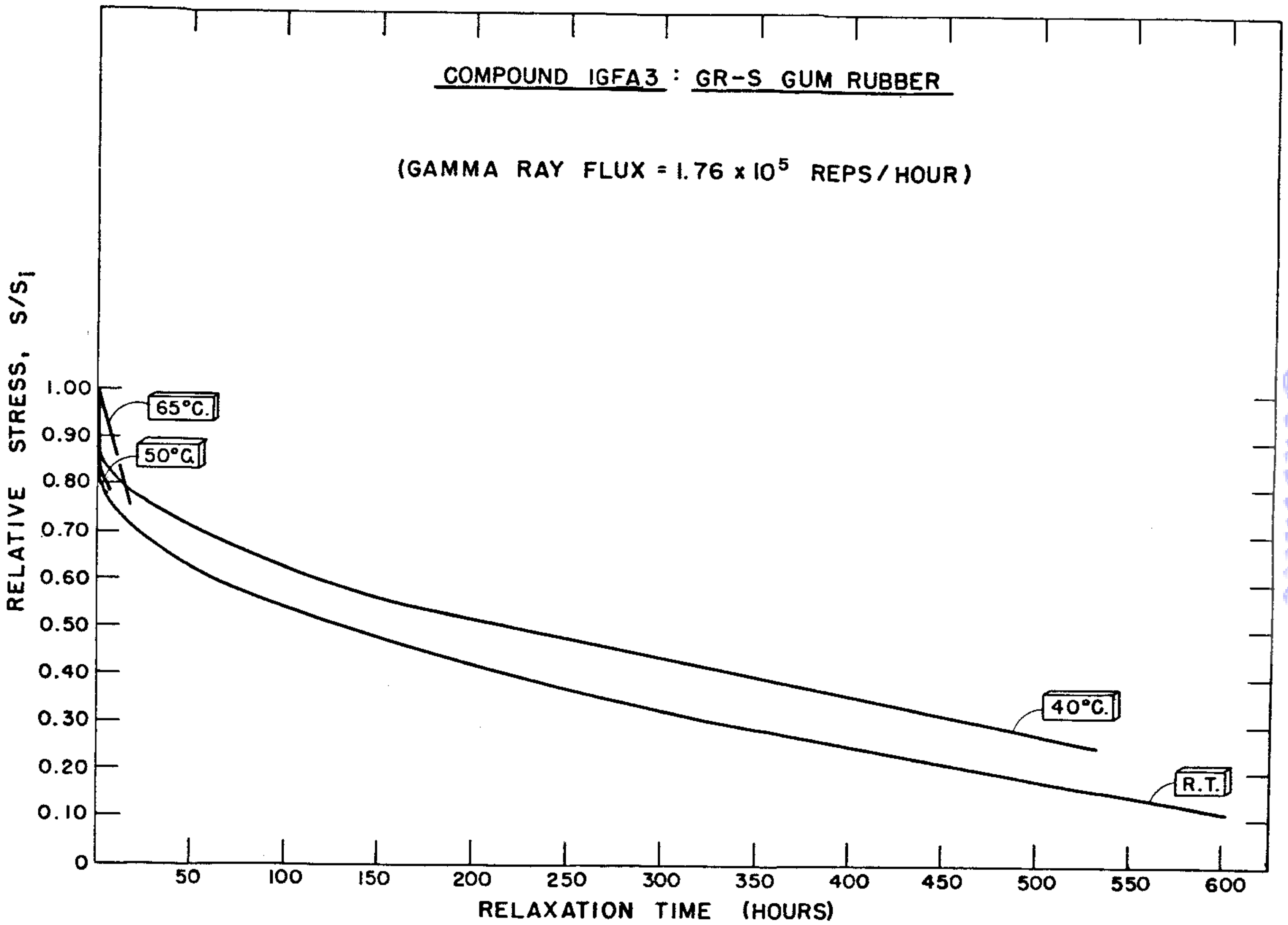

FIGURE 12. CONTINUOUS STRESS RELAXATION OF GUM GR-S DURING IRRADIATION AND HEATING IN AIR

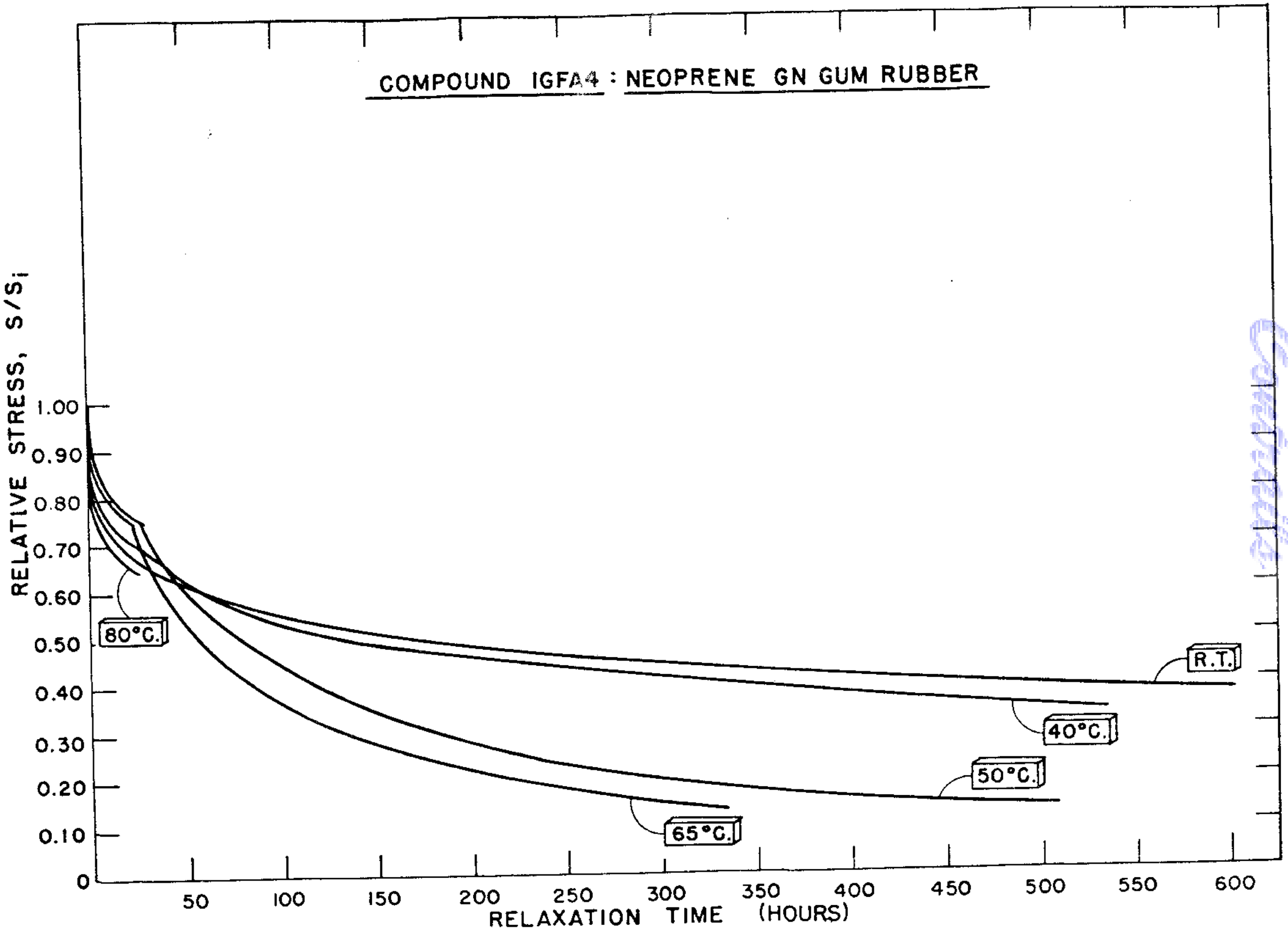

FIGURE 13. CONTINUOUS STRESS RELAXATION OF GUM NEOPRENE GN DURING HEATING IN AIR

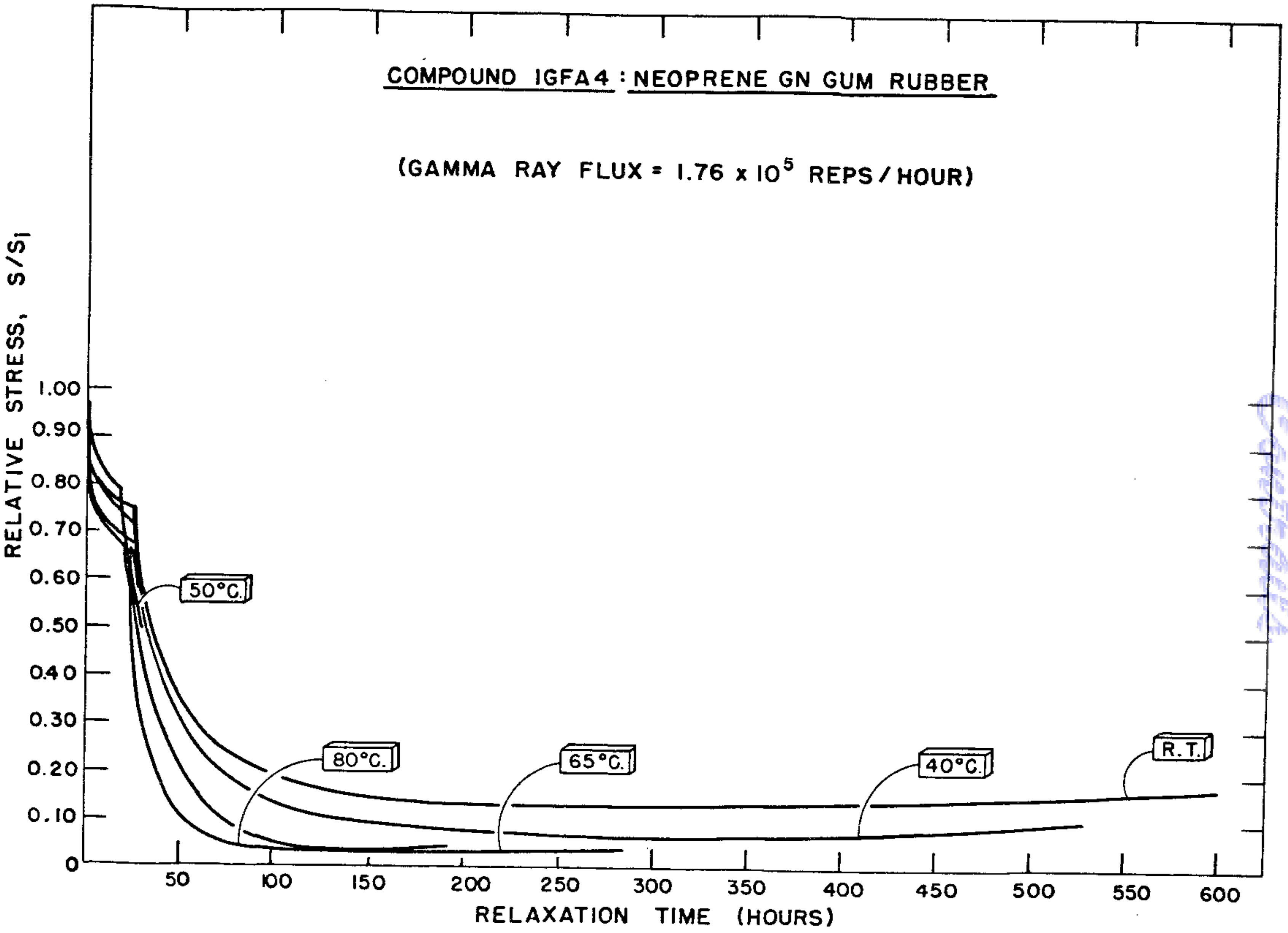

FIGURE 14. CONTINUOUS STRESS RELAXATION OF GUM NEOPRENE GN DURING IRRADIATION AND HEATING IN AIR

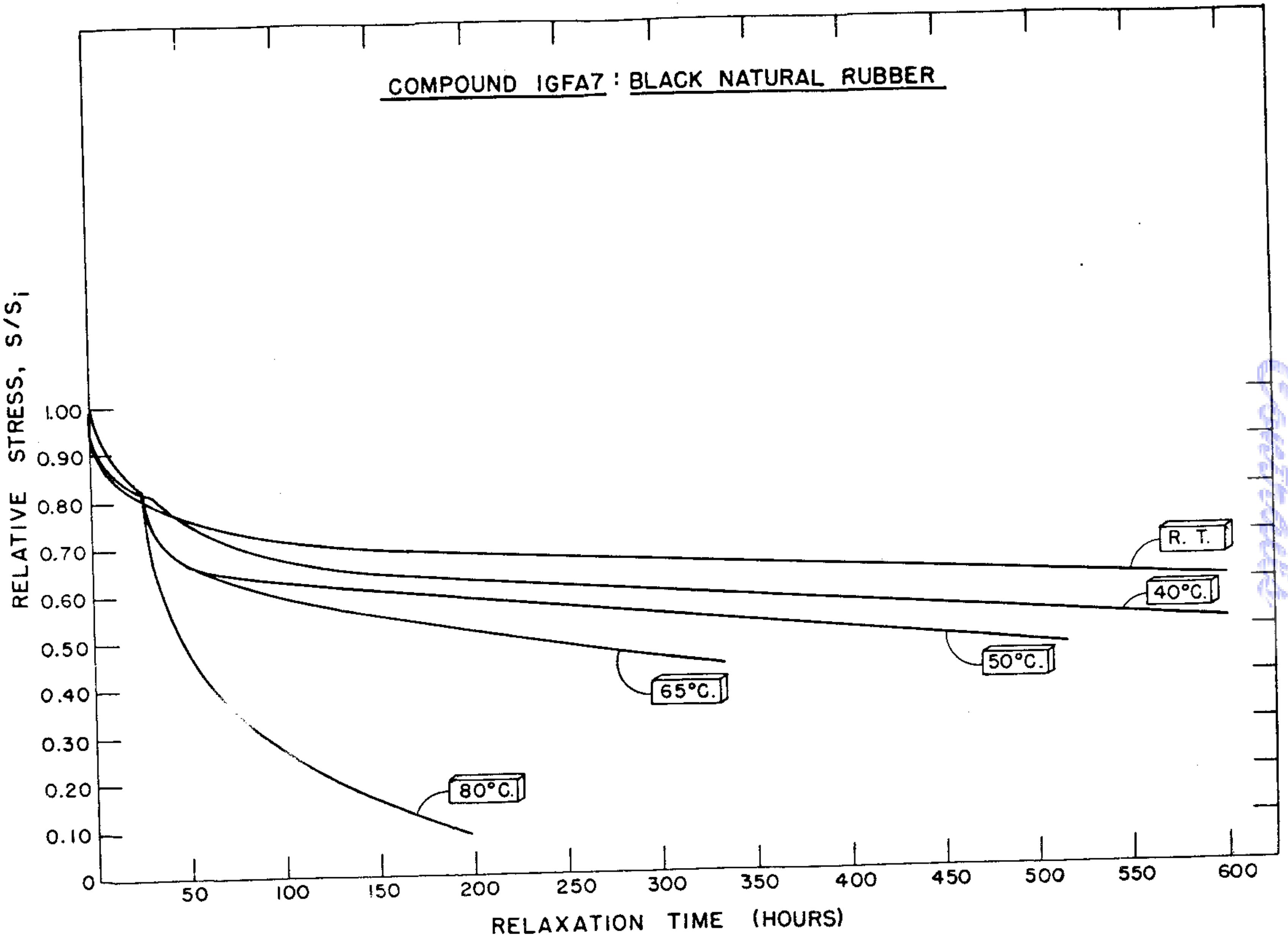

FIGURE 15. CONTINUOUS STRESS RELAXATION OF A BLACK NATURAL RUBBER COMPOUND DURING HEATING IN AIR

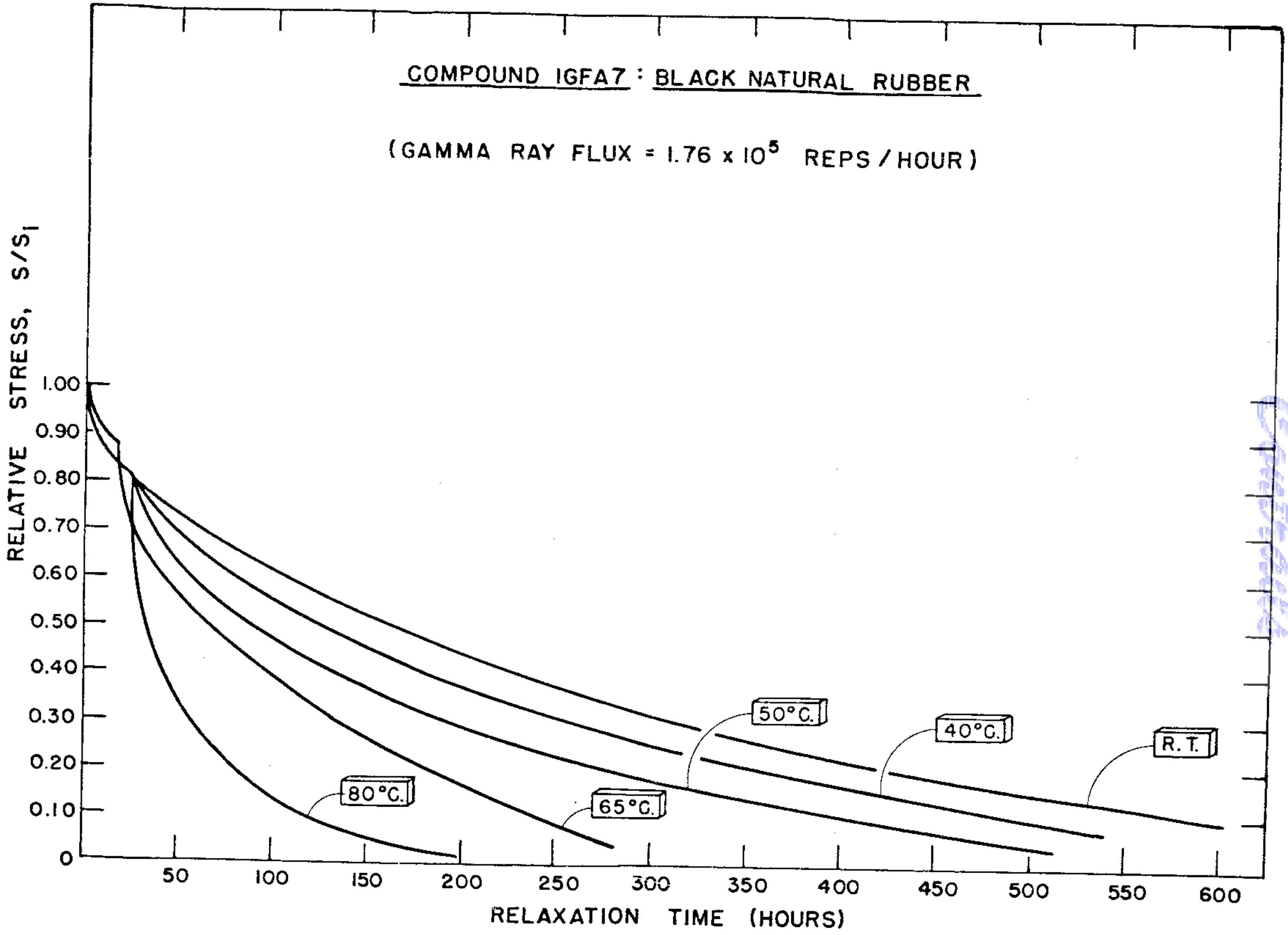

FIGURE 16. CONTINUOUS STRESS RELAXATION OF A BLACK NATURAL RUBBER COMPOUND DURING IRRADIATION AND HEATING IN AIR

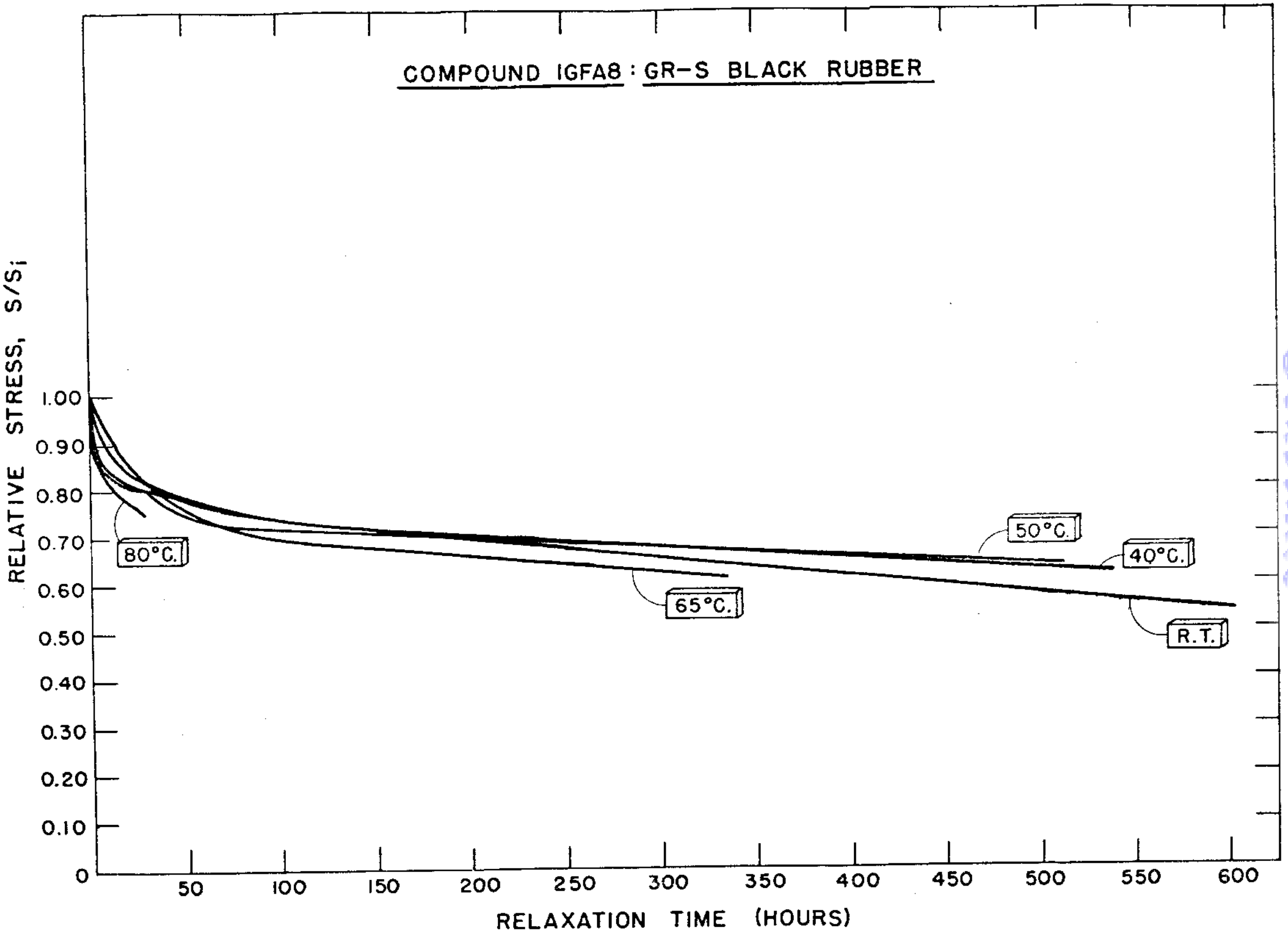

FIGURE 17. CONTINUOUS STRESS RELAXATION OF A BLACK GR-S COMPOUND DURING HEATING IN AIR

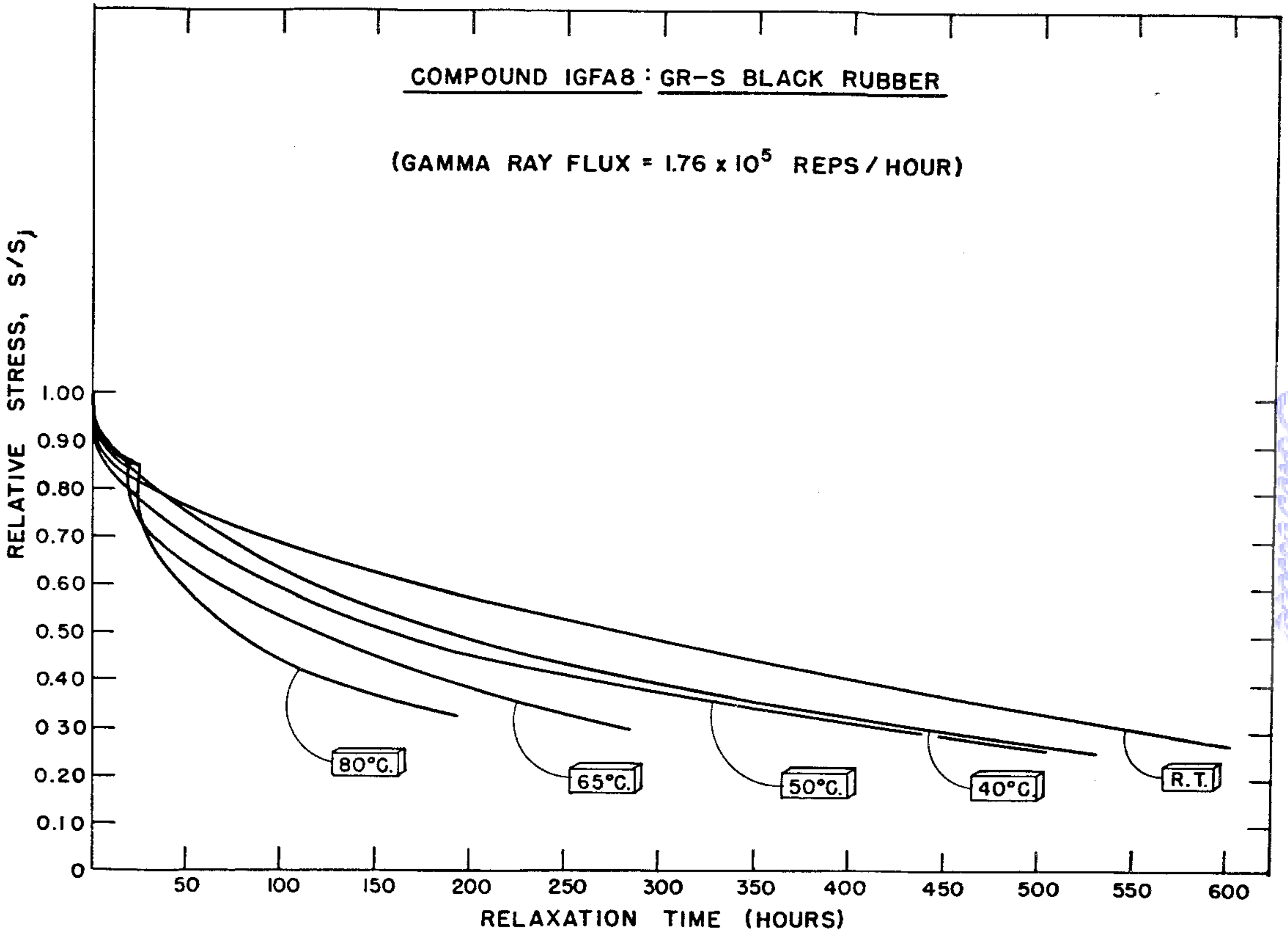

FIGURE 18. CONTINUOUS STRESS RELAXATION OF A BLACK GR-S COMPOUND DURING IRRADIATION AND HEATING IN AIR

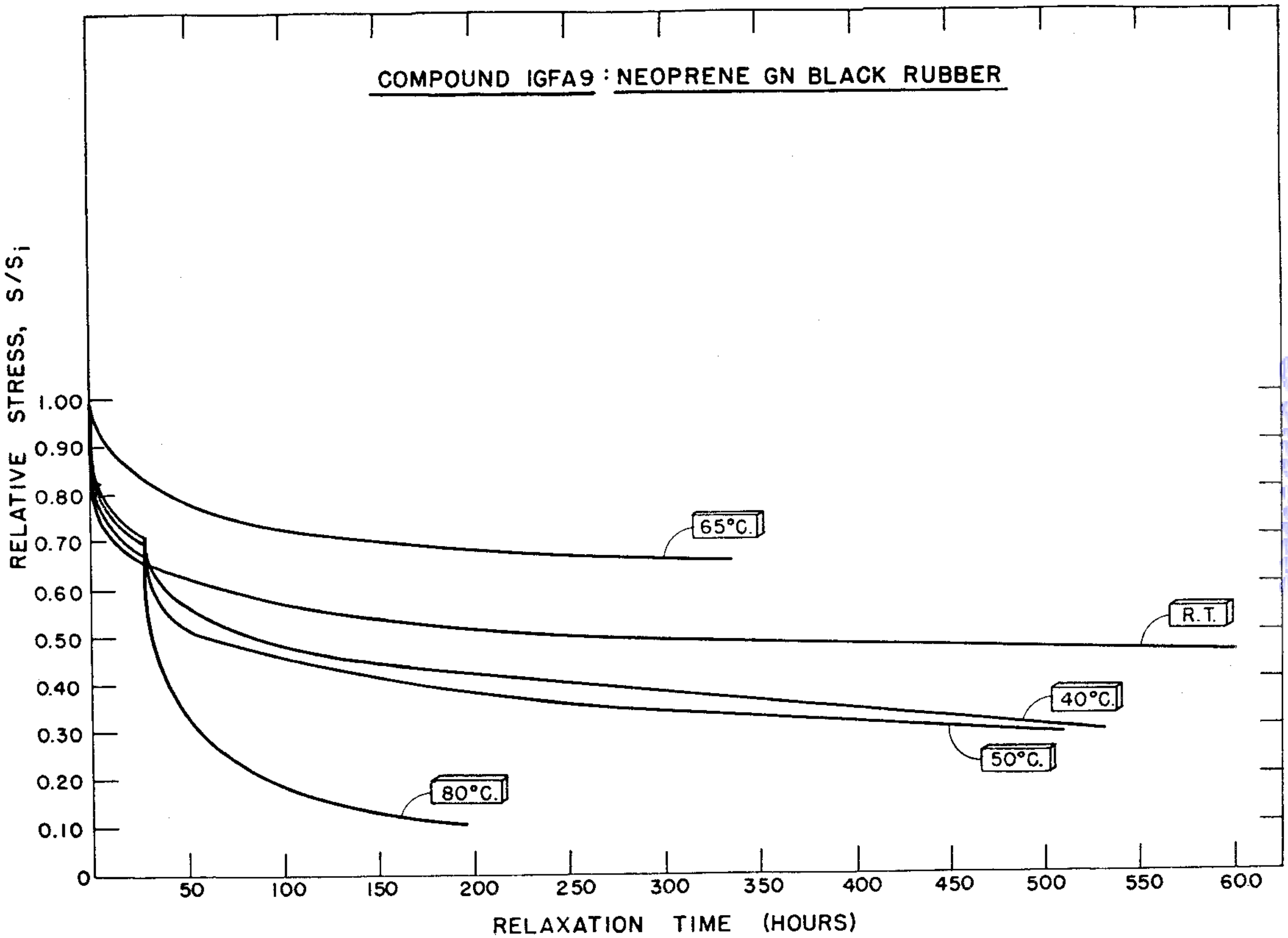

FIGURE 19. CONTINUOUS STRESS RELAXATION OF A BLACK NEOPRENE GN COMPOUND DURING HEATING IN AIR

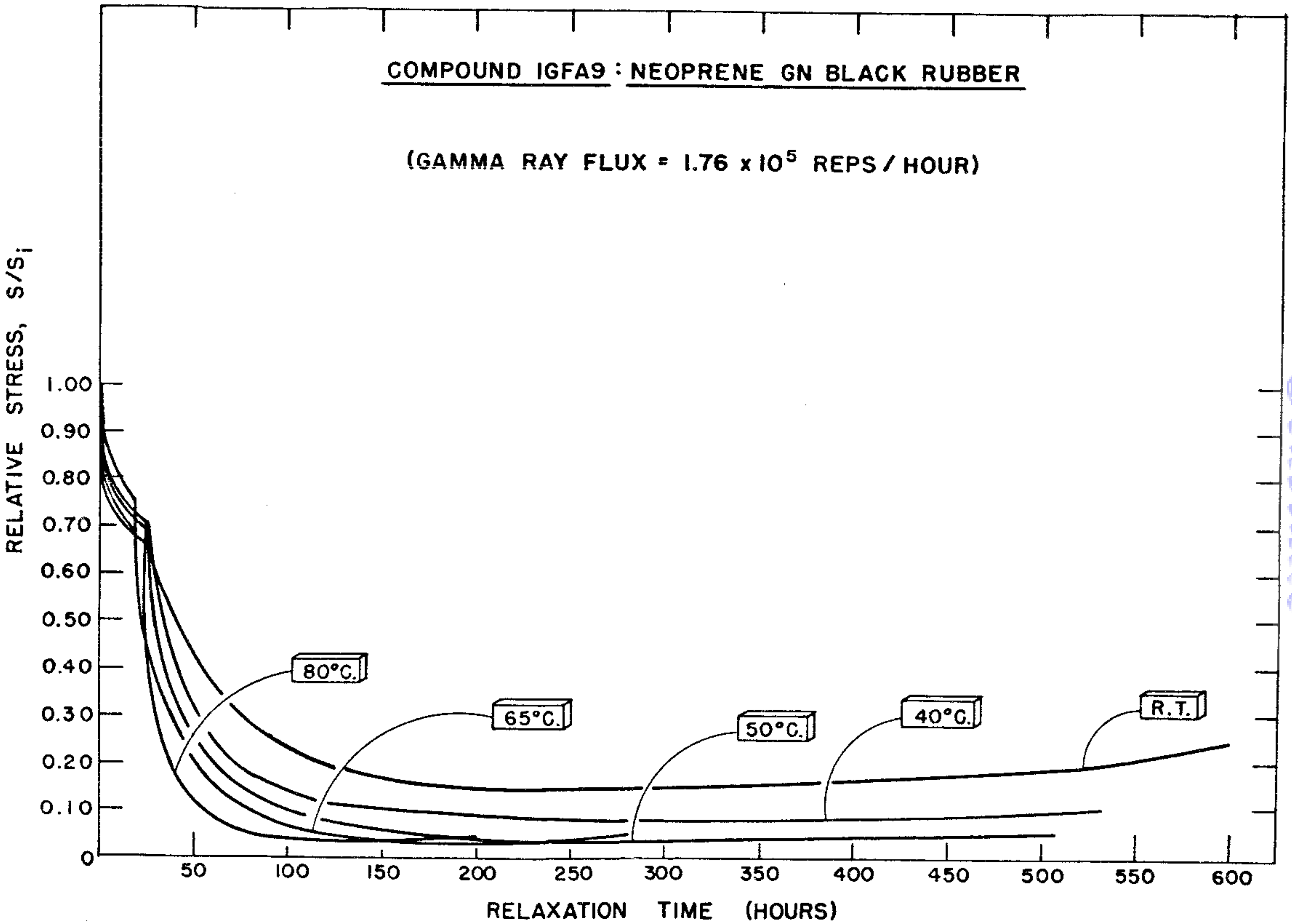

FIGURE 20. CONTINUOUS STRESS RELAXATION OF A BLACK NEOPRENE GN COMPOUND DURING IRRADIATION AND HEATING IN AIR

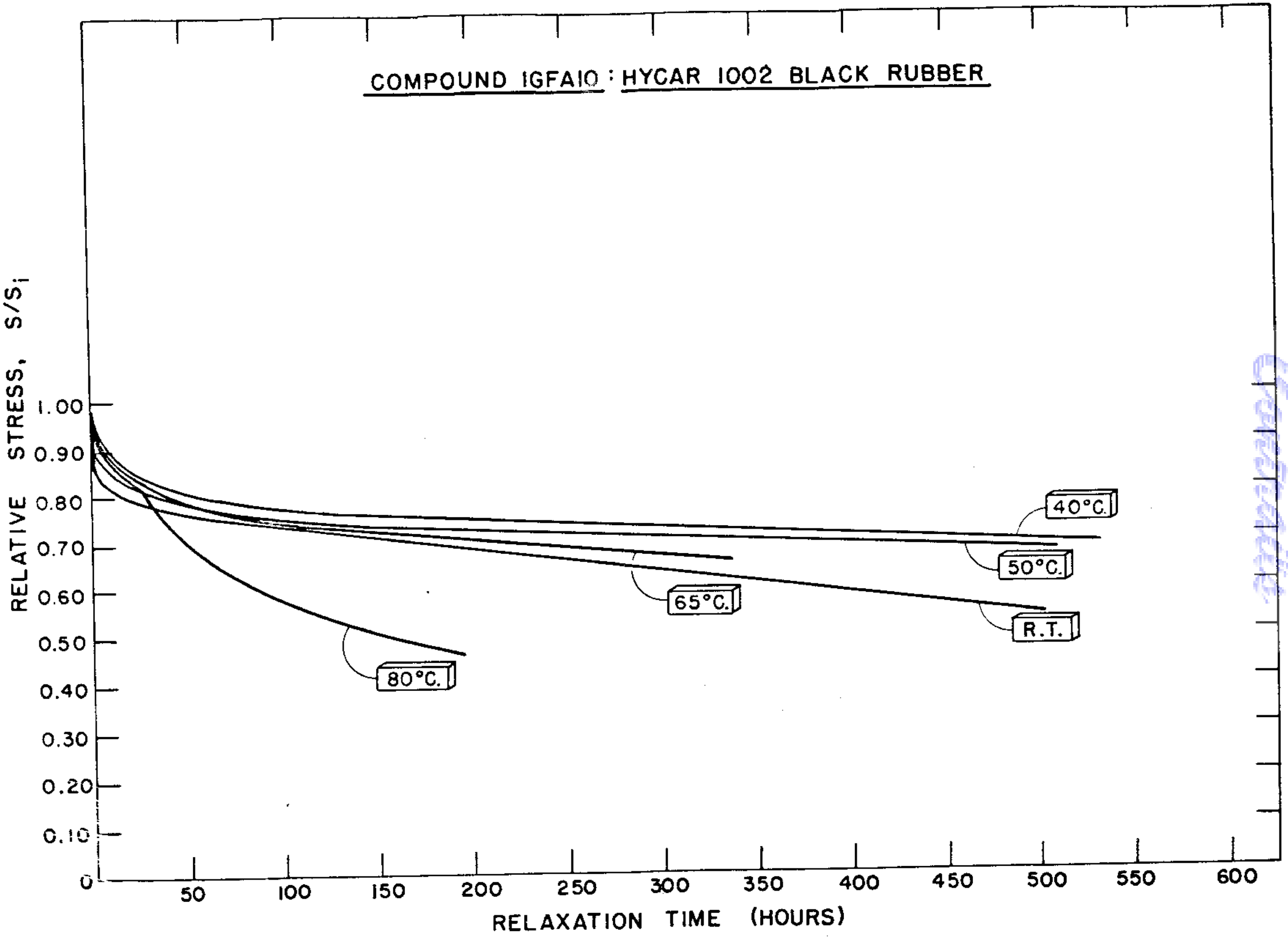

FIGURE 21. CONTINUOUS STRESS RELAXATION OF A BLACK HYCAR 1002 COMPOUND DURING HEATING IN AIR

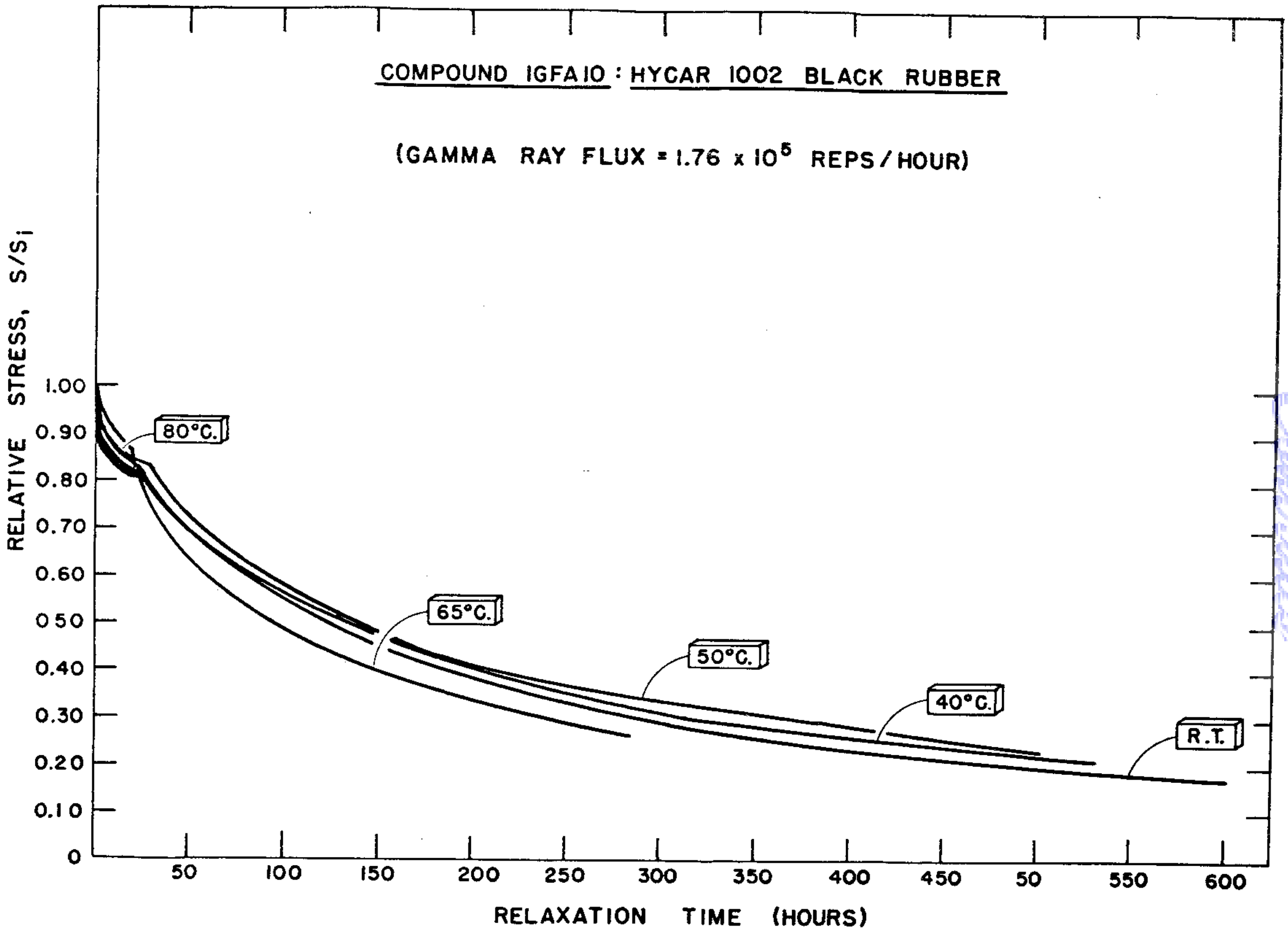

FIGURE 22. CONTINUOUS STRESS RELAXATION OF A BLACK HYCAR 1002 COMPOUND DURING IRRADIATION AND HEATING IN AIR

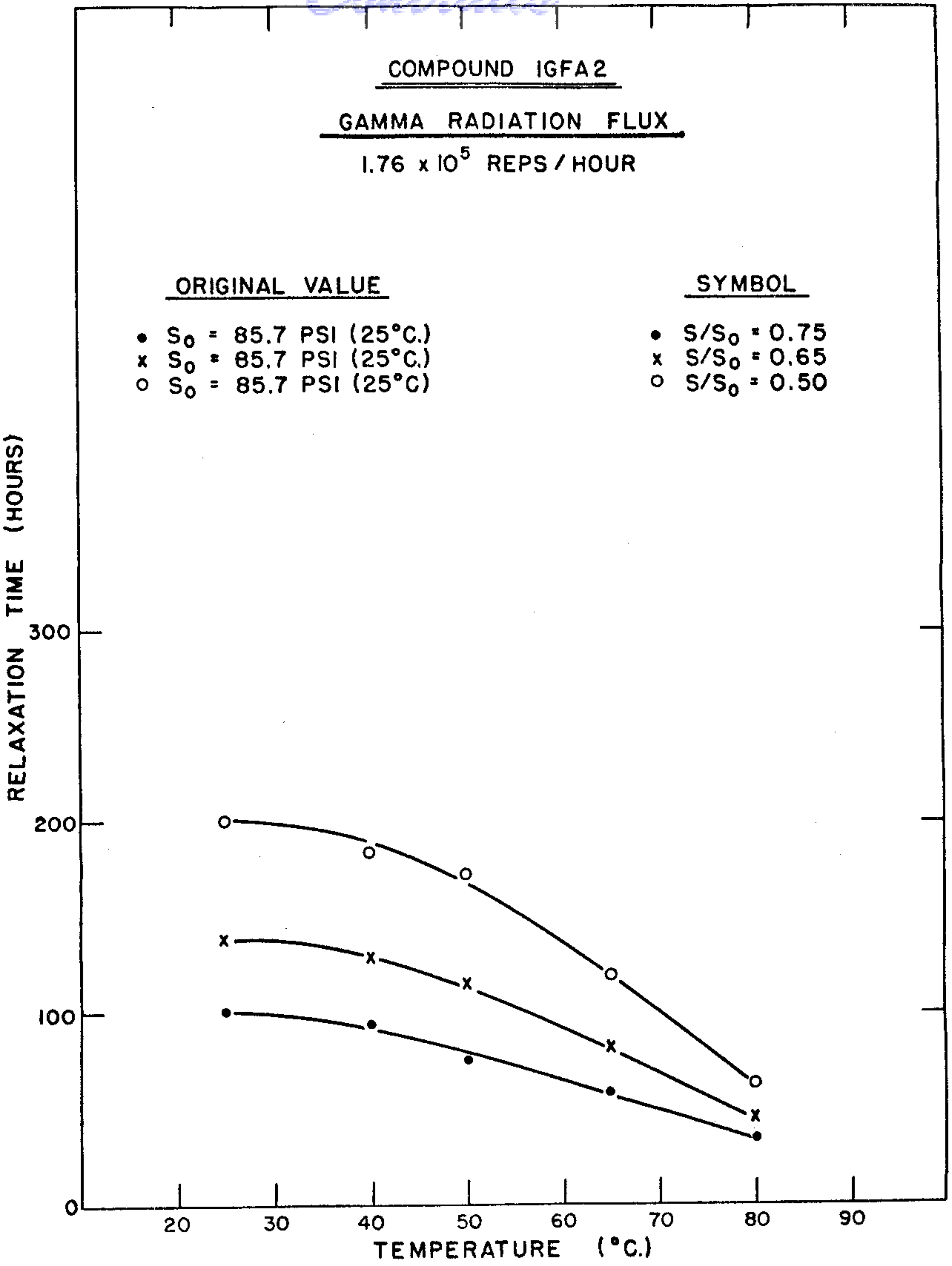

FIGURE 23. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF GUM NATURAL RUBBER DURING IRRADIATION IN AIR.

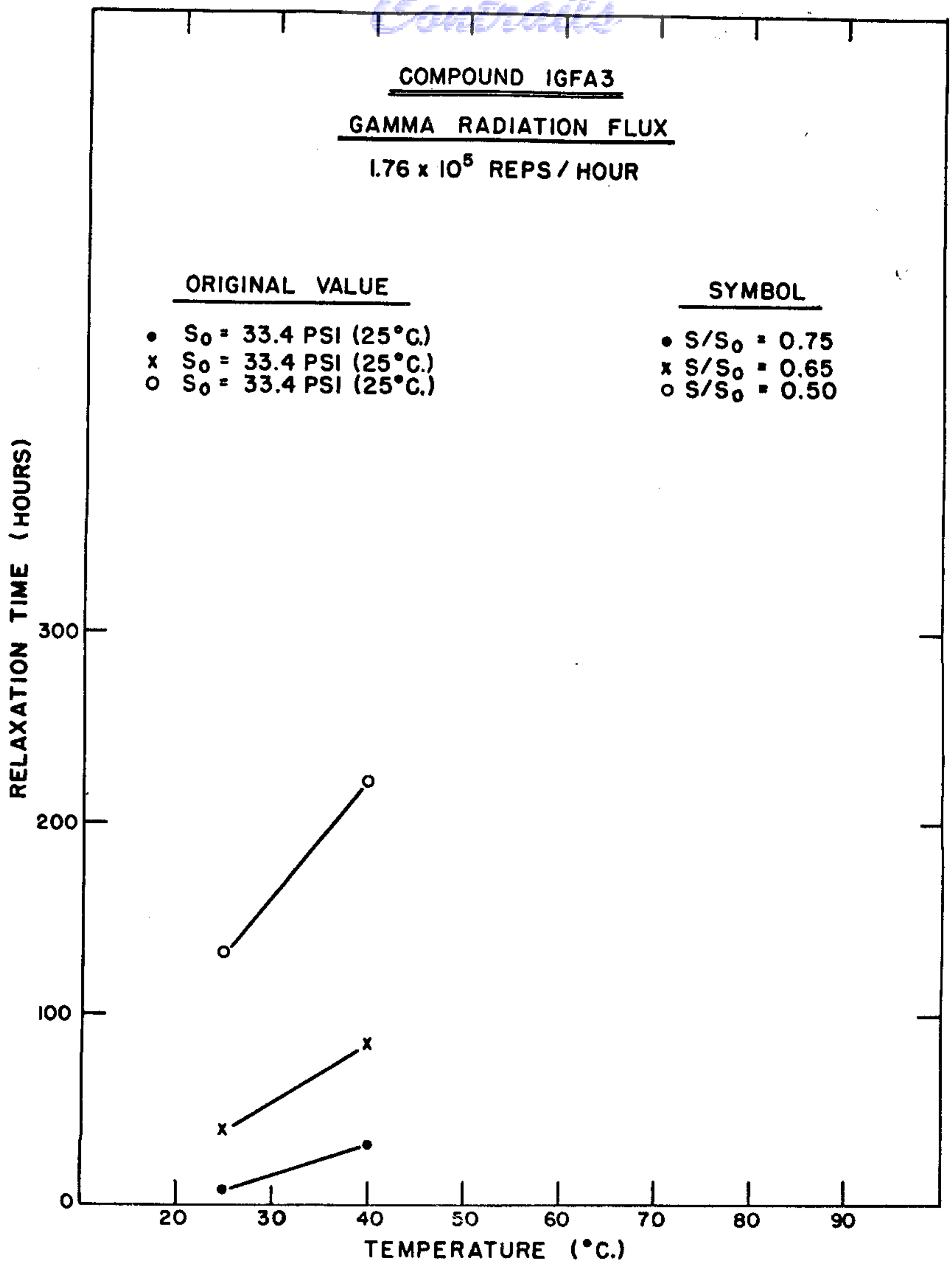

FIGURE 24. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF GUM GR-S DURING IRRADIATION IN AIR

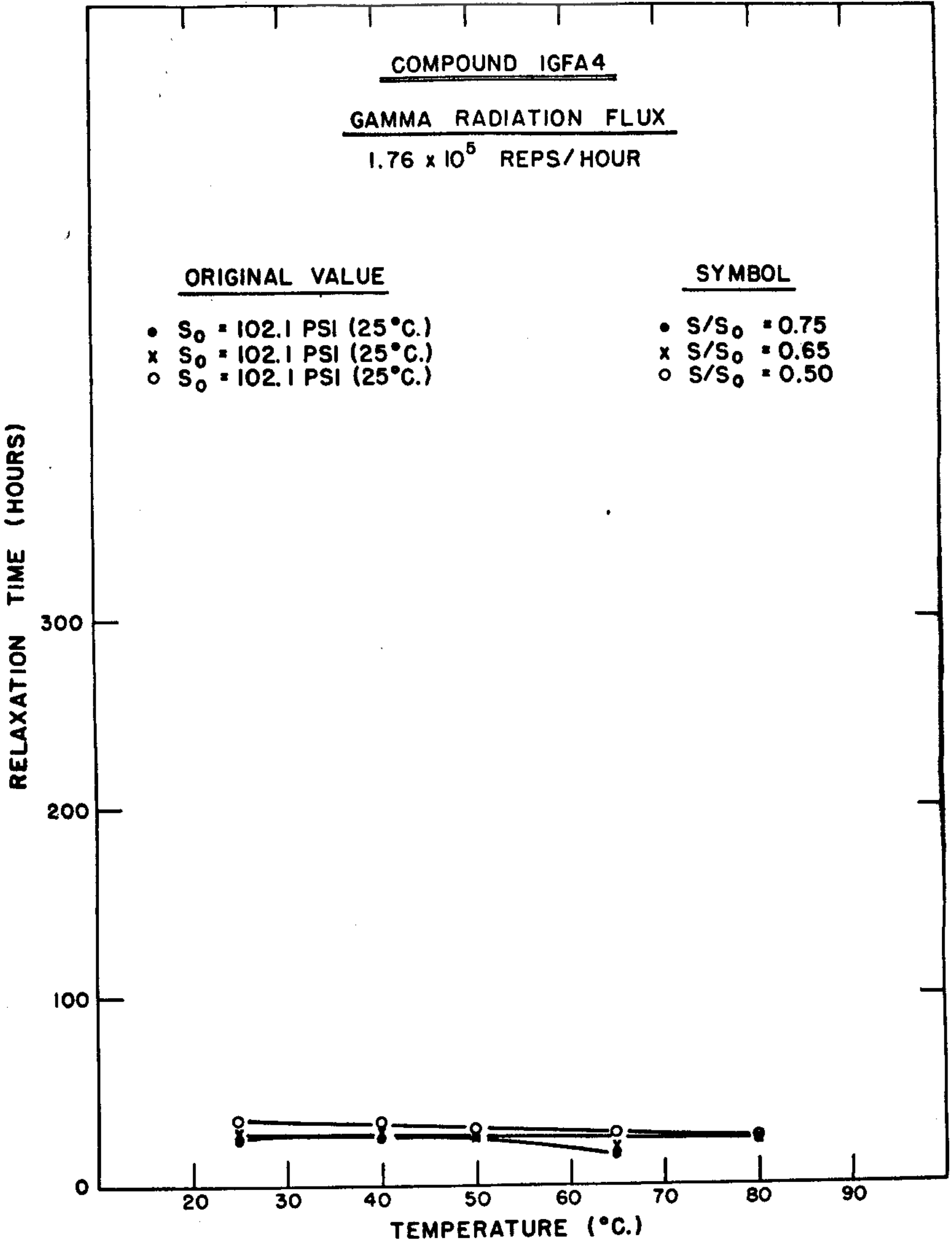

FIGURE 25. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF GUM NEOPRENE GN DURING IRRADIATION IN AIR

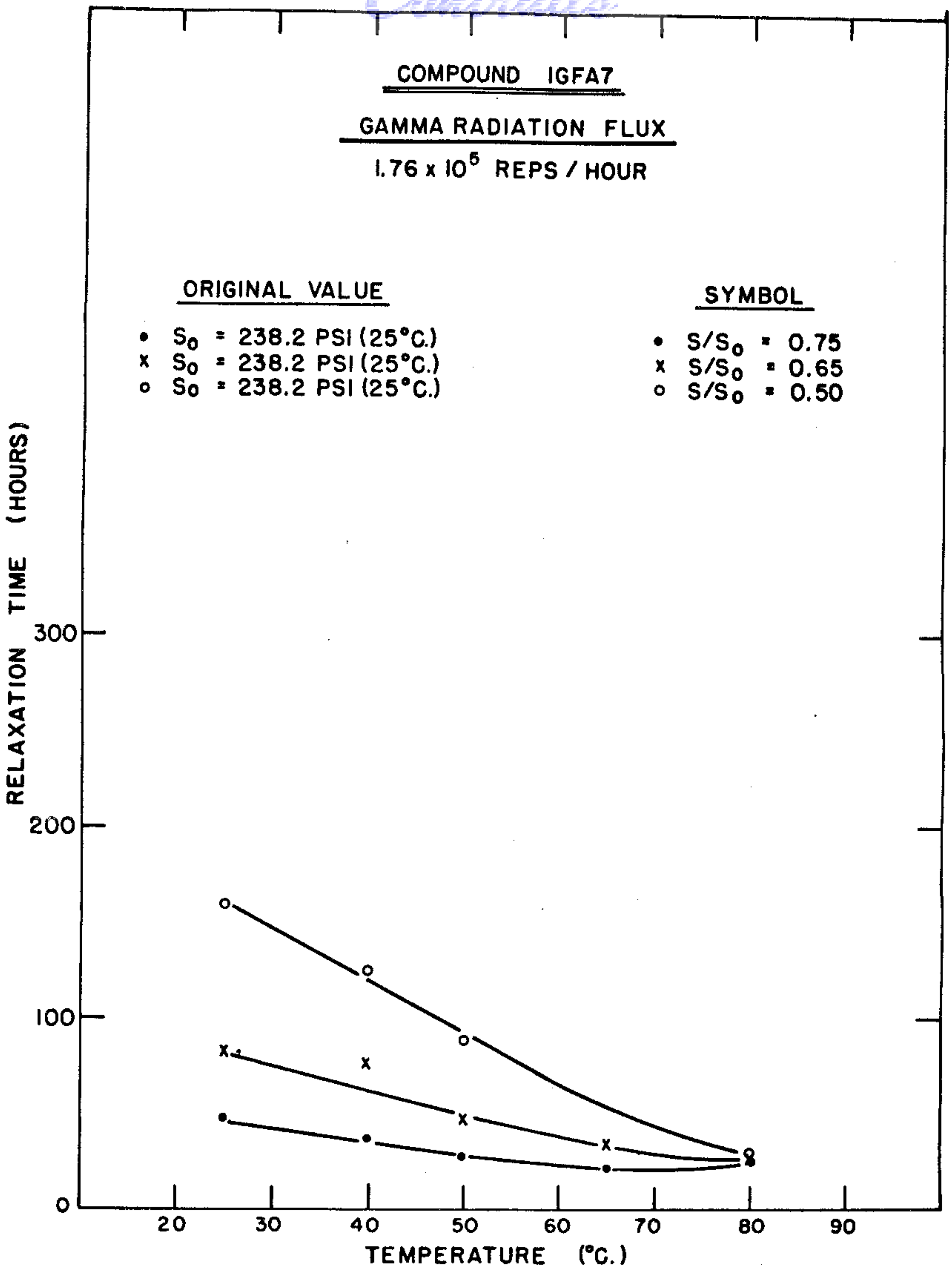

FIGURE 26. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF A BLACK NATURAL RUBBER COMPOUND DURING IRRADIATION IN AIR

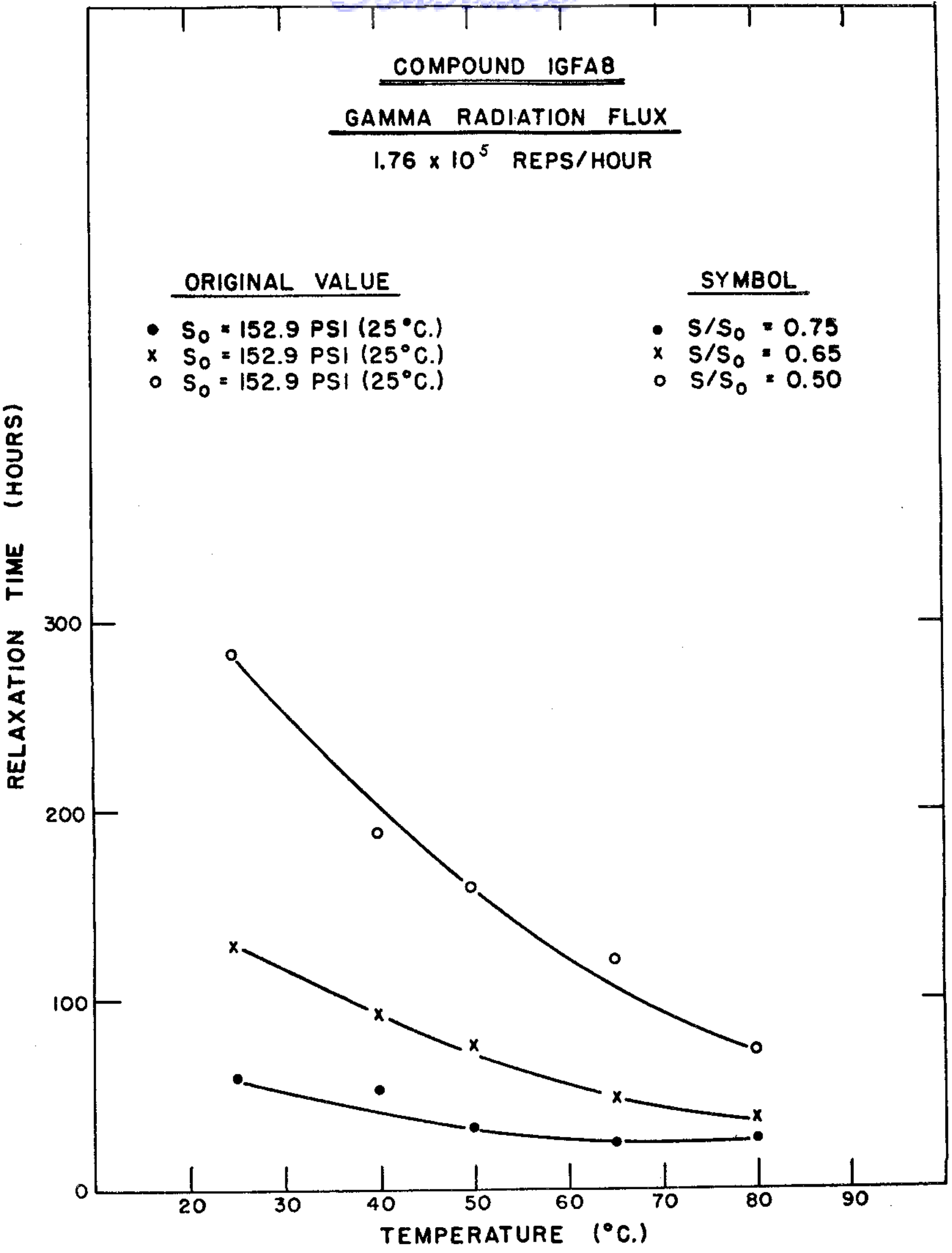

FIGURE 27. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF A BLACK GR-S COMPOUND DURING IRRADIATION IN AIR

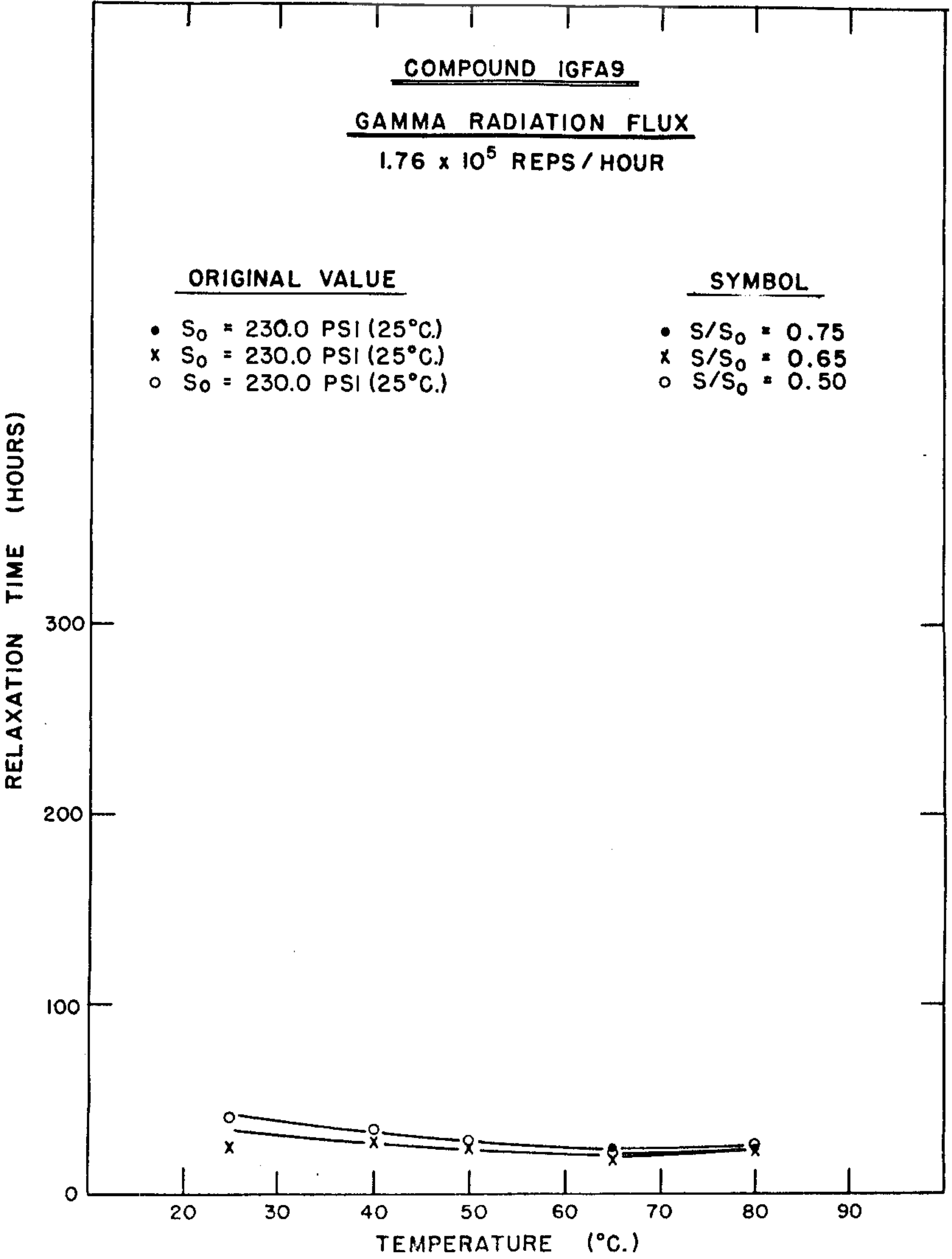

FIGURE 28. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF A BLACK NEOPRENE GN COMPOUND DURING IRRADIATION IN AIR

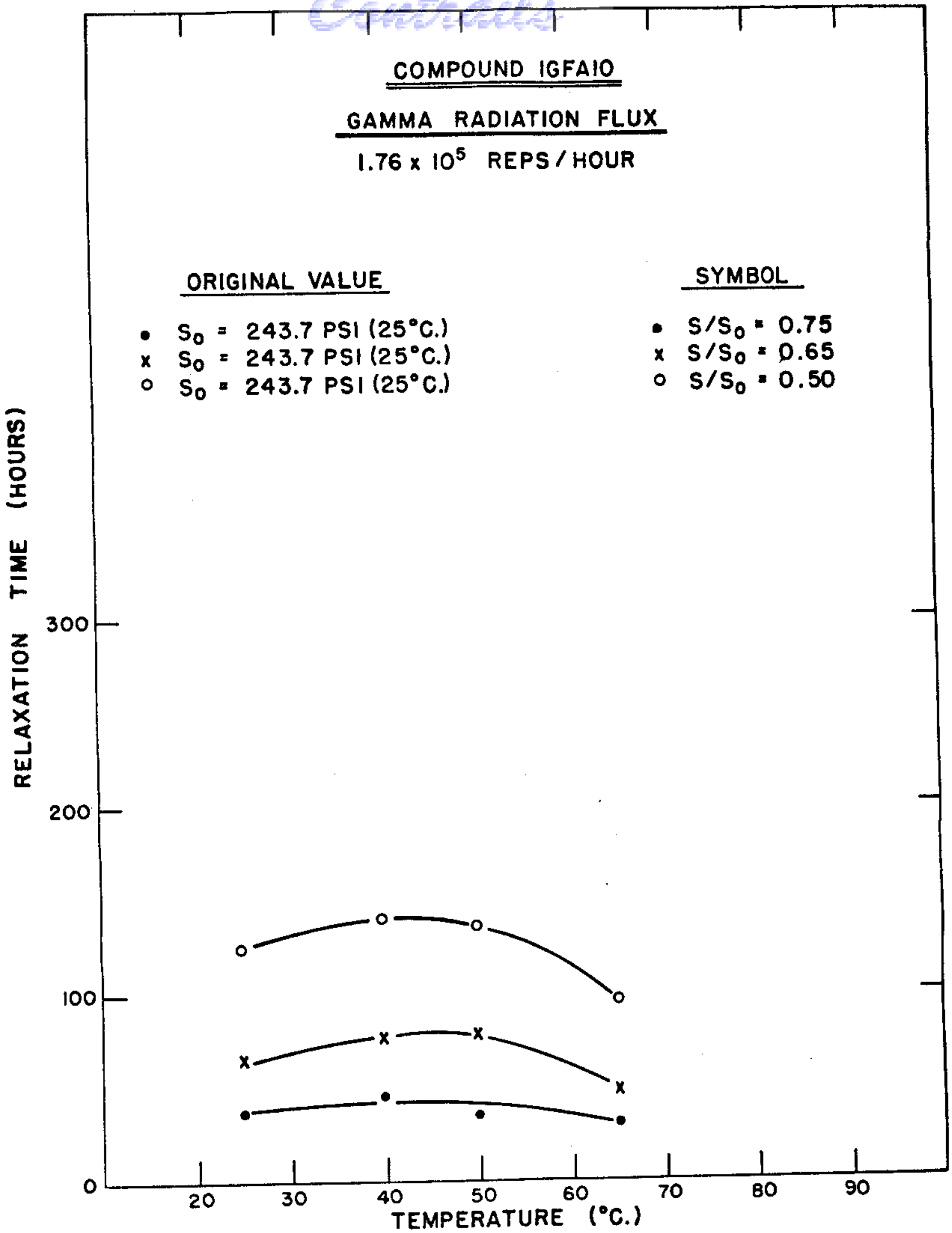

FIGURE 29. THE EFFECT OF TEMPERATURE ON THE RELAXATION TIME OF A BLACK HYCAR 1002 COMPOUND DURING IRRADIATION IN AIR

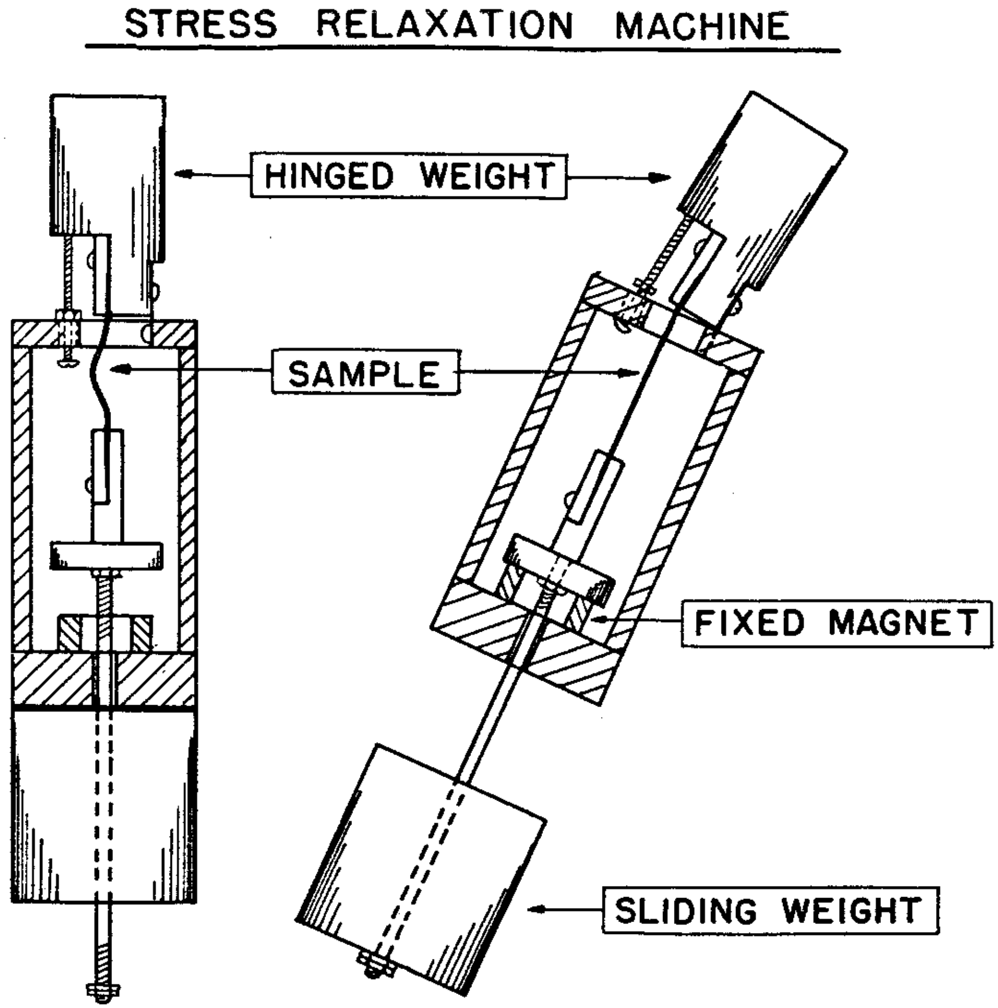

Figure 30. SCHEMATIC DRAWING OF A DIPSOMETER

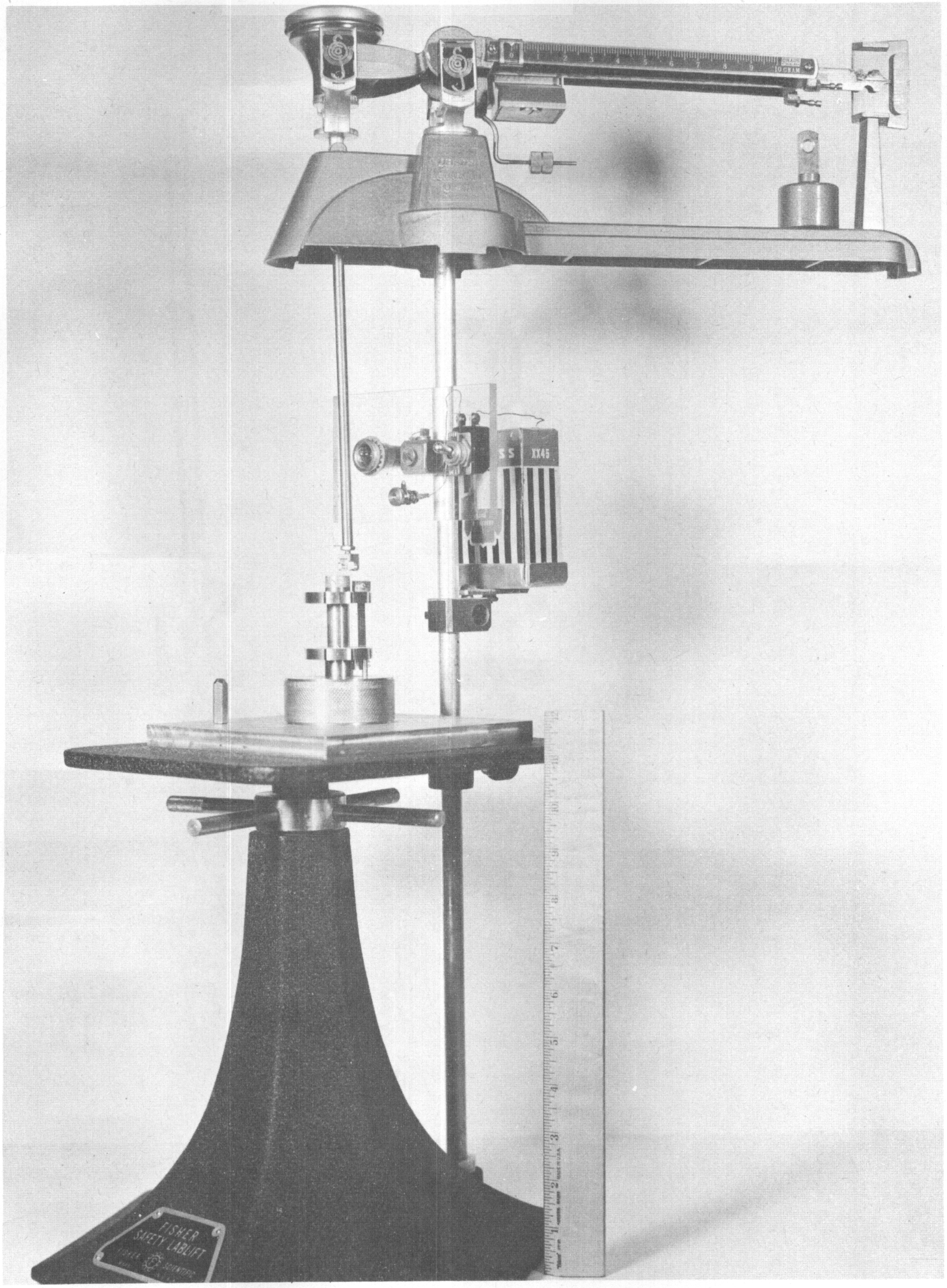

Figure 31 THE STRESS RELAXATION READER ASSEMBLY

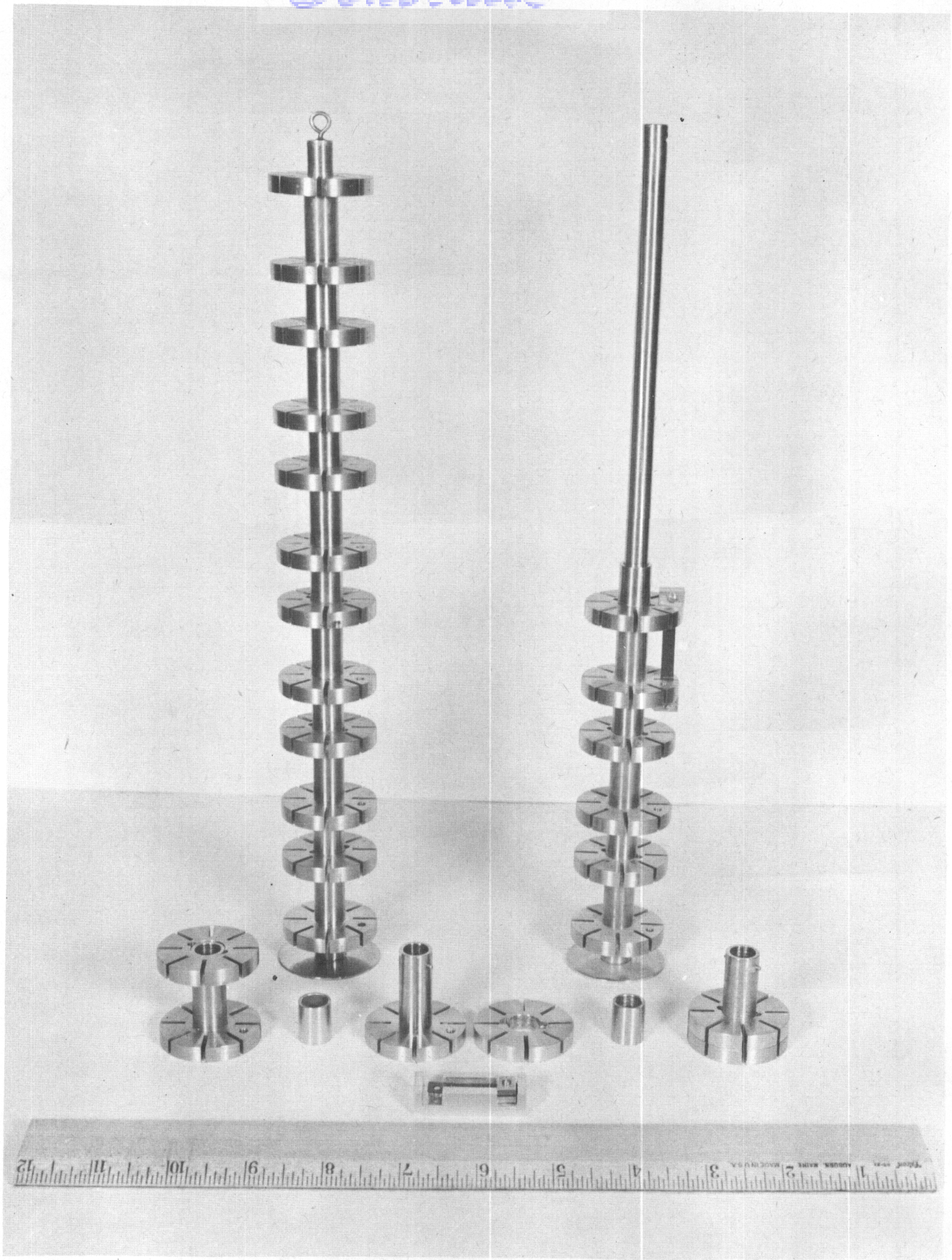

Figure 32 . THE STRESS RELAXATION RACK ASSEMBLY

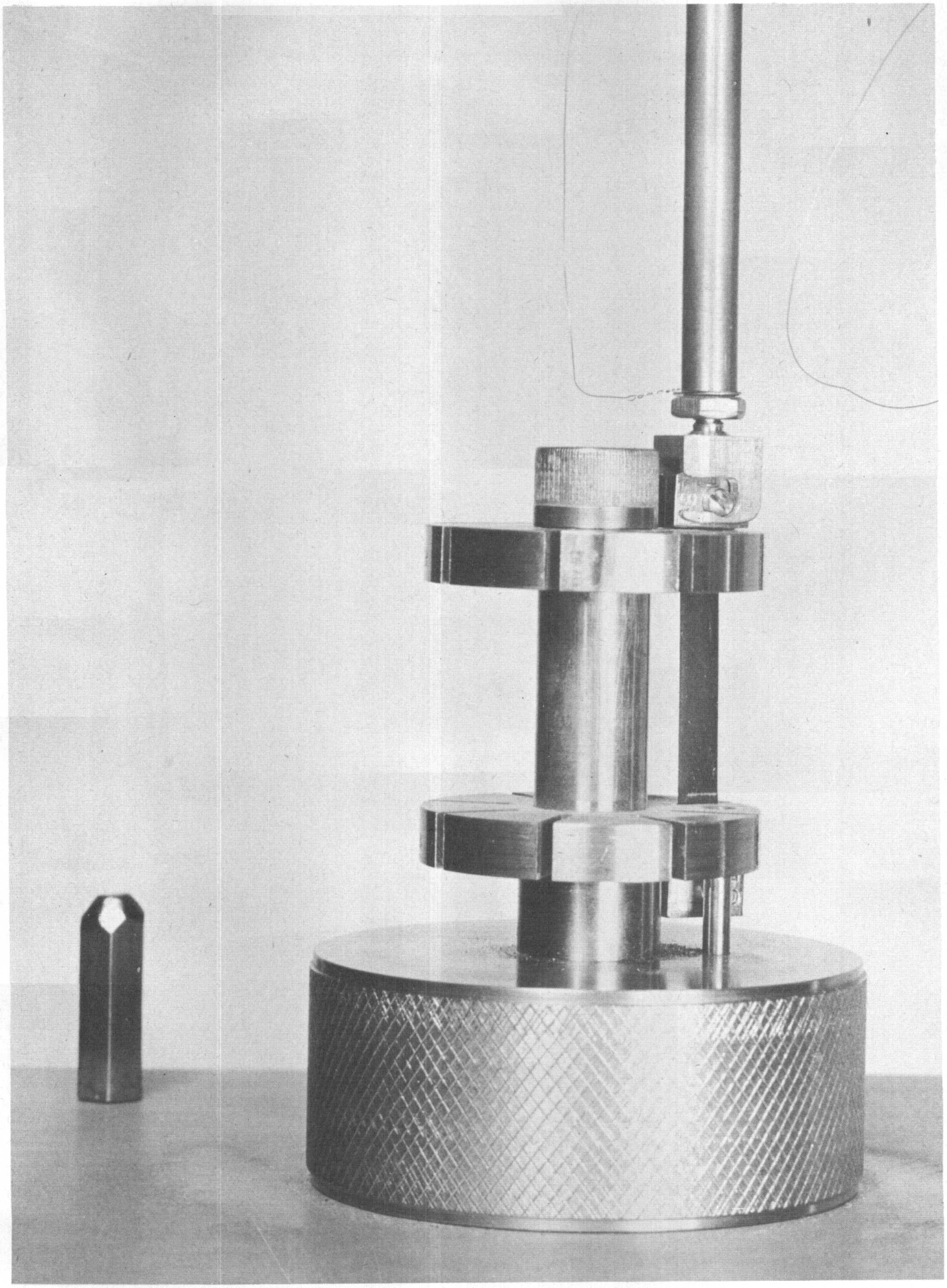

Figure 33 ATTACHMENT OF HOOK TO JAWS IN DETAIL

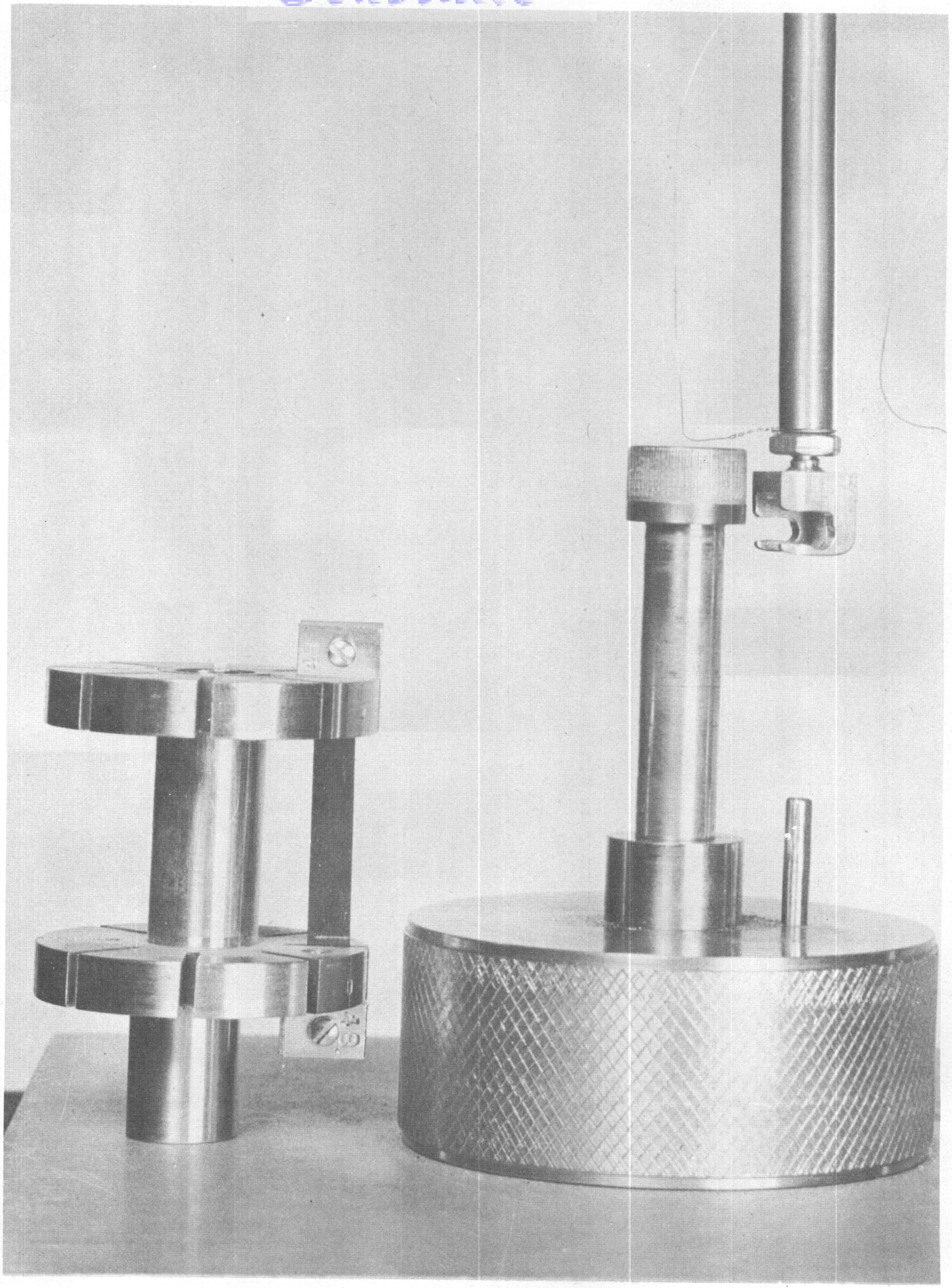

Figure 34 . DESIGN OF HOOK IN DETAIL

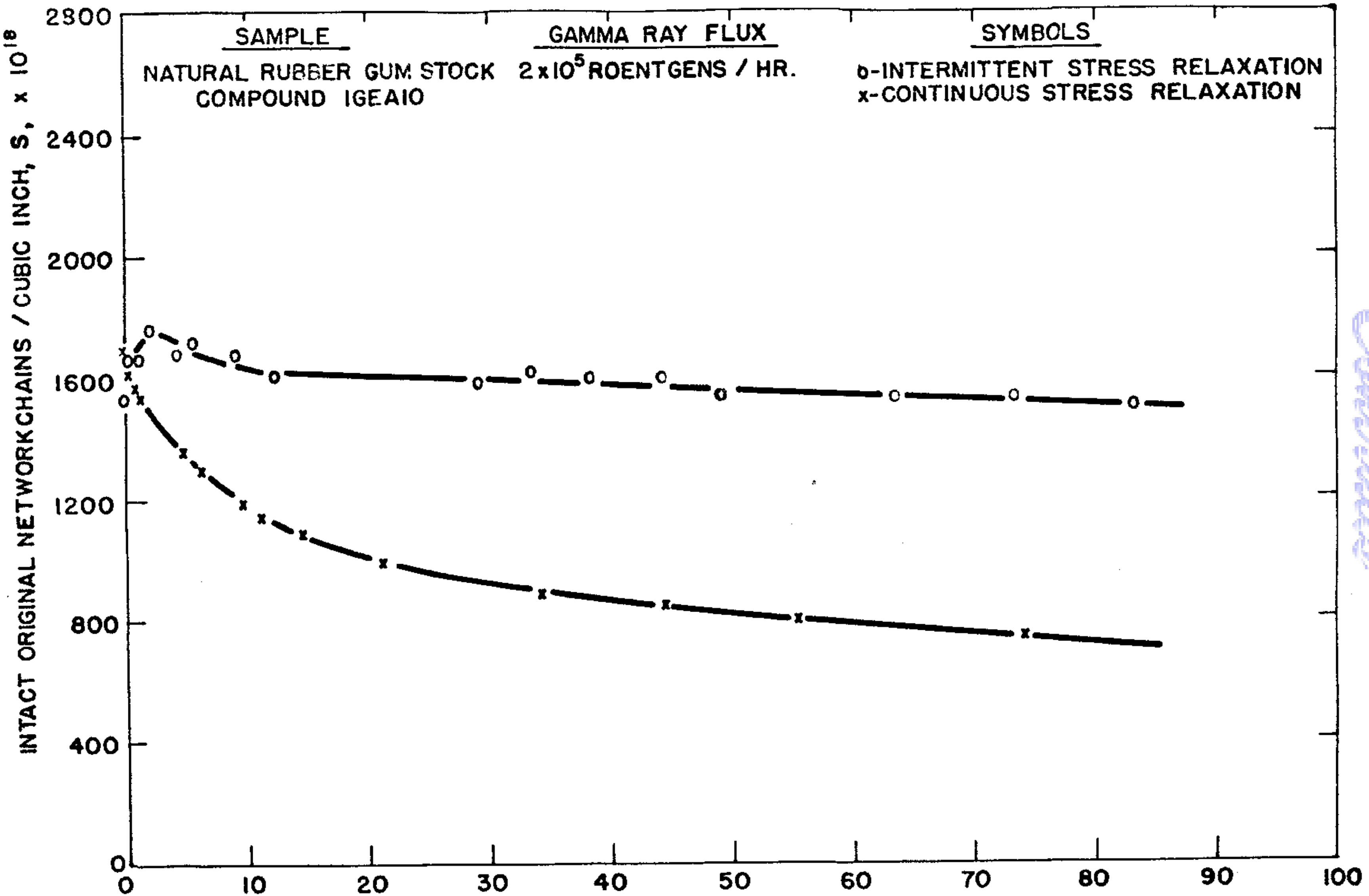

FIGURE 35 RADIATION EFFECTS: STRESS RELAXATION IN VACUUM.

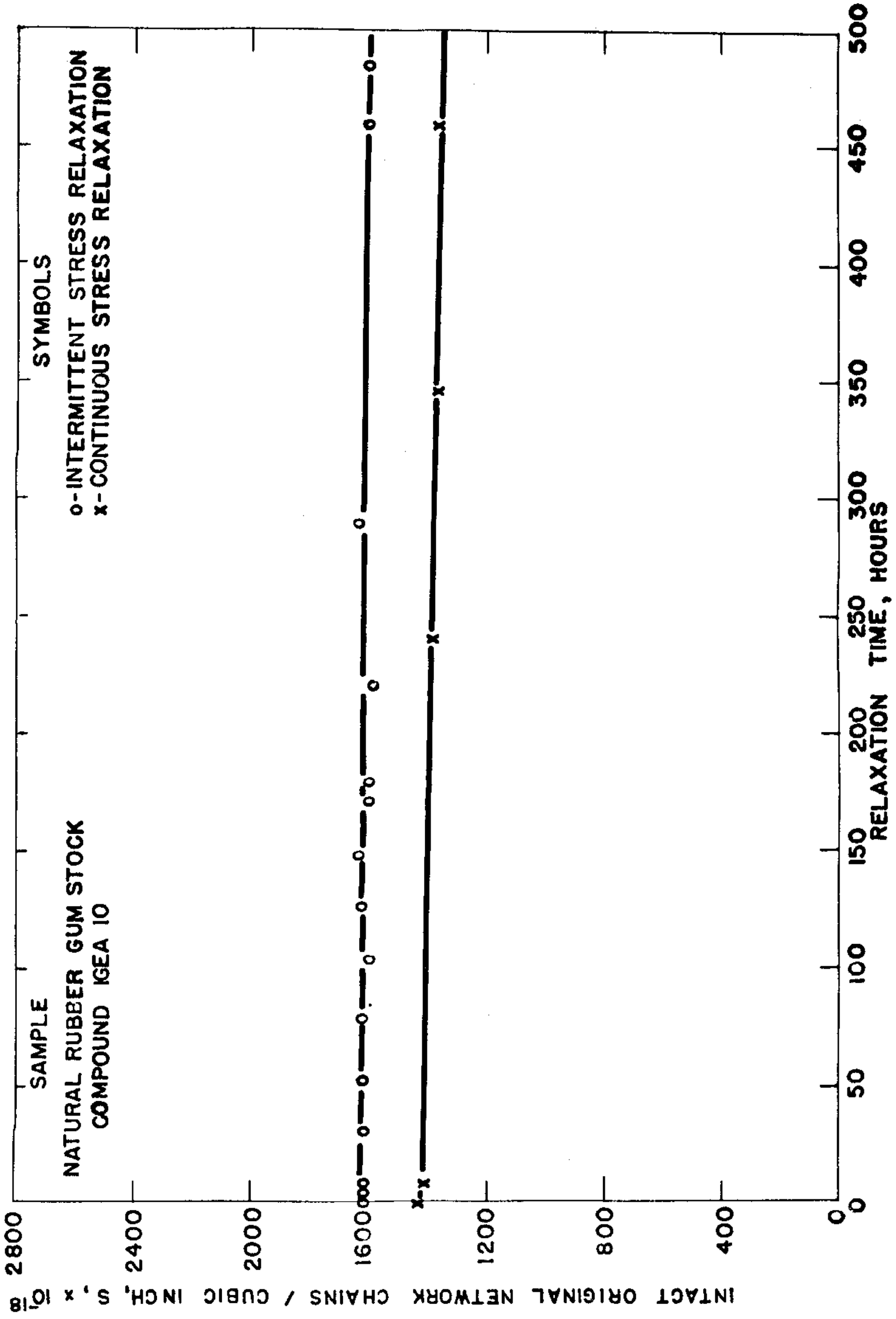

FIGURE 36 CONTROL STUDY: STRESS RELAXATION IN VACUUM

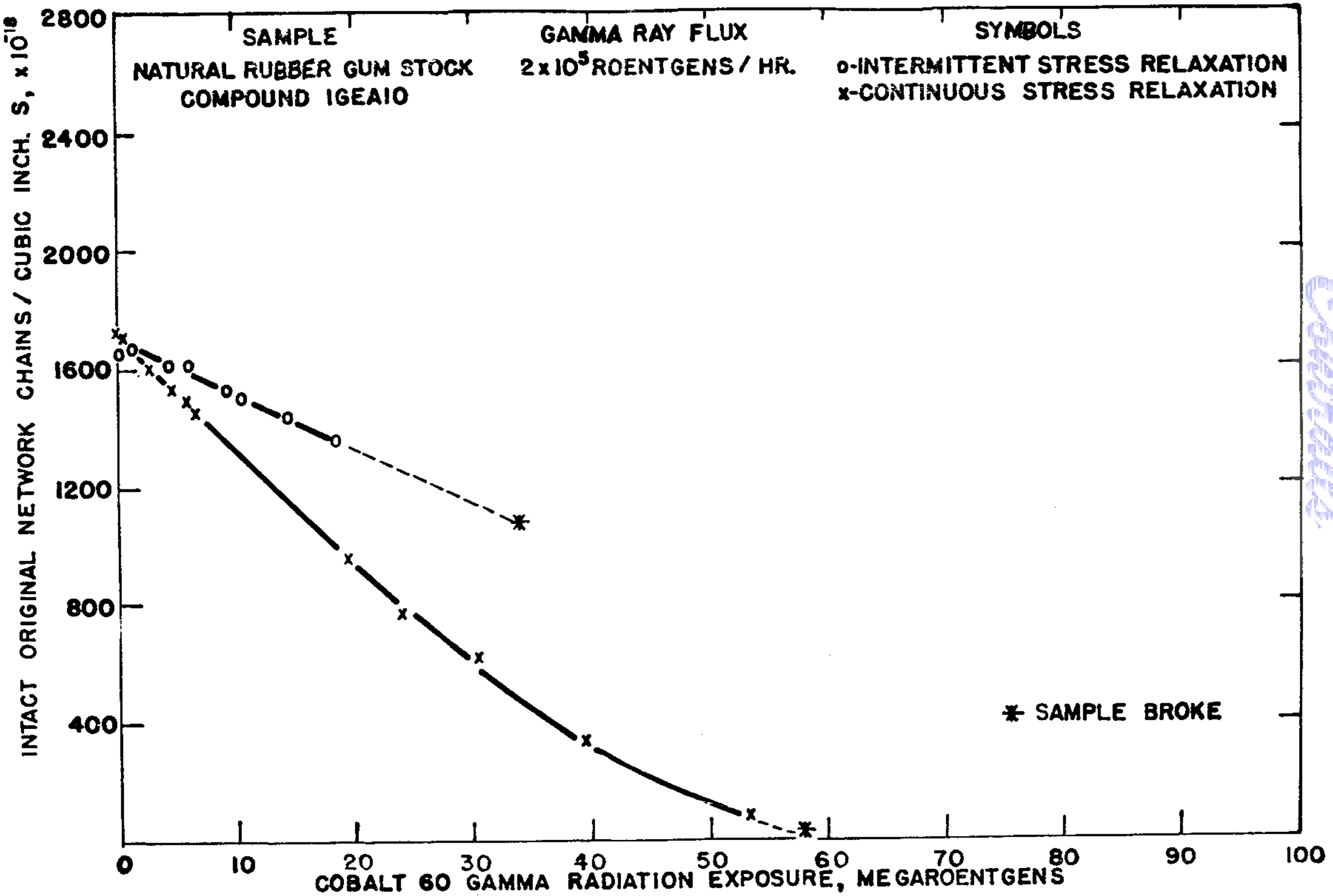

FIGURE 37 RADIATION EFFECTS: STRESS RELAXATION IN AIR.

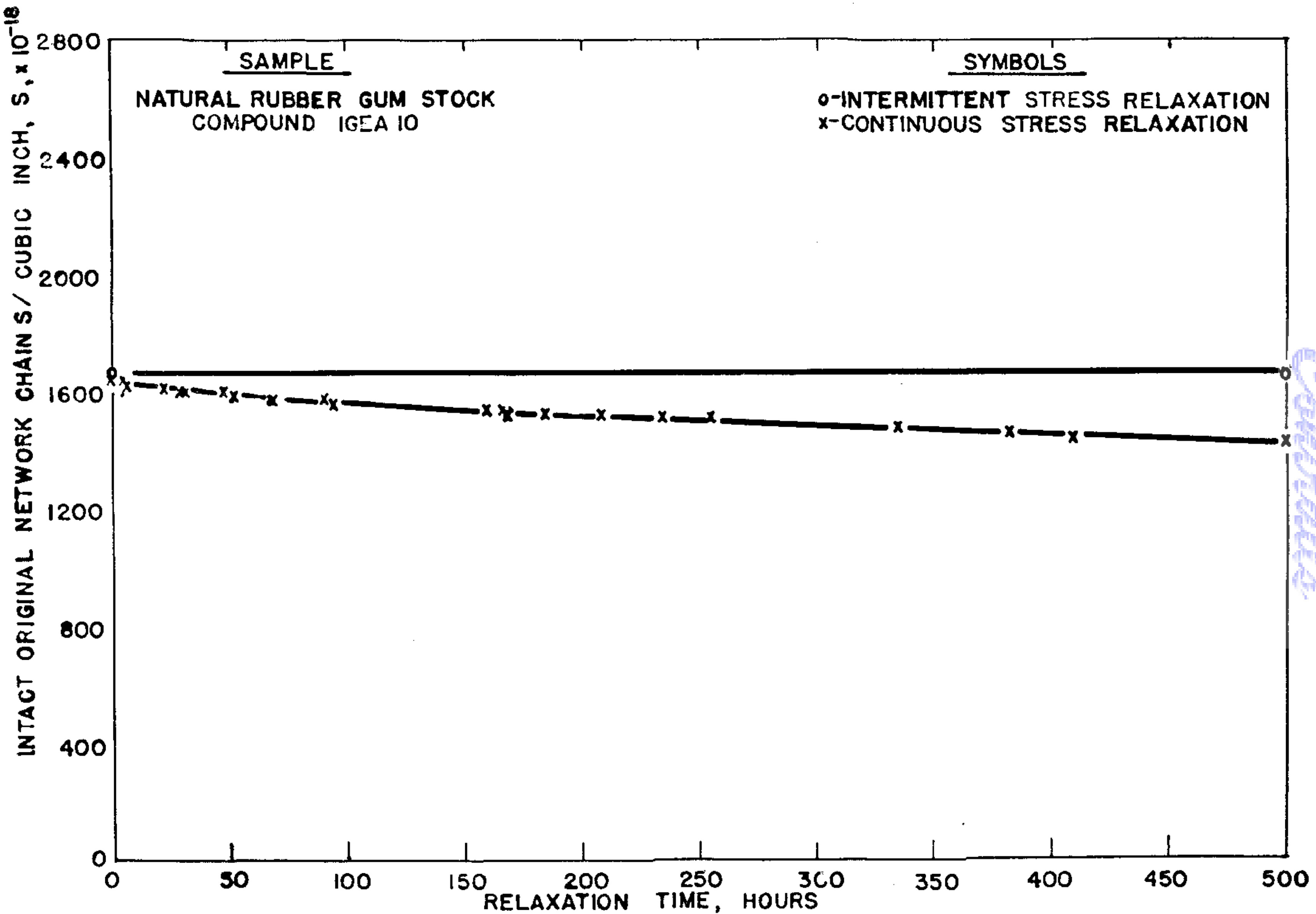

FIGURE 38 CONTROL STUDY: STRESS RELAXATION IN AIR.