

General Electric Company
KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York

THE INTERACTION OF TRITIUM
WITH POLYMERIC MATERIALS

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B. A. Hemmer
C. F. Pachucki

August 21, 1953

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ACKNOWLEDGMENT

We are grateful to D. H. Ahmann for his continued interest in the work and to H. C. Matraw for his assistance in the interpretation of mass spectrometric data. We are indebted to C. C. Harris of the duPont Company with whom we have had repeated discussions concerning many aspects of the problem.

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ABSTRACT

The effect of tritium on a number of polymeric materials has been investigated. The exchange rates of tritium with the following polymers increase in the order:

Hypalon X-53 < Hycar DR-25 < GR-S, X-478 < Natural Rubber < Neoprene Type WRT

The extent of hardening as a result of exposure to tritium is in the following increasing order.

GR-S, X-478 \leq Hycar DR-25 < Natural Rubber < Neoprene Type WRT < Hypalon X-53
< Hypalon X-52 < Hypalon X-50 < Buna-N*

Elongation tests indicate a differing hardening mechanism in the case of Neoprene Type WRT and Natural Rubber. Tritium fluoride was the only decomposition product identified in the case of Teflon and Kel-F exposed to tritium. On the basis of these experiments, GR-S, X-478 and Hycar DR-25 seem to be the most suitable of the candidate rubbers for use as gasket materials and valve seats.

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THE INTERACTION OF TRITIUM WITH POLYMERIC MATERIALS

L. M. Dorfman, B. A. Hemmer, C. F. Pachucki

INTRODUCTION

The metal vacuum systems used in the processing of tritium require the use of organic polymers, such as rubbers or plastics, as o-rings in metal flanges and seat materials in vacuum valves. A serious problem in the use of these polymers results from their rapid deterioration under the radiation effects of the tritium β -particles.

In order to obtain information about the nature of the physical and chemical processes occurring and to provide some basis for the selection from candidate materials for use in the metal tritium lines, an investigation of the interaction of tritium with a number of polymers was undertaken.

A brief mention of the possible primary processes involved in the attack on the polymer is in order. Some of these are:

- I. Ionization by β -particles originating in the gas phase.



followed by decomposition:



where RH represents the polymer molecule. A consequence of this primary process would be exchange with the tritium:



The formation of the hydrocarbon radical $R\cdot$ in the polymer could lead to cross-linking and subsequent hardening of the polymer. Primary process I will be predominantly a surface effect because of the short range of the β -particles. (The tritium β -spectrum has an end-point energy of 0.018 Mev.¹) This will not be the sole primary process since at tritium pressures approaching one atmosphere, most of the ionization by β -particles will occur in the gas phase, leading to:

- II. Hydrogen abstraction from the polymer molecule by tritium atoms.



Secondary reactions of cross-linking and exchange would follow process II.

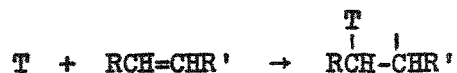
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III. Ionization of the polymer by β -particles from tritium within the polymer itself.

β -particles resulting from the decay of tritium which has found its way into the polymer by diffusion and by exchange with hydrogen in the polymer molecule would be absorbed almost completely by the polymer leading to ionization and the various secondary reactions. This would not be only a surface phenomenon.

IV. Addition of tritium atoms to ethylenic linkages.



Partial saturation of the polymer molecules could lead to reactions of cross-linking and exchange.

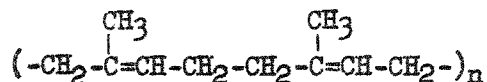
In the case of the rubbers the rates of exchange with tritium and the extent of hardening were measured. Elongation changes were determined for two rubber samples. In the case of halogenated polymers, decomposition products were determined.

POLYMERS INVESTIGATED

The following polymers were subjected to tests. The first five of these were obtained from the duPont Company. The first four were compounded by the duPont Rubber Development Laboratory for this specific purpose.

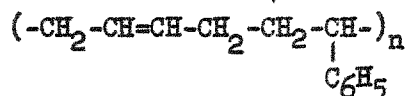
1. Natural Rubber

polyisoprene



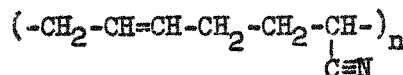
2. GR-S, X-478[‡]

a Buna-S rubber, a copolymer of butadiene and styrene



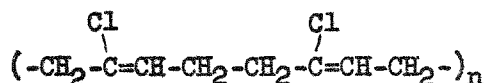
3. Hycar, DR-25[‡]

a Buna-N or Perbunan rubber, a copolymer of butadiene and acrylonitrile



4. Neoprene Type WRT[‡]

polychloroprene



[‡] These are duPont Rubber Laboratory designations.

5. Hypalon, Types X-50, X-52, and X-53[†] chlorosulfonated polythene
6. Teflon polytetrafluoroethylene
 $(-CF_2-CF_2-)_n$
7. Kel-F Polytrifluoromonochloroethylene
 $(-CF(CCl)-CF_2-)_n$
8. Silicone The compounding of this particular silicone rubber sample was not known to us at the time of writing.
9. Buna-N*, Type OR-15 This particular sample was obtained from The Canfield Rubber Co. and was identified as a Buna-N rubber by analysis at the Rubber Development Laboratory of the duPont Company.

EXPERIMENTAL METHODS

Exchange Rates

These determinations were carried out on all the hydrocarbon polymers. A sample of each of the rubbers, 1 inch by 1 inch by 1/8 inch, was sealed inside a cylindrical pyrex tube of approximately 35-cc volume. The type of sample tube used may be seen in the photograph, Figure 11. The tube was closed off by two vacuum stopcocks in series enclosing a capillary lock of volume approximately 0.4 cc. With this arrangement small gas samples could be withdrawn from time to time for mass spectrometric analysis without any substantial reduction in the gas pressure inside the tube. It has been shown² that the mass spectrometric sensitivities for hydrogen and tritium, with the General Electric analytical mass spectrometer in use here, are equal to within less than 2%.

The tube containing the polymer sample was first evacuated to a pressure of less than 10^{-5} mm after which tritium (containing some 10 to 15% hydrogen) was introduced from a uranium bed, usually to a pressure of about 120 mm. The exchange rates were followed for several weeks, during which time some six or seven analyses were done on each tube. The stopcocks were lubricated with fluorothene grease to avoid the exchange which is known to occur with hydrocarbon greases.

[†]These are duPont Rubber Laboratory designations.

Hardness Measurements

The extent of hardening as a result of exposure to tritium was determined for all of the first five rubbers listed above and for the sample of Buna-N* using a Shore Durometer, Hardness Type A2. At the end of the exchange tests the tritium in the sample tubes was taken up on a uranium bed and the rubber sample removed from the tube. The hardness of the exposed samples was measured on a steel surface. In addition to the samples obtained from the exchange experiments, further samples for hardness tests were placed in tubes (four or five in a single tube) and exposed to tritium for periods up to three months to determine extent of hardening.

Elongation Changes

Only the samples of Neoprene Type WRT and Natural Rubber were subjected to elongation tests. A ring of each of these rubbers, 14-mm diameter, 1-mm thickness, was suspended in the apparatus shown in the photograph, Figure 10a. The weight, 429 grams, consisted of a pyrex tube filled with mercury and sealed under vacuum. The entire outer tube was filled with tritium to a pressure of about 100 mm. A small inverted wire basket was placed inside the tube at the bottom as a precaution in the event of rupture of the ring sample. The standard taper of the outer jacket was sealed with Apiezon W wax. The stopcocks were lubricated with fluorothene grease. Elongation measurements were made once or twice daily using a cathetometer. When readings were not being taken, the apparatus was placed on its side to remove the stress from the rubber ring.

Decomposition

Rates of formation of decomposition products were determined only for the samples of Teflon and Kel-F. Small solid pieces of each polymer were placed in tubes and exposed to tritium for several weeks. These tubes were fitted with capillary locks for sampling. In two cases the stopcocks were lubricated with fluorothene grease. Since it was suspected that fluorothene grease could conceivably give rise to similar decomposition products, two experiments were set up in which the stopcocks were lubricated with Apiezon W grease. In addition, a sample of shredded Teflon, weight 4.607 grams, with an extremely large surface area was placed in a similar tube and exposed to tritium gas. The sample and tube used in this latter experiment may be seen in the photograph, Figure 11.

To check on the possibility of dimensional changes in the Teflon, two pieces which were carefully machined were exposed to tritium. These were accurately measured with a micrometer before and after the exposure.

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In general, proper vacuum technique was employed in all the foregoing experiments. Sample tubes were thoroughly degassed before tritium was added. The tritium, which was handled on uranium beds and with Toepler pumps, was free of impurities other than hydrogen. All the apparatus was handled in hoods. The normal safety precautions, such as the use of gloves and air masks, were taken in handling the rubber samples after exposure to tritium.

RESULTS AND DISCUSSION

Exchange Rates

The only change observed in the tritium gas in contact with the rubber samples is a continuous decrease in the percentage of tritium and a corresponding increase in the percentage of hydrogen. These results may be seen in Figures 1 to 5 in which are plotted the mole per cent of tritium and of hydrogen versus the time in days for each of the first five rubbers listed in the Section, Polymers Investigated. The composition change is clearly due to exchange of tritium with the hydrogen in the rubber rather than increase of hydrogen from decomposition of the rubber. This is established by the following evidence. Although there is no direct pressure reading device connected with the sample tubes, any pressure change greater than a few per cent would manifest itself in a similar change in the sum of the mass spectrometer peak heights for H_2 , HT , and T_2 . Each analytical sample is taken as a constant aliquot of the whole. The mass spectrometer sensitivity for these peaks is constant to within $\pm 5\%$ during the period of the experiments. The sum of these peaks has therefore been examined for constancy for the series of analyses carried out on each sample. There is no pressure change within $\pm 5\%$. A graphical comparison of the exchange rates has been made in Figure 6 in which all five composition-time curves are shown on a single graph.

A numerical comparison of the rates of exchange with the rubbers may be made from the slopes of the composition-time curves. The slopes should be measured at the same composition point on each curve since it is clear that the exchange rate falls off as the percentage of tritium in the gas phase decreases.

The numerical computation may be made most easily by tabular differentiation using the method of finite differences. For a plot of y as a function of x , if the values of y for equispaced intervals in x are available, the slope of the curve at any point x_0 may be obtained from the equation:

$$\frac{dy}{dx} \Big|_{x=x_0} = \frac{1}{h} \left(a_0 - \frac{b_0}{2} + \frac{c_0}{3} - \frac{d_0}{4} \dots \right)$$

where h is the magnitude of the equispaced intervals in x , and $a_0 = y_1 - y_0$, $b_0 = a_1 - a_0$, etc, are the 1st, 2nd, etc, finite differences in the values of y . Although the composition points in Figures 1 to 5 are not for equispaced time intervals, the plots are smooth enough so that this information can be obtained from the curves. The values of the change in percentage of tritium per day have been obtained for each of the exchange curves at the composition point corresponding to 84.0% tritium. The results are shown in the following table, which includes, in addition to the decrease in the percentage of tritium per day, a column showing the total pressure for each run.

TABLE I

EXCHANGE RATES OF TRITIUM WITH RUBBERS

Rubber Sample	Initial Pressure (mm)	Exchange Rate at 84.0% T ₂ (%/day)	Exchange Rate Pressure x 10 ² (%/day/mm)
Natural Rubber	112.9	2.17	1.92
GR-S, X-478	127.7	1.67	1.31
Hycar, DR-25	117.8	1.53	1.30
Neoprene Type WRT	115.7	3.43	2.96
Hypalon X-53	109.2	1.30	1.19

As may be seen from Table I, the relative rates of exchange of these samples are in the following order of ascending rates.

Hypalon X-53 < Hycar DR-25 < GR-S, X-478 < Natural Rubber < Neoprene Type WRT

The Neoprene Type WRT has by far the fastest rate of exchange with the tritium.

Differences in the tritium pressure may affect the rates of exchange. Since the pressures are not exactly the same for each sample tested, the rates have been "normalized" to equal pressure and the results are shown in the last column, which lists the rate (at 84% T₂) divided by the pressure. The comparison of these "corrected" rates does not change the order:

Hypalon X-53 < Hycar DR-25 = GR-S, X-478 < Natural Rubber < Neoprene Type WRT

A very rapid exchange rate would be undesirable in a candidate material for the following reasons. Firstly, the loss of tritium by exchange to gasket and valve seat materials could make a small but significant contribution to material balance deficiencies. One gram of a hydrocarbon rubber, in which half the hydrogen had been exchanged for tritium, would contain over 400 standard cc of tritium. Secondly, a greater extent of radiation damage by way of direct ionization by the tritium β -particles might be expected in compounds holding a larger amount of tritium in the molecule itself.

Hardness Measurements

The results of the determination of hardness after exposure to tritium are listed in Table II for eight types of rubbers. The values given have been obtained with a Shore Durometer, Hardness Type A-2. The rubber sample and identified as Buna-N rubber (by analyses at the Rubber Development Laboratory of the duPont Company) showed by far the greatest

TABLE II

HARDNESS AFTER EXPOSURE TO TRITIUM

Exposure Time (days)	19	36	45	68	87
T ₂ Pressure (mm)	103.5	107.4	97.5	76.7	101.4

<u>Rubber Sample</u>	<u>Original Hardness</u>					
Natural Rubber	64	66	-	68	-	70
GR-S, X-478	60	64	-	66	-	67
Hycar DR-25	59	61	-	66	-	68
Neoprene Type WRT	62	67	-	68	-	73
Hypalon, X-53	70	-	-	-	74	77
Hypalon, X-52	< 79	-	-	-	84	-
Hypalon, X-50	< 86	-	-	-	91	-
Buna-N*	61	-	96	-	-	-

hardening of the rubbers tested. Only the Hycar DR-25 and GR-S, X-478 rubbers showed a hardness of less than 70 units after 87 days exposure to tritium. A sample of silicone rubber which had been tested in an earlier experiment³ became completely brittle after exposure and crumbled on being handled. The samples of Hypalon X-50 and X-52 seemed to be easily torn after exposure. The extent of hardening is in the following order of increasing hardness:

GR-S, X-478 < Hycar DR-25 < Natural Rubber < Neoprene Type WRT < Hypalon X-53
< Hypalon X-52 < Hypalon X-50 < Buna-N*

This order is based on the absolute hardness. It is clear that a correlation based on the percentage increase in hardness would lead to quite a different order. From the point of view of performance, however, the actual hardness, rather than the percentage increase, resulting from exposure to tritium is the value which should be used in evaluating candidate materials. The Teflon and Kel-F polymers have a hardness equal to or greater than 100, the maximum readable on the Shore Durometer. No hardness experiments were carried out on these two polymers.

Elongation Measurements

The results of the elongation measurements carried out on the samples of Neoprene Type WRT and Natural Rubber are shown graphically in Figure 7 and 8. These figures show a plot of the elongation in millimeters against the exposure time in days. Both rubber samples show a marked decrease in elongation with increasing exposure time. The two rubbers, however, exhibit a basically different hardening process which brings about the change in elongation. The Neoprene Type WRT shows a regular decrease with no discontinuities in the curve. The Natural Rubber shows first a regular decrease and then an increase in elongation with several sharp discontinuities in this latter portion of the curve. The experiment with the Neoprene Type WRT was stopped by the breakage of the rubber ring.

The hardening and embrittlement in the case of the Neoprene Type WRT seem to occur throughout the body of the ring sample. In the case of the Natural Rubber, the hardening is predominantly a surface effect which produces a decrease in elongation until cleavage occurs in the hardened surface later. This cleavage is readily visible in the exposed ring sample which may be seen in the photograph, Figure 10b. After this rupture of the surface, there is then exposed an unhardened inner layer of rubber and the elongation increases. The surface cleavage occurs again, eventually leading to the complete rupture of the ring sample. No elongation tests were carried out on the other samples.

Decomposition

The formation of decomposition products as a result of exposure to tritium was evaluated only for the Teflon and Kel-F polymers. Only one decomposition product was found for these plastics. This was a gas having its major mass spectral peak at mass 85. It was identified⁴ as silicon tetrafluoride, SiF_4 . The actual decomposition product from the interaction of tritium with these plastics is TF. The SiF_4 is formed as a result of interaction of the tritium fluoride (and hydrogen fluoride) with the glass. This was confirmed by filling a similar pyrex sample tube with HF. The mass 85 peak appeared in the mass spectrum, indicating the immediate formation of SiF_4 . The mass spectral sensitivity for SiF_4 was found to be 2.2 times that for hydrogen.

The rate of formation of SiF_4 was found to be appreciable only for the shredded sample of Teflon. The results of this experiment may be seen in Figure 9 which is a plot of mole per cent SiF_4 versus time in days. This compound amounted to 11% of the gas phase after 33 days exposure time. Of this 11%, some 1 to 2% originated from the fluorothene grease.

The small solid samples of these polymers, 2 inches by 3/4 inch by 1/16 inch, were exposed in tubes, with Apiezon grease used as the stopcock lubricant. The analysis gave the results shown in Table III.

TABLE III

AMOUNT OF DECOMPOSITION OF PLASTICS EXPOSED TO TRITIUM

<u>Polymer Sample</u>	<u>Sample Weight</u>	<u>Exposure Time</u>	<u>Tritium Pressure</u>	<u>Per Cent SiF_4</u>
Teflon	3.43 grams	29 days	114.1 mm	1.0
Kel-F	3.66 grams	31 days	122.0 mm	0.9

These results for the small solid samples amount to a rate of formation of SiF_4 of 1.3×10^{-3} cc/day, corresponding to a TF rate of formation of approximately 5×10^{-3} cc/day.

The experiment with the machined pieces of Teflon, exposed to approximately 100 mm of tritium, showed clearly that there was no measurable dimensional change after 30 days.

CONCLUSIONS

1. The rates of exchange of tritium with the various polymers tested increase in the following order.

Hypalon X-53 < Hycar DR-25 < GR-S, X-478 < Natural Rubber < Neoprene Type WRT

2. The extent of hardening as a result of exposure to tritium is in the following increasing order.

GR-S, X-478 < Hycar DR-25 < Natural Rubber < Neoprene Type WRT < Hypalon X-53
< Hypalon X-52 < Hypalon X-50 < Buna-N*

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3. The ring samples subjected to elongation tests show that in the case of Neoprene Type WRT the hardening occurs throughout the body of the rubber. In the case of the Natural Rubber the hardening seems to be chiefly a surface effect.

4. Only TF (and HF) was found as a decomposition product from Teflon and Kel-F exposed to tritium. The rate of formation of this product with small solid samples is extremely slow and would seem to present no serious problem.

5. On the basis of these experiments, GR-S, X-478 and Hycar DR-25 seem to be the most suitable of the candidate rubbers for use as gasket materials and valve seats. No choice, on the basis of the experiments, can be made between Teflon and Kel-F.

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2. H. C. Matraw, C. F. Pachucki and L. M. Dorfman, "Mass Spectrometric Determination of the Hydrogen-Tritium Equilibrium," J. Chem. Phys. 20, 926 (1952).

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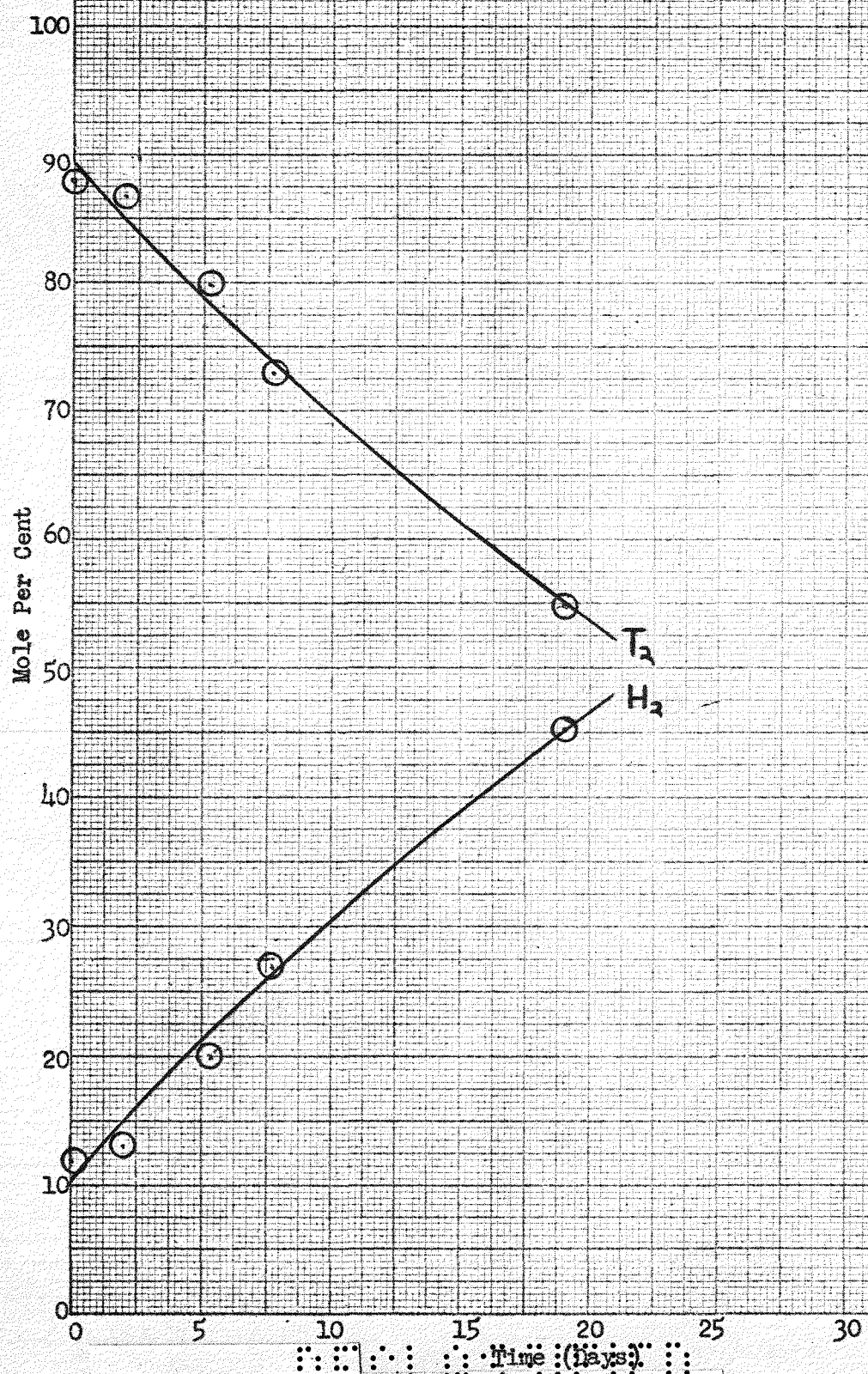
APPENDIX
Figures 1 through 11

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FIGURE 1

Rate of Exchange of Tritium with Natural Rubber

Press = 112.9 mm

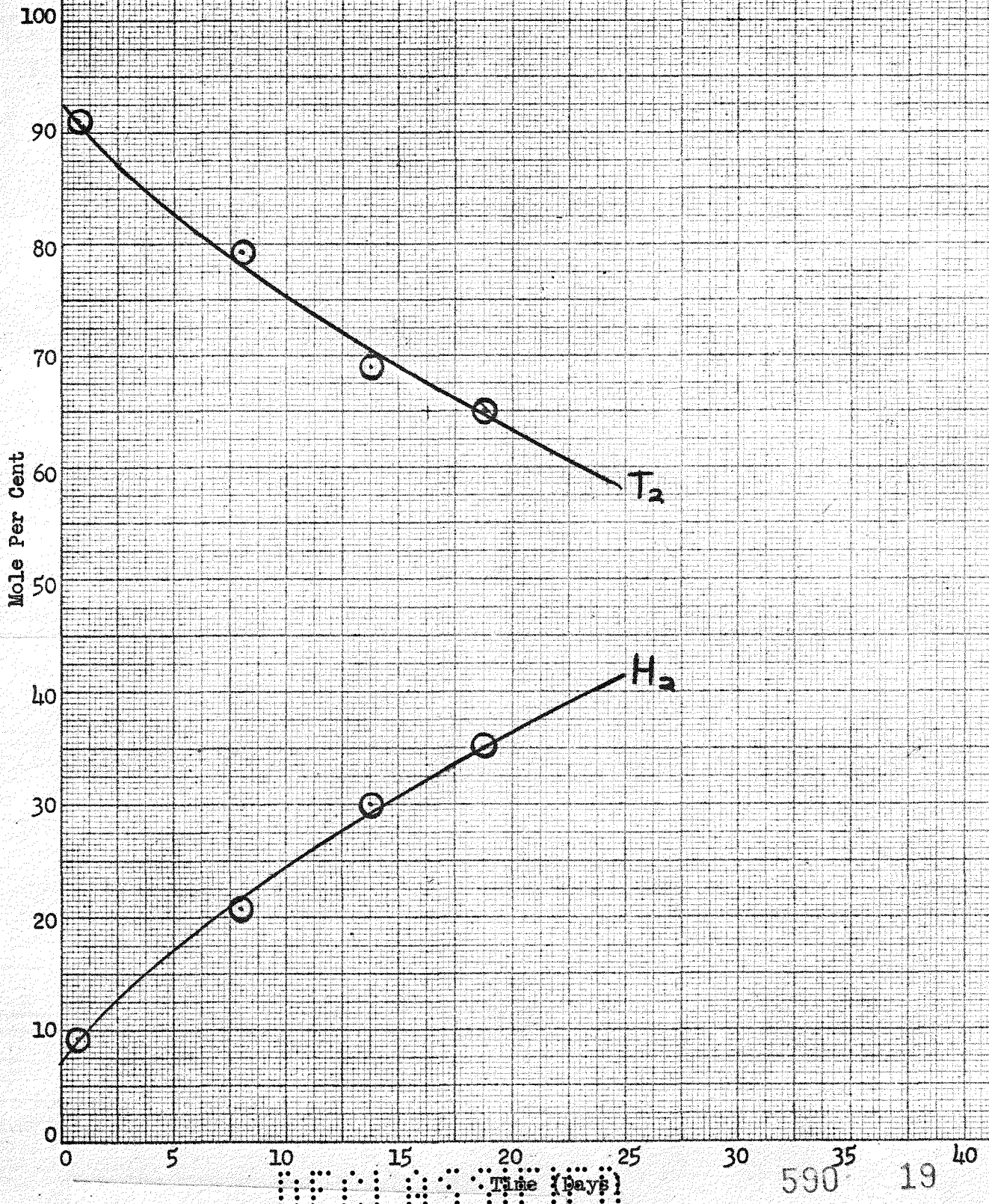


ENCLOSURE

GENERAL ELECTRIC COMPANY, KNOLLS ATOMIC POWER LABORATORY
180X250 1mm DIVISIONS

Figure 2

Rate of Exchange of Tritium with GR-S, X.478
Press = 127.7 mm

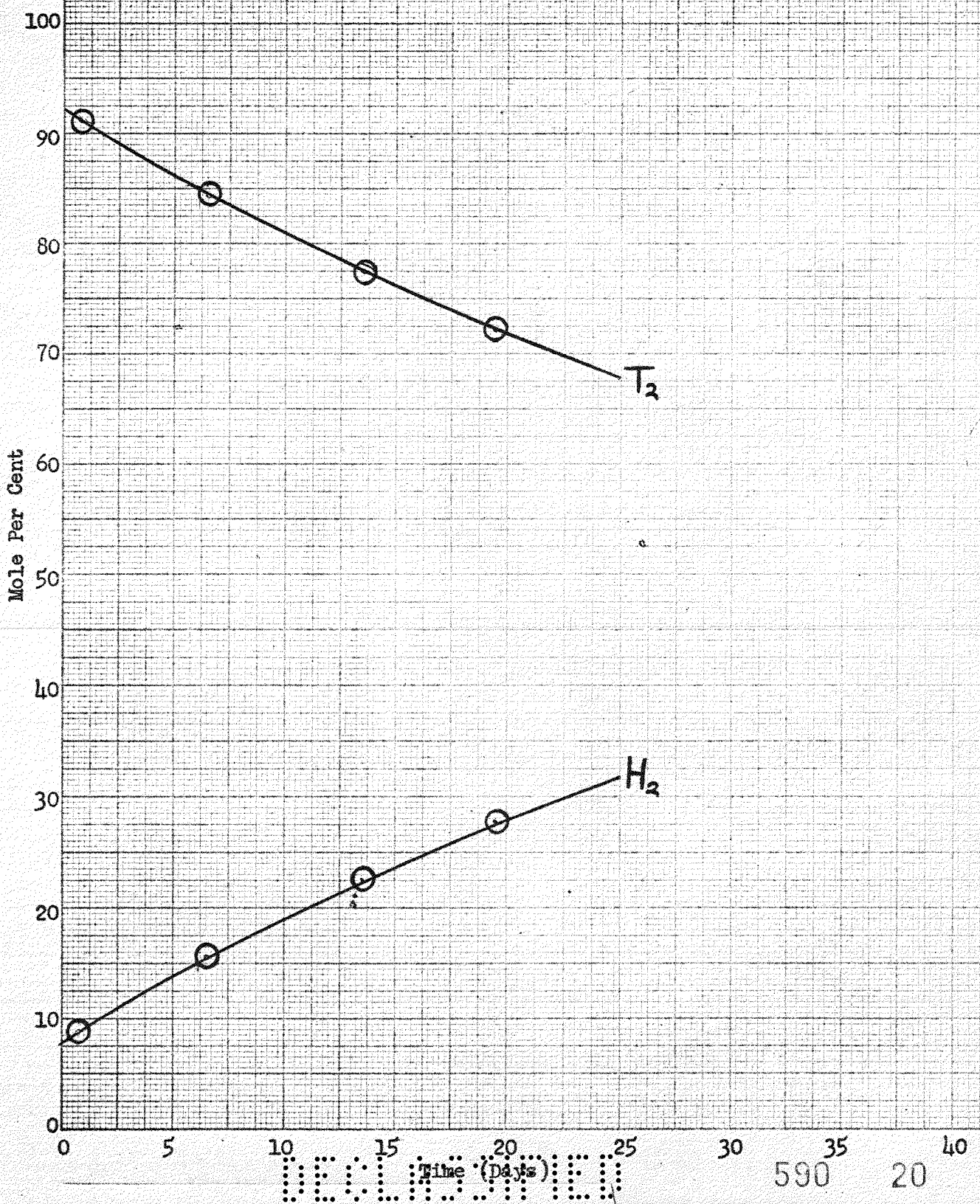


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Figure 3

Rate of Exchange of Tritium with Hycar DR-25
Press = 117.8 mm



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Figure 4

Rate of Exchange of Tritium with Neoprene-Type WRT

Press = 115.7 mm

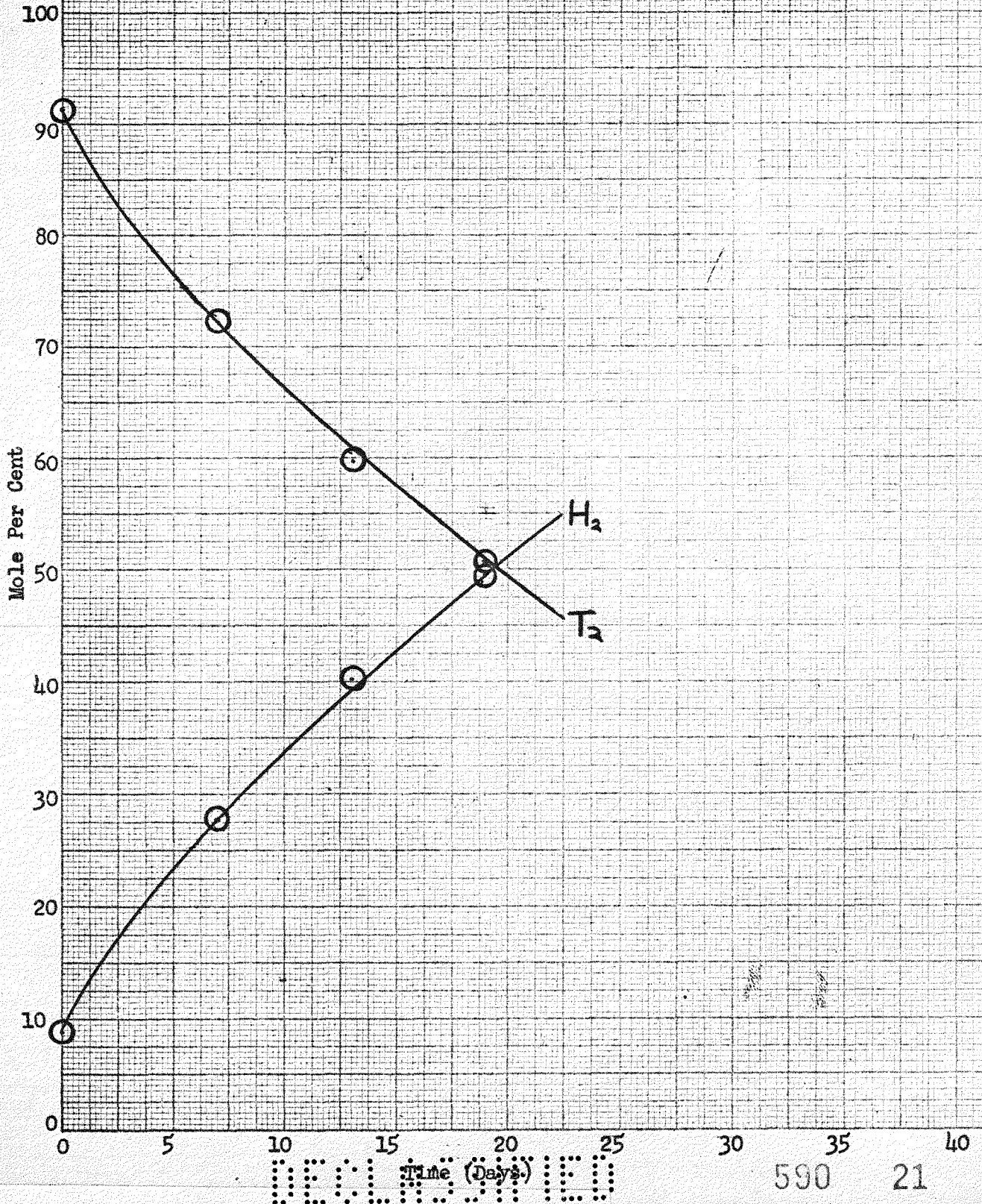
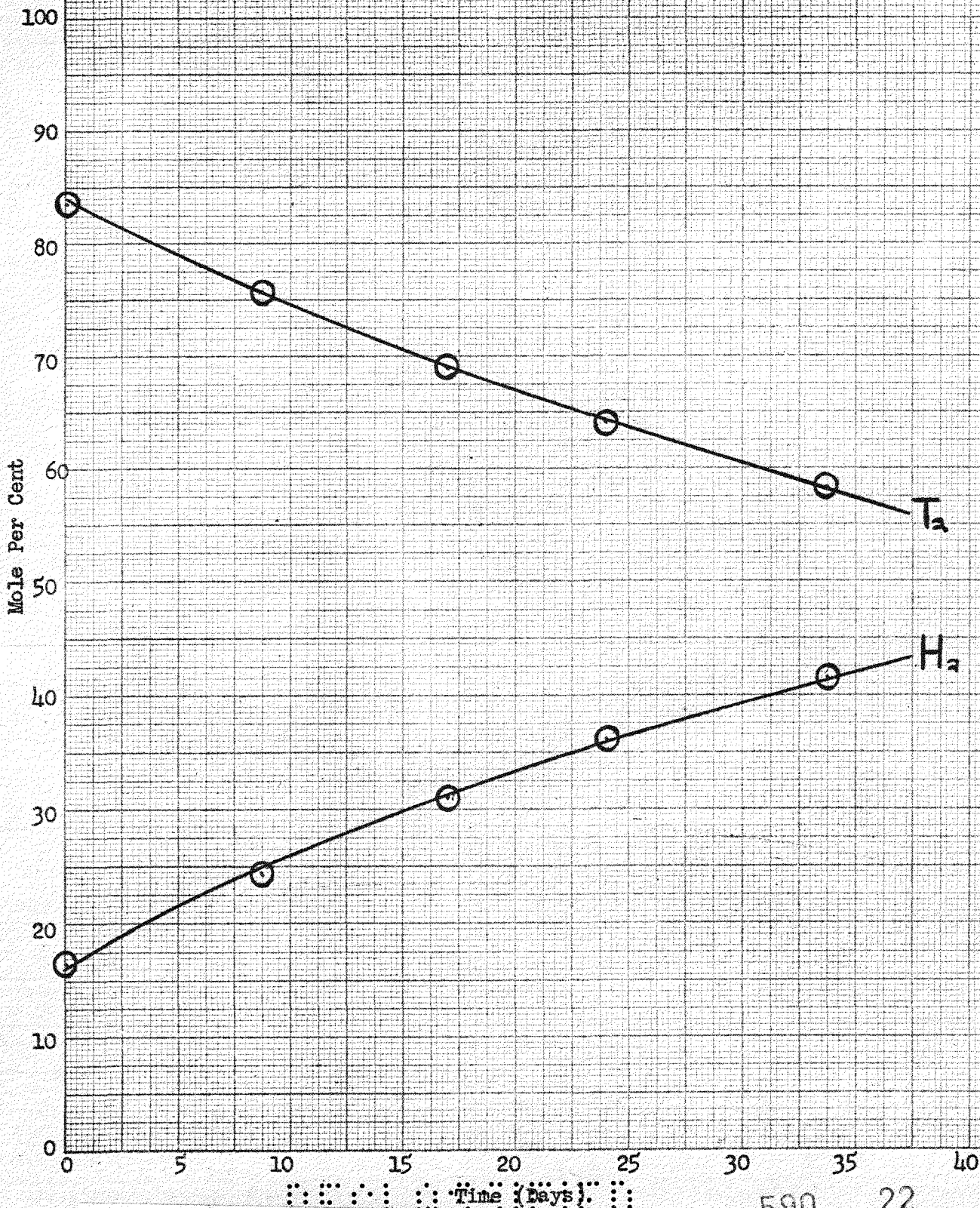


Figure 5

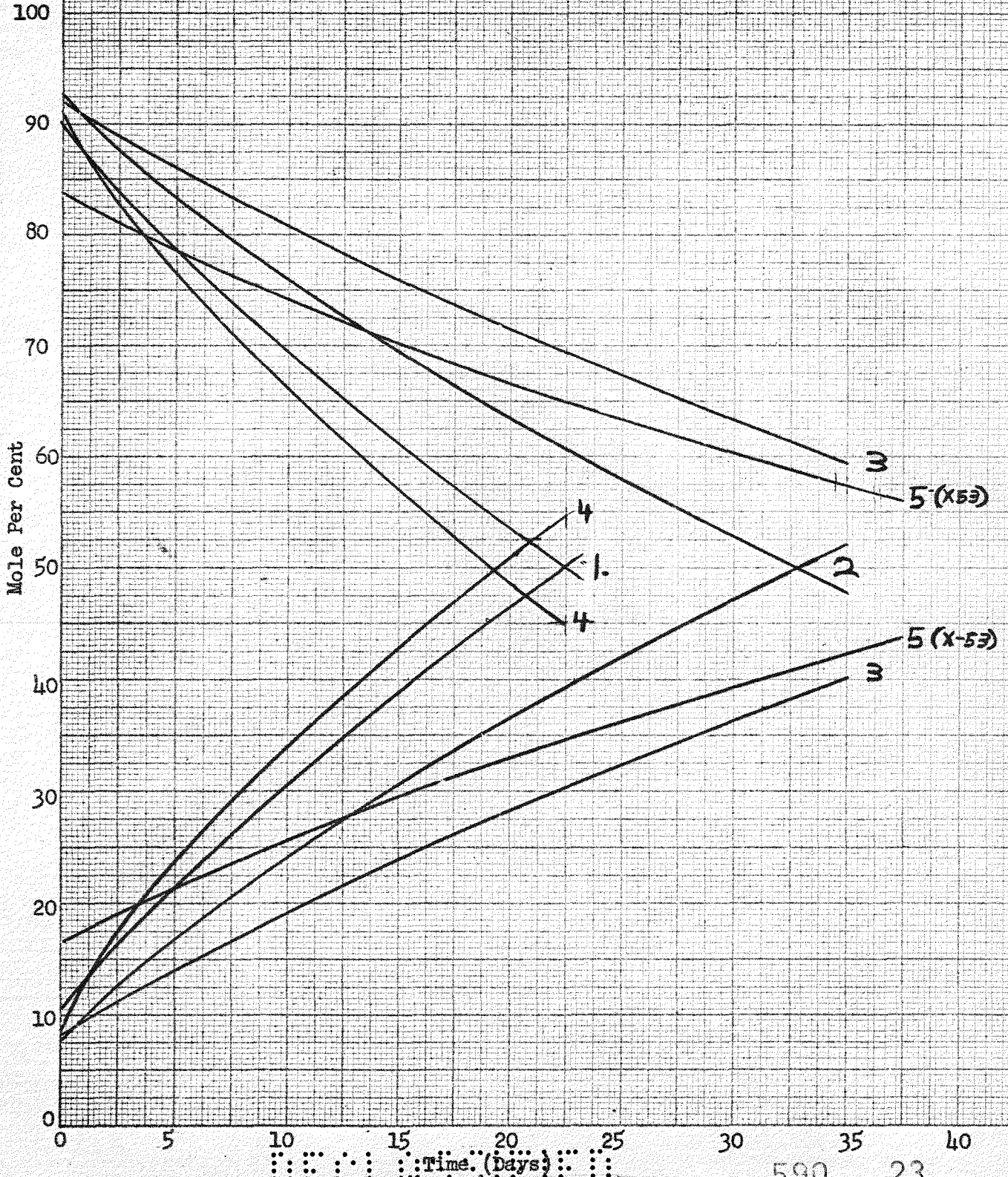
Rate of Exchange of Tritium with Hypalon Type X-53
Press = 109.2 mm



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Figure 6

Exchange Curves For Rubbers 1 to 5



Time (Days)

590 23

Figure 7

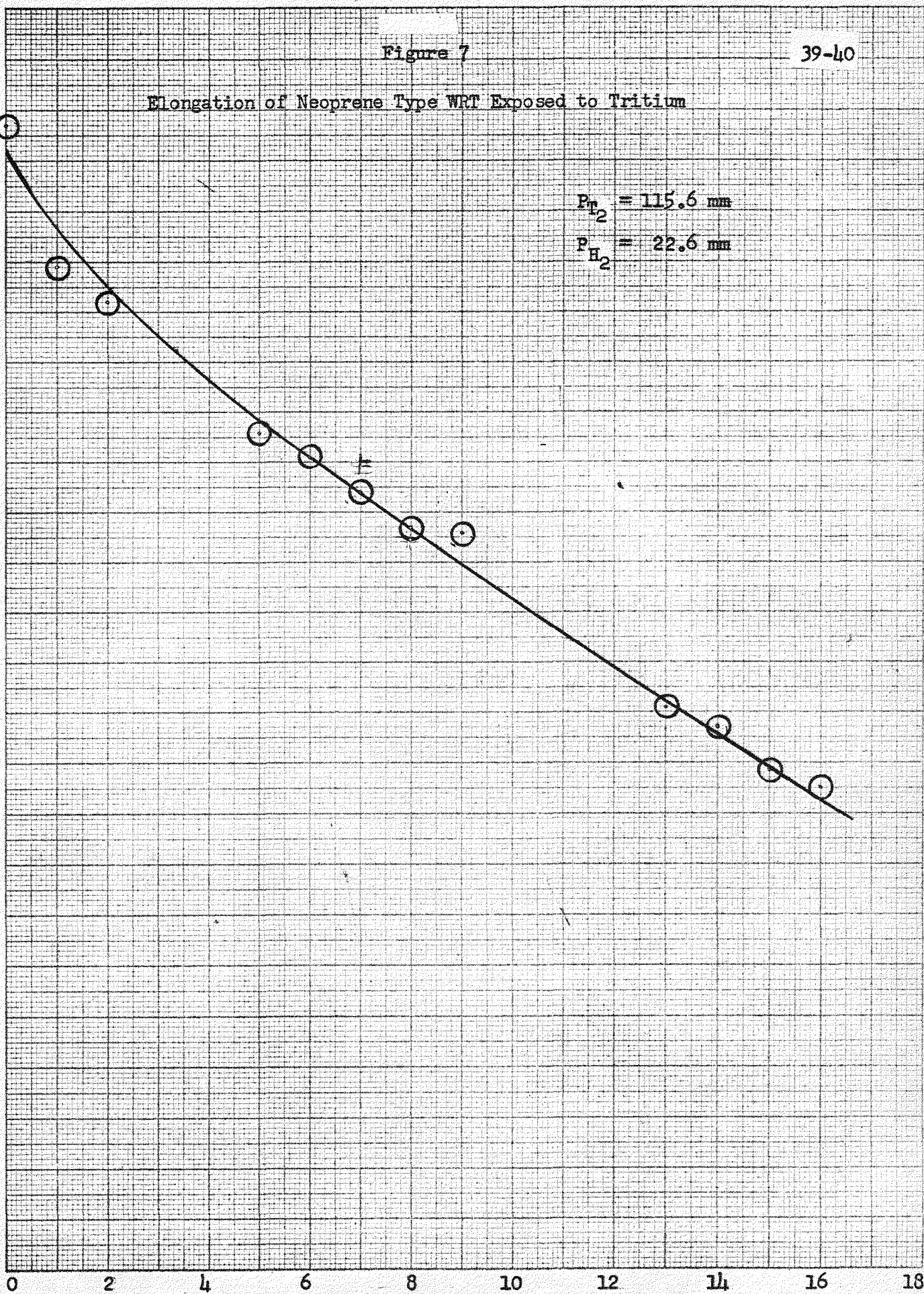
Elongation of Neoprene Type WRT Exposed to Tritium

$P_{T_2} = 115.6 \text{ mm}$
 $P_{H_2} = 22.6 \text{ mm}$

GENERAL ELECTRIC COMPANY, KNOLLS ATOMIC POWER LABORATORY

Elongation in mm

180X250 1mm DIVISIONS



0 2 4 6 8 10 12 14 16 18

Time (Days)

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Figure 8

41-42

Elongation of Natural Rubber Exposed to Tritium

$P_{T_2} = 93.5 \text{ mm}$
 $P_{H_2} = 11.5 \text{ mm}$

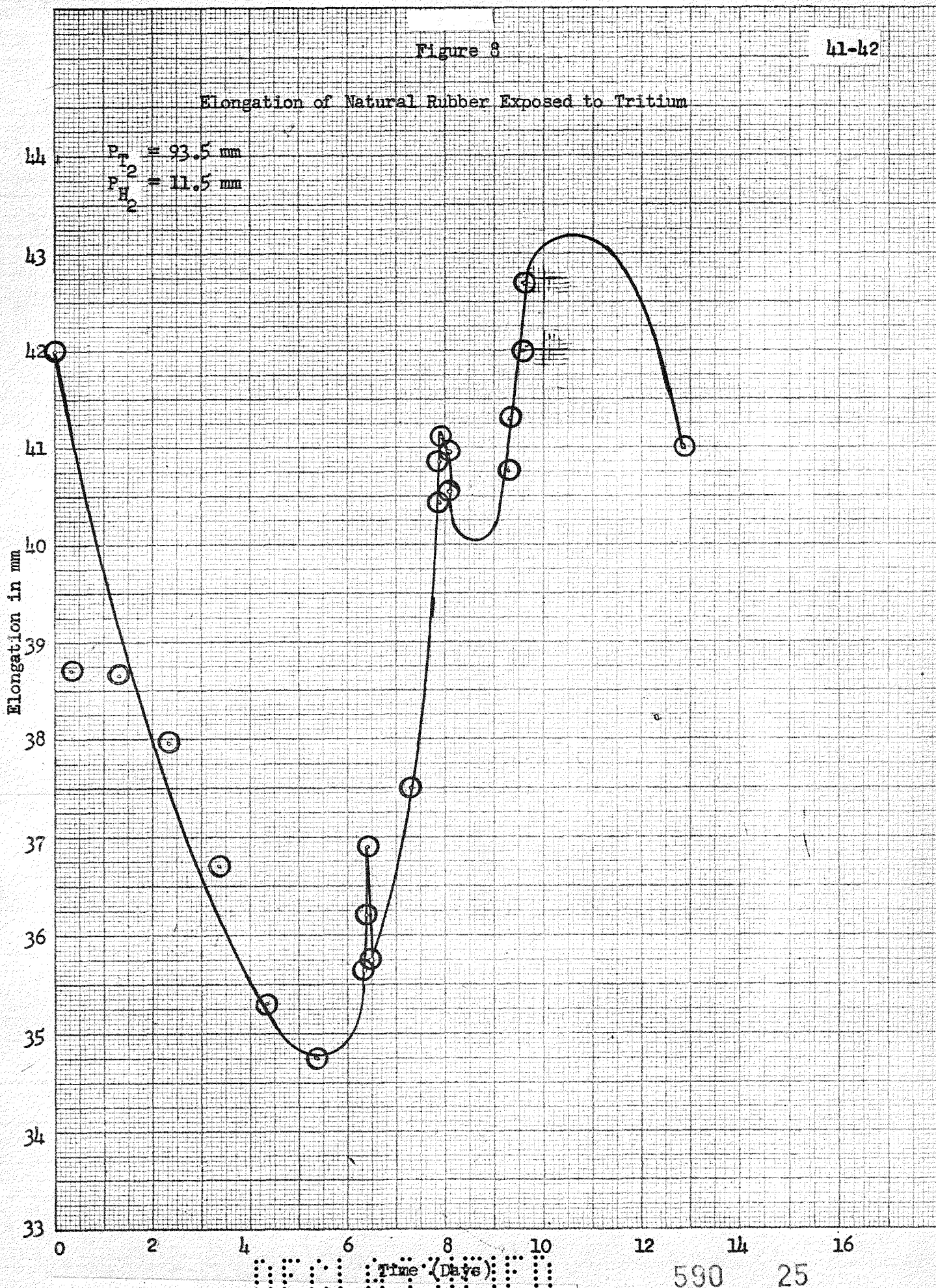
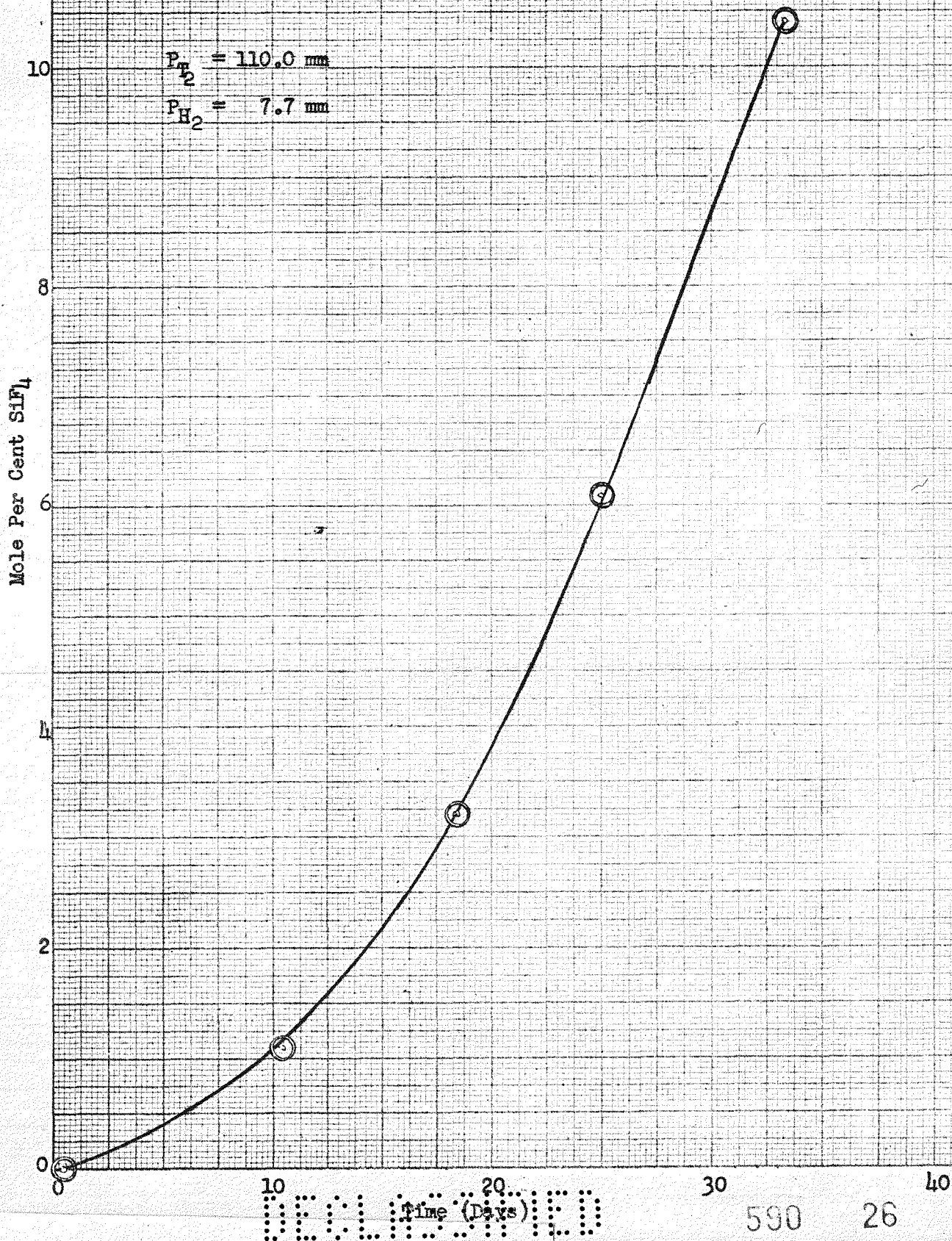


Figure 9

43-44

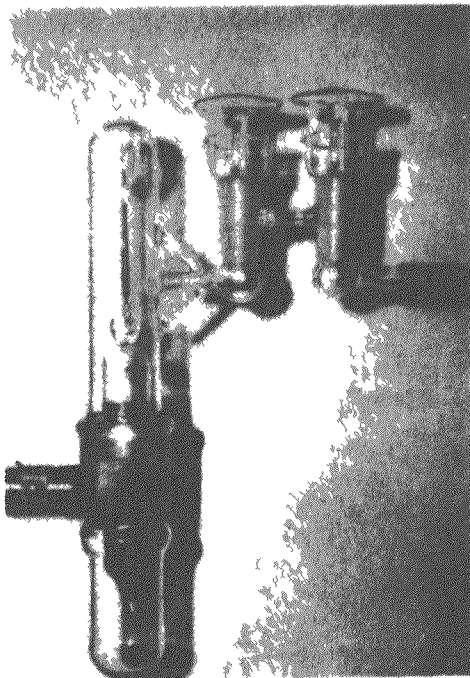
Rate of Formation of SiF_4 for Shredded Teflon Sample



Time (Days)

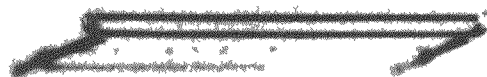
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FIGURE 10a

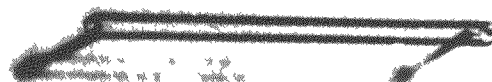


ELONGATION TEST APPARATUS

FIGURE 10b



UNEXPOSED

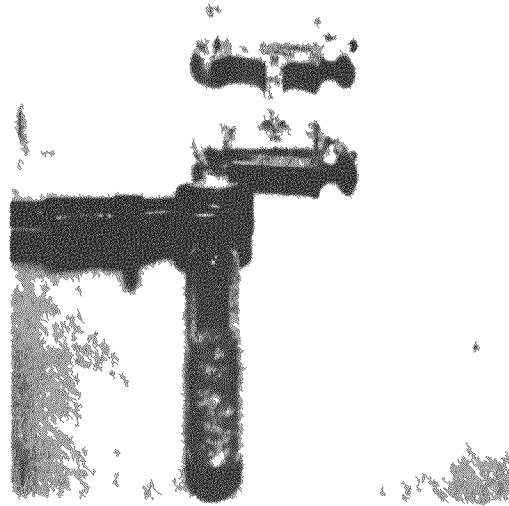


EXPOSED

NATURAL RUBBER

1121618

FIGURE 11



SAMPLE TUBE CONTAINING
SHREDDED TEFLON

1121619