UNCLASSIFIED

AD NUMBER:	AD0434216

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to US Government agencies and their contractors; Administrative/Operational Use; 15 Dec 1963. Other requests shall be referred to Naval Air Engineering Center, Philadelphia, PA 19112.

AUTHORITY

AML/NAEC ltr dtd 28 Mar 1966

THIS PAGE IS UNCLASSIFIED

BEST
POSSIBLE
SCAN

AD 434216

434216

U. S. NAVAL AIR ENGINEERING CENTER

PHILADELPHIA, PENNSYLVANIA

CATALOGED BY DDC
AS AD No.

AERONAUTICAL MATERIALS LABORATORY

FOUNDATIONAL RESEARCH PROJECT NAEC-AML(16)-R360FR101

(15 Dec 1963)

MOLECULAR CHANGES IN POLYAMIDE AND ELASTOMERIC POLYMERS DUE TO NUCLEAR, ULTRAVIOLET AND THERMAL RADIATION

FINAL REPORT

Qualified requesters may obtain copies of this
report direct from DDC

DDC
APR 9 1964

THIS REPORT MAY BE RELEASED OUTSIDE OF THE MILITARY
DEPARTMENTS AND EXECUTIVE AGENCIES OF THE UNITED
STATES GOVERNMENT ONLY WITH PAGES ______ REMOVED

NO OTS

PLATE NO 11749

NOTICE

Reproduction of this document in any form by other than naval activities is not authorized except by special approval of the Secretary of the Navy or the Chief of Naval Operations as appropriate.

The following Espionage notice can be disregarded unless this document is plainly marked CONFIDENTIAL or SECRET.

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

NAVAL AIR ENGINEERING CENTER
PHILADELPHIA, PENNSYLVANIA 19112

AERONAUTICAL MATERIALS LABORATORY

FOUNDATIONAL RESEARCH PROJECT NAEC-AML(16)-R360FR101

(15 Dec 1963)

MOLECULAR CHANGES IN POLYAMIDE AND ELASTOMERIC POLYMERS DUE TO NUCLEAR, ULTRAVIOLET AND THERMAL RADIATION

FINAL REPORT

PREPARED BY:
G Hargreaves
G. HARGREAVES
Principal Investigator

APPROVED BY:
MBHays
M. B. HAYS, HEAD
Textiles Branch

C A Cassola
C. A. CASSOLA, SUPERINTENDENT
High Polymer Division

GKHolmes
G. K. HOLMES
Technical Consultant

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
Continued

LIST OF TABLES

ABSTRACT

The object of this investigation was to determine the molecular changes in polyamide and elastomeric polymers due to nuclear, ultraviolet, and thermal radiation.

Several types of nylon fibers were exposed to gamma, ultraviolet and thermal radiation and different atmospheric conditions. The unexposed and exposed specimens were examined by the following techniques for the purpose of obtaining information concerning the physical and chemical changes in the structure of the polymer; viscosity of solutions, melting point, infrared spectra, ultraviolet absorption, and microscopy. The tensile strength was measured in some instances. Results show that no one method gives a complete picture, but the combined results from many methods give some insight into the molecular changes taking place as a result of irradiation. Some of these changes are; 1) the molecules break at the C-N bonds creating smaller molecules and appreciable changes in the physical state, 2) the degree of crystallinity changes.

The ultraviolet resistance of some nylons is improved by small doses of gamma irradiation.

I. INTRODUCTION

A. This final report describes research on the radiation effects on some polymers performed in the High Polymer Division of the Aeronautical Materials Laboratory, Textile Branch during the period 5 May 1960 - 31 December 1963. This research was initiated under TED NAM ES 7045 Foundational Project No. 16, established 5 May 1960 "Molecular Changes in Polyamide and Elastomeric Polymers Due to Nuclear, Ultraviolet and Thermal Radiation" and was administered under the Directorate of the Aeronautical Materials Laboratory, Naval Air Engineering Center.

B. The Space Age has created a need for materials capable of withstanding radiation prevalent in both the lower and upper atmosphere and in outer space. The elements of space environment that may have the greatest effect on materials and are also amenable to laboratory studies are: ionizing, ultraviolet, thermal radiation and high vacuum. Knowledge of the changes taking place in the molecule as a result of radiation is essential as a basis for developing methods of preventing degradation whether by modifying the polymer or by additive treatments. With these factors in mind, this study was begun.

C. The degradation of these polyamides was studied as a part of the research program to find the fundamental reactions that occur when such high polymers are exposed to gamma, ultraviolet or thermal radiation and varied atmospheric conditions. The term degradation is used to describe irreversible changes in the chemical structure of the polymer as a result of external influences.

D. The early months of this investigation were spent in; 1) searching the literature for information pertaining to the subject of polymer degradation; 2) determining suitable laboratory methods, required chemicals, laboratory equipment and apparatus; and 3) negotiating arrangements for the installation of certain laboratory equipment in a suitable work space.

II. EQUIPMENT AND MATERIALS

A. An ultraviolet radiation source was designed and built. With this source, materials may be irradiated with light of 2537 A wavelength and intensity of 3.02×10^{-2} watts/hr/in^2, under controlled conditions of temperature and humidity, in air, a vacuum or an inert atmosphere. (Figure 1) Gaseous products of the irradiation may be collected in the gas collecting bottles for infrared or gas chromatographic analysis.

B. Thermal Irradiation was carried out in a Hevi-duty combustion furnace. (Figure 2) Temperatures up to 1000°C could be obtained and held for extended periods. The exposure could be made in air, vacuum or an inert atmosphere. The gaseous product of combustion could be collected for analysis.

C. The Gammacell 220 was used for the gamma irradiation. If the gaseous products were to be collected and the atmosphere controlled, the specimens were placed in flasks with tubes leading out of the irradiation chamber to the gas collecting bottles. (Figure 3) Some samples were sealed in ampules before irradiation, after being evacuated, filled with nitrogen or with a normal atmosphere. The dose rate ranged from $1.16 - 0.82 \times 10^6$ rads/hr.

D. In order to learn the effect of combined gamma and ultraviolet radiation, a 2537 A wavelength light with intensity of 5.83×10^{-5} watts/hr/in^2 was built to fit into the Gammacell (Figure 4), with the specimens suspended around it. Irradiation was done in air or in nitrogen. The construction of the Gammacell did not permit evacuating the chamber when combining ultraviolet with gamma radiation.

E. Nylon 66, nylon 6, and Nomex a more heat resistant nylon, obtained in the form of commercial yarns from several manufacturers were used as the polymers for the study. These were designated as:

Fiber #0 300/210 bright high tenacity nylon 66
Fiber #4 Nomex/200 modified more heat resistant nylon, formerly HT-1
Fiber #7 SD/200 semidull nylon 6
Fiber #9 330/210 bright sunlight resistant nylon 66

III. EXPERIMENTAL PROCEDURE

A. The yarns were reeled into 100 yard skeins, scoured, rinsed, dried in an oven at 105°C, and placed in a desiccator until used.

1. The skeins or specimens were placed in the quartz tube of the ultraviolet irradiation apparatus. (Figure 1) The exposure chamber was closed and the gas collecting bottle attached. (Alternately the yarns were cut into 1/4" lengths before placing in the irradiation tube). When normal atmosphere was used, the ultraviolet light was turned on, temperature brought up to 38°C and the temperature in the chamber held at that point for the desired length of time. Or the system was evacuated to 10^{-5} mm of Hg. for 24 hours and then the stopcocks to the chamber were closed and the ultraviolet light turned on. For other specimens the system was first evacuated, then flushed with nitrogen for 1/2 hour and sealed off under slight pressure of nitrogen then irradiated as before.

2. For thermal irradiation the skeins or specimens were placed in combustion boats, covered and inserted in the combustion tube as shown in Figure 2. The system could be evacuated, filled with nitrogen, etc. as it was for ultraviolet irradiation. Temperatures were controlled by rheostats incorporated in the apparatus.

3. For gamma irradiation the specimens were placed in 100 ml flasks connected to tubes leading from the irradiation chamber to the gas collecting bottles. (Figure 3) The system could be evacuated or filled with nitrogen. In one series the specimens were sealed in ampules with air, nitrogen or a vacuum, and placed in the irradiation chamber.

4. For combined gamma and ultraviolet irradiation the skeins were suspended around the ultraviolet source in the gamma irradiation chamber. These specimens were irradiated in the normal atmosphere or while continuously flushed with nitrogen. No arrangements for the use of a vacuum were practical. No gases were collected.

B. Viscosity - After the specimens were exposed to gamma ultraviolet or thermal radiation under controlled conditions, the breaking of the polymer chains was determined by viscosity measurements of dilute solutions of the nylon specimens in a solvent made from a saturated solution of calcium chloride in methanol ($CaCl_2CH_3OH$) (14). The viscosities were measured at 30°C using calibrated Ostwald-Fenske viscometers. (3,4,6) Duplicate runs were made using the average of five efflux time measurements determined to the nearest 0.1 sec. Nomex was dissolved in H_2SO_4.

C. Melting points were determined with a Kofler Hot Stage and microscope. The magnification was 100X.

D. The infrared characteristics of the gaseous products and residues after irradiation were measured in order to determine any possible chemical changes in the structure of the nylon. The infrared transmission spectra were obtained with a Beckman IR 4 Recording Spectrophotometer.

E. Transmittance in the ultraviolet and visible region of the spectrum was measured with a Beckman DU Spectrophotometer, using quartz cells. The fibers were dissolved in $CaCl_2$-CH_3OH, m-cresol or H_2SO_4. The transmittance was measured against the solvent used with each fiber.

F. Light microscopy - The changes in the nylon fibers as a result of exposure to radiation were studied by microscopical techniques(17). Photomicrographs of samples of nylon #0, #4, #7, (see Figure 19) differentiate the types of nylon and illustrate their relative resistance to gamma irradiation. A petrographic microscope was used for these studies. Photomicrographs were taken under crossed nicols at 450X magnification, using a vertical microscope camera, with a filament light source. A ground glass plate was used in the illuminator when the photographs were made.

C. Breaking strength - of the yarns was measured with the Instron by the method given in reference (12).

IV. ANALYSIS OF RESULTS

A. Viscosity data as shown in Table 1 indicate that some chain scission occurred as a result of irradiation. The data shows progressive degradation or chain breaks with increasing amounts of radiation, by the lowering of the relative viscosity (η r), the inherent viscosity ($\ln \eta_r/C$), and the intrinsic viscosity $[\eta]$ (11, 20, 28, 29).

1. Table 2 relates relative viscosity, tensile strength, and melting point as affected by gamma, ultraviolet and thermal radiation, in different atmospheres for nylon 66, nylon 6 and Nomex, a more heat resistant nylon. As indicated by tensile strength measurements and viscosity measurements Nomex is improved by from 0.86×10^6 -6.88×10^6 rads of gamma irradiation and shows little evidence of degradation after more than 1.72×10^8 rads of gamma radiation alone or in combination with 1.2×10^{-2} watts of ultraviolet radiation. This may be explained by the fact that in Nomex the basic nylon structure has been modified by the addition of one or more aromatic substituents. Radiation protection is afforded by the benzene ring which has many energy levels. Polymers containing this group show unusual resistance to thermal and gamma radiation.(15)

B. Melting point - Figure 5 illustrates the effect of gamma irradiation on the melting point of nylon 66.(21) There is relatively little change in the melting point after 1.16×10^7 rads of gamma irradiation, progressive lowering after 1.16×10^7 - 4.48×10^8 hours irradiation, and a rapid lowering of the melting point for doses greater than 4.48×10^8 rads. Melville (24) states that one reason for the high melting point of nylon 66 is the hydrogen bonding between neighboring polymer chains. For this to be effective, it is necessary that the NH groups of one chain be opposite the CO group of another chain, since hydrogen bonding can occur only over short distances - a few Angstrom units - it is expected that as the number of methylene groups between the CONH groups increases, lateral adhesion between the chains is less frequent and the melting point is lowered. The decrease, however, is not uniform, but alternating. The reason is that with the odd numbered acids, the CO and NH groups are not always in the most favorable position and lateral adhesion is decreased with the consequent lowering of the melting point. While this theory relates directly to nylon 66 the melting point of nylon 6 was affected in the same manner.

1. Schwertassek (26) studied the structure of polyamide fibers as regards their thermal behavior (melting region). He stated that the partially crystalline state of the fiber is one of the main causes for the fact that the fibers gradually soften before attaining the melting temperature, and that the fiber skin shows a higher melting temperature than the fiber core. Under the microscope as the temperature increases the fibers were observed to move more or less slowly, then bend slightly or straighten out and shrink. This is probably due to the non-uniformity of the interior tensions of the fibers, especially in the amorphous regions. According to Hill (18) the mobility of the molecular segments in the amorphous region is greater than in the crystalline region. Next, the fibers curl with greater speeds and shrink strongly. The temperature observed at this stage is evidently the melting temperature of the fiber core. At this stage, the skin is still present and maintains the fiber shape. When two fibers touch they do not flow together. Finally, the fiber structure is lost, the fibers flow together and the boundaries of the fiber surface disappear. This is the melting region of the fiber skin. The two points are the range in the usual melting point tables. Melting point determinations after ultraviolet and thermal irradiation of nylon indicated the same relationships between radiation dose and change in melting point. (21,22)

2. Nomex has no melt-flow characteristics, even at temperatures above 400°C. It chars and becomes brittle but does not melt. Neither ultraviolet nor gamma irradiation causes Nomex to have a melting point.

C. Infrared

1. The infrared analysis of Nomex as compared to that of nylon 66 Fiber #0 is shown in Figure 6. In the (8, 25, 27) wave length range of 2 - 6.4 microns (μ) the absorption curve is the same for Nomex and nylon 66. At 6.5μ Nomex has a peak which is not seen in the nylon 66 spectrum. From 6.7 - 7.7μ the spectra are the same. At 7.7 - 8μ nylon 66 has a broader band than Nomex. Nylon 66 has a definite absorption peak at 10.7μ which is not found in Nomex. These data indicate that Nomex is a polyamide with the addition of an aromatic factor. Figure 7 shows spectra of gases from pyrolysis of nylon (Fiber #0) at 316°C and Nomex (Fiber #1) at 816°C. The nylon spectrum shows peaks at 3.35, 4.25, 4.60 - 4.70 and 10.35 - 10.75μ. These indicate (8) the production of CH_4, CO_2, CO and NH_3. The Nomex spectrum has a peak at 3.35μ indicating production of CH_4, and a very weak peak at 4.35μ for CO_2, stronger peaks at 4.60 - 4.70μ indicating CO, and at 7.45μ probably CH_4. Figure 8b - 10b giving infrared analysis of Fiber #0 show no significant changes in the spectra of the residue after 1.72 x 10^8 rads of gamma irradiation, whether in air, nitrogen or a vacuum. However, Figure 8a on the gaseous products after gamma irradiation in air of Fiber #0 shows weak

absorption at $3.35\ \mu$, $4.25\ \mu$, and $4.60 - 4.70\ \mu$, indicating the production of CH_4, CO_2, and CO. Figure 9a infrared analysis of Fiber #0 after 1.72×10^8 rads gamma irradiation in nitrogen shows absorption peaks at $4.25\ \mu$, and $4.60 - 4.70\ \mu$, but none at $3.35\ \mu$. The peak at $2.60 - 2.70\ \mu$ probably indicates water vapor of atmospheric origin. Figure 10a, after gamma irradiation in a vacuum the gaseous products are limited to CO. Since these irradiations were carried out in a closed system, it is possible that secondary reactions occur during the irradiation. For this nylon 66 fewer gaseous products resulted from irradiation in a vacuum than in air or in nitrogen. Figure 11a is the infrared spectra of the gaseous products after ultraviolet irradiation of Fiber #0 in air for a total dose of 6.04×10^{-2} watts, and shows CO_2 and CO only. The infrared spectrum of the residue shows no significant changes after 6.04×10^{-2} watts of ultraviolet irradiation.

2. In Figure 12a gamma irradiation in air of Fiber #4 (Nomex) produces CO_2, CO, C-C, CH_2-CH_2, groups as indicated by peaks at $2.60 - 2.70\ \mu$, $4.25 - 4.30\ \mu$, $5.70 - 5.90\ \mu$, $6.50 - 6.60\ \mu$, $7.10 - 7.40\ \mu$ and at $13.90\ \mu$. This is also a closed system and some of the products are probably the result of secondary reactions. Figure 13a shows only one peak at $4.20 - 4.30\ \mu$. This probably indicates residual CO_2 in the system. Figure 14a is the infrared spectra of Fiber #4 after 1.72×10^8 rads of gamma irradiation in a vacuum. There was no evidence of any gas being evolved. Figures 12b - 14b - infrared spectra of the residues from gamma irradiation of Fiber #4 in air, nitrogen and a vacuum, appear unchanged. Figure 15 gives the infrared spectrum of Fiber #4 after 6.04×10^{-2} watts of ultraviolet irradiation. There are no significant changes. The gaseous products were analyzed by the gas chromatograph and showed CO and CO_2 to be present. Figure 16a&b gives the infrared spectra of Fiber #0 and Fiber #4 after 1.72×10^8 rads of gamma irradiation at the same time with 1.2×10^{-2} watts of ultraviolet irradiation. A comparison of these spectra with those of the same fibers shown in Figure 6 indicate that the combined radiation has produced structural changes in the molecules which are accompanied by changes in the infrared spectra in the $10.5 - 15.0\ \mu$ region. The nylon (Fiber #0) showing the more pronounced effect in the almost complete absence of absorption at $13.25\ \mu$ and $14.40\ \mu$. In Figure 16b the Fiber #4 spectra shows the peaks at $9.75\ \mu$ $11.0\ \mu$ to be missing. This indicates a change in the number of free hydrogen atoms, and CH out of plane deformations.

D. Ultraviolet - Visible

1. Figure 17 illustrates the effects of gamma, and ultraviolet irradiation of Fiber #0 as revealed in the Ultraviolet-Visible region of the spectrum.(23) The solvent used was $CaCl_2CH_3OH$. Gamma irradiation causes complete absorption in the $220 - 300\ m\mu$ region

than an increase in transmission in the region 400 - 700. Ultraviolet irradiation shifts the 2.80 mu peak to the right and produces a new peak at 340 mu. Transmission of Fiber #9 is unchanged by 5.90 x 10^{-2} watts/in of uv irradiation.

2. Figure 18 shows the transmission characteristics of Fiber #4 (Nomex) in the 320 - 700 mu region before and after irradiation. The solvent was H_2SO_4. After 16.51 x 10^8 rads of gamma irradiation, the absorption shifts toward the longer wavelengths. After 2.89 x 10^{-2} watts/in^2 of ultraviolet radiation, there is an absorption peak at 395 mu and a decrease in absorption 400 - 700 mu. The solvent - H_2SO_4 absorbs completely in the 220 - 320u ultraviolet region, and is less desirable as a solvent than $CaCl_2CH_3OH$.

E. Figure 19a shows nylon 66 fibers before irradiation. The typical stress patterns of nylon 66 as they appear when seen with polarized light may be seen. Figure 19b shows nylon 66 fibers after 2.08 x 10^7 rads of gamma irradiation. Breakdown of the crystalline structure is well advanced as evidenced by the crystal fragments at the point where the two fibers are crossed. Figure 19c shows Nomex nylon before irradiation. Figure 19d shows Nomex after 8.6 x 10^7 rads of gamma irradiation. There are no visible changes in the fiber. Figure 19e is the before picture of nylon 6. Figure 19f shows nylon 6 after 2.08 x 10^7 rads of gamma irradiation. As with nylon 66, the fiber has begun to disintegrate at the point where the two fibers cross. The degradation of nylon 66 and nylon 6 increases rapidly with increasing dose and finally loses all fiber characteristics. Nomex after four times as much radiation shows no crystalline breaks after irradiation.

V. DISCUSSION

A. The degradation of Polyamides may by described by a series of reactions. A primary reaction probably is one in which an $-NH-CH_2-$ bond in the polyamide chain is broken, the main products being a polyamide chain with a nitrile end-group, a polyamide chain with a hexanoic end-group and a molecule of water. The water may hydrolyze an amide linkage; end-groups formed in this manner may react to form a secondary amine group; carboxylic end-groups will give a keto group. Part of the reaction products may contain unsaturated hydrocarbon chains.(30)

B. When examined by X-ray or electron diffraction (1,15) many polymers including the nylons show evidence of crystalline structure. The crystals are small and each long chain molecule runs through a number of crystals with amorphous structure between them. These crystals are responsible for the solidity and strength of nylon. When a polymer is irradiated, cross links may be formed but crystallinity may also be destroyed by increased doses of radiation. Figure 19 shows some of this. The progressive destruction of crystal orientation in the nylon 6 and 66 fibers was illustrated in an earlier paper (13). The energy absorbed from a beam of ionizing radiation is captured at random throughout the irradiated specimen, however the reactions which take place depend largely on the chemical structure of the polymer. The benzene ring is known to provide a considerable degree of radiation protection to the molecules of which it forms a part. For example, in this study Nomex the more heat resistant nylon is known to contain an aromatic structure in the molecule. The fact that this protection arises from the resonant nature of the aromatic group has been demonstrated by Charlesby (5) and others (2,7,10). While the benzene ring affords excellent protection when the polymer is exposed to ionizing or thermal radiation it does not afford the same protection to ultraviolet radiation. This is shown in the results given in Table 2. (10,16) Fiber #9 the more sunlight resistant nylon 66 has the same infrared spectra as Fiber #0 the conventional nylon 66. While that of Fiber #4 Nomex nylon indicate the presence of aromatic substituents. #0 and #4 are affected by ultraviolet radiation to about the same degree, #9 is much less affected by ultraviolet than either of the other two. Fibers #0 and #9 are affected by gamma radiation to the same degree, while Fiber #4 can withstand massive doses of gamma irradiation.

VI. CONCLUSIONS

A. This study has left many questions unanswered, many gaps in the data, and it has also raised other questions. Such as, why is Nomex nylon resistant to gamma and thermal radiation yet affected by ultraviolet radiation to about the same extent as nylon 6 and 66? On the positive side it has been shown that Nomex has many desirable properties and these may be enhanced by suitable doses of gamma radiation. Particularly, the resistance to ultraviolet radiation is improved by small doses of gamma radiation. This may also be true of nylon 6 and 66 under certain circumstances.

B. This work was carried out on filament yarn. The results of other work on film or fiber indicate that the molecular changes that take place as a result of irradiation are the same for film or fiber (1,22,29,30).

C. The gaps in the data should be filled. Some phases of the investigation should be carried out under more rigorous conditions, such as a higher vacuum, a purer nitrogen supply, and a more intense ultraviolet source. Specimens should be given small doses of gamma irradiation and then exposed to ultraviolet and/or thermal radiation in order to determine if the resistance to ultraviolet radiation can be improved consistently by previous gamma irradiation. Even, if it should prove to be true only, for Nomex nylon and not for nylon 6, or 66, that in itself would be valuable knowledge.

VII. PERSONNEL

This work was done by the principal investigator and A. Milo of the Textile Branch.

VIII. ACKNOWLEDGEMENT

The cooperation of E. R. Wright and M. Perlman of the Chemical Engineering Division for obtaining the infrared spectrophotometric data is acknowledged.

BIBLIOGRAPHY

1. Achhammer, B. G., Reinhart, F. W., and Kline, G. M., Mechanism of the Degradation of Polyamides, J. RES. N.B.S. 46,391,1951

2. Bopp, C. D., and Sisman, O., How Radiation Changes, Polymer Mechanical Properties, NUCLEONICS 13,51,1955

3. Boulton, J., and Jackson, D. L. C., The Fluidity of Nylon Solutions in m-Cresol, J. Soc. Dyers and Colourists 59,21,1943

4. IBID The Fluidity of Nylon Solutions in m-Cresol, Part II, J. Soc. Dyers and Colourists 61,40,1945

5. Charlesby, A., Atomic Radiation and Polymers, Pergamon Press New York, 1960

6. Charlesby, A., Some Radiation Effects on Long Chain Polymers, Trans. Plastics Inst., London, 23,133,1955

7. Charlesby, A., Effect of High Energy Radiation on Long Chain Polymers, NATURE 171,167,1953

8. Colthrup, N. B., Spectra Structure Correlations in the IR Region, J. Opt. Soc. of Am., 40,397,1950

9. DuPont, High Temperature Twins, DuPont Magazine, Sep - Oct 1963

10. Florin, R. E., and Wall, L. A., Radiation Chemistry of Monomers and Polymers NBS,WADC, Report No. 33 (61 57-14 Project No. 7 (8-7360) Task No. 70347, 1959

11. Flory, P. J., Molecular Weights and Intrinsic Viscosities of Polyisobutylenes, J. Amer. Chem. Soc., 65,372,1943

12. Hargreaves, G., NAMATCEN Report No. NAMC AML AE 1076, Final Report TED NAM AE 5293 of 18 Dec 1958

13. Hargreaves, G., Radiative Degradation of Nylon 66 as Shown with a Polarizing Microscope, Text. Res. J. 32,704,1962

14. Hargreaves, G., Viscosity of Dilute Solutions of Nylon 66 in $CaCl_2CH_3OH$, J. Poly. Letters 2,29,30,1964

15. Harwood, J. J., Hausner, H. H., Morse, J. G., & Rauch, W. G., The Effects of Radiation on Materials, Reinhold, Publishing Corp. N. Y., 1958

16. Harmon, D. J., Effects of Gamma Radiation (Co^{60}) on the Physical Properties of Textile Cords, Text. Res. J. 27,318,1957

17. Heyn, A. N. J., Fiber Microscopy, Interscience Publishers, Inc., N. Y., 1954

18. Hill, R., Fibers From Synthetic Polymers Elsvier Press London 1953

19. Huggins, M. L., Viscosity of Dilute Solutions of Long Chain Molecules, V. Dependence on Solvent, J. Applied Physics, 14,246, 1943

20. Huggins, M. L., Physical Chemistry of High Polymers, John Wiley & Sons, Inc., N. Y., 1958

21. Kozlov, P. V., Endrykhovskaya, A., and Kargin, V. A., Investigations into the Temperature Transitions in Synthetic Polymers with Rigid Chains, Dokl. Akad. Nauk. SSSR, 129,844,1959, abstr. in J. Text. I. 51,A225,1960

22. Little, K., The Effect of High Doses of Ionizing Radiations on Organic High Polymers, A.E.R.E. Harwell, March 1954

23. Lothian, M. A., Adsorption Spectrophotometry, Hilger and Watts Ltd. London 1958, 2nd Ed.

24. Melvile, Sir Harry, Twenty-Five Years ~~of Manmade~~ Fibers, J. Text. I., 71,382,1960

25. Nichols, J. B., X-ray and IR Studies on the extent of Crystallization of Polymers, J. Applied Phys. 25,840,1954

26. Schwertassek, K., Structure of Polyamide Fiber, Faserforsch, Textiltech., 2,45,1955

27. Scott, R. B. and Vandenbelt, J. M., Infrared Spectroscopy, Beckman Bulletin No. 14, 1954

28. Taylor, G. B., The Relation of the Viscosity of Nylon Solutions in Formic Acid, J. Am. Chem. Soc., 69,635,1947

29. Tobolsky, A. V., Properties and Structure of Polymers, J. Wiley & Sons, N. Y.

30. Kamerbeek, B., Kroes, G. H., and Grolle, W., Thermal Degradation of Polymers, Soc. of Chem. Ind., London, 1961

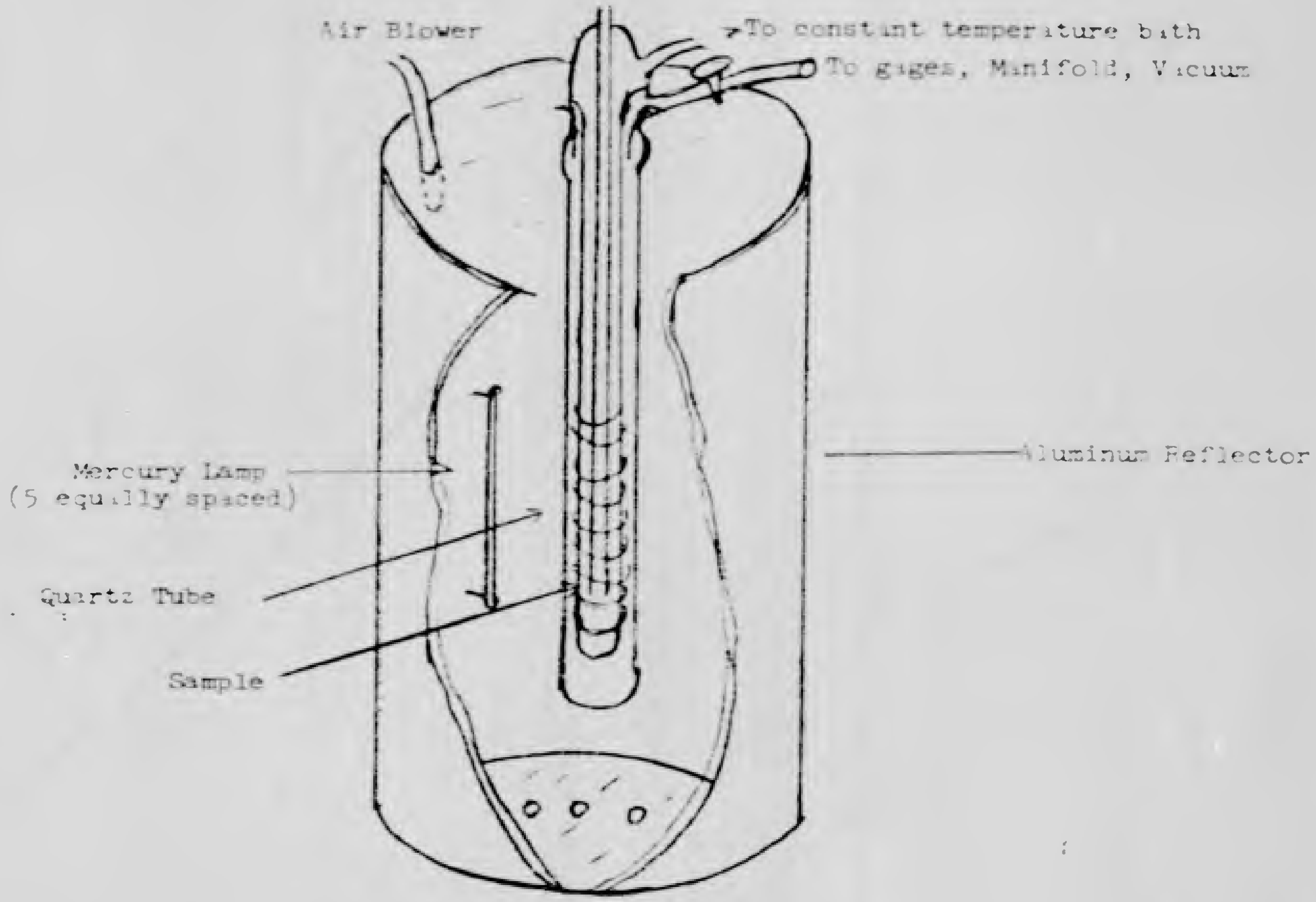
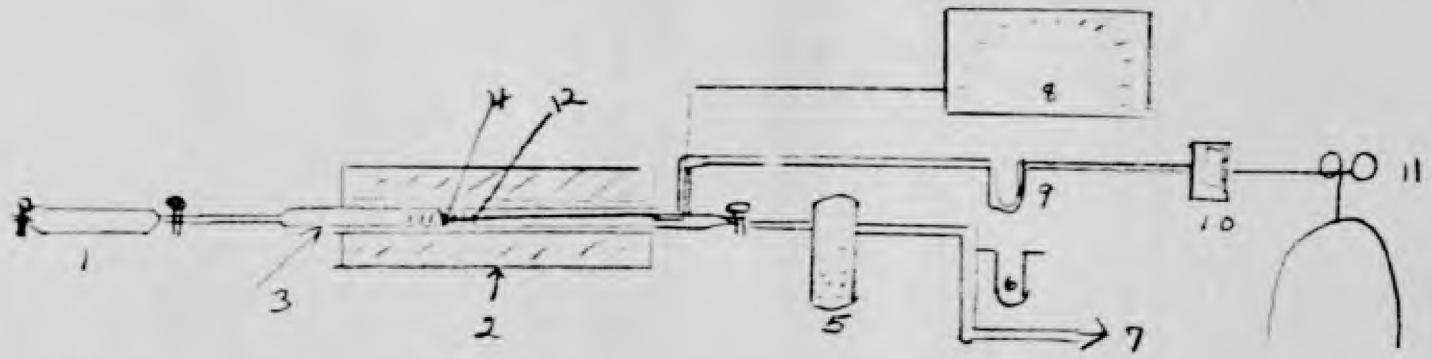
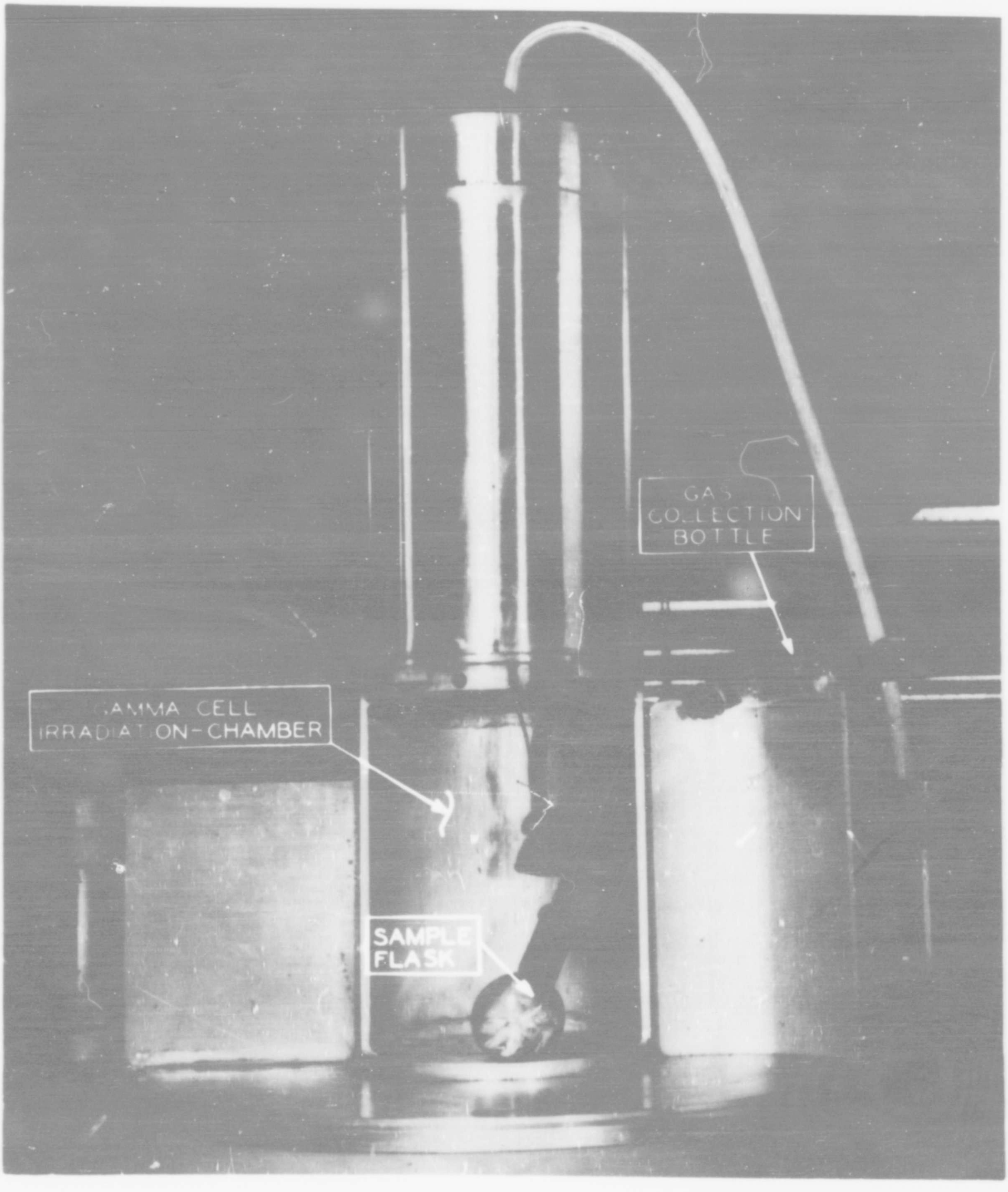


Figure 1 - UV IRRADIATION APPARATUS



1. Gas collecting bottle with vacuum stopcock
2. Combustion furnace
3. Unterzaucher combustion tube
4. Sample
5. Drying tube
6. Vacuum gauge
7. Vacuum pump
8. Temperature recorder
9. Drying tube
10. Flow meter
11. Gas cylinder
12. Thermocouple in sample

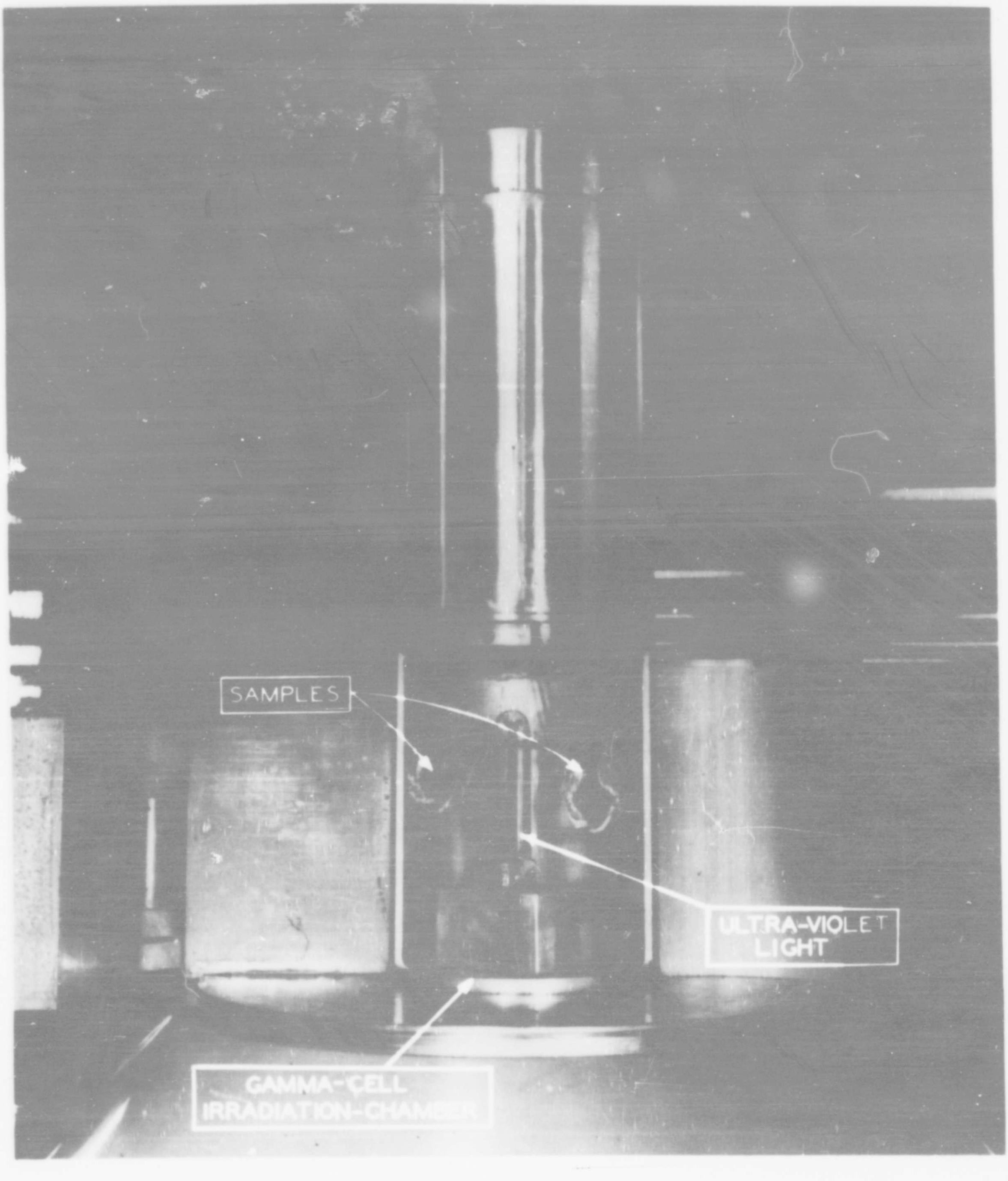
FIGURE 2 - THERMAL IRRADIATION APPARATUS



GAMMA IRRADIATION APPARATUS

PHOTO NO: CAN-356971(L)-12-63

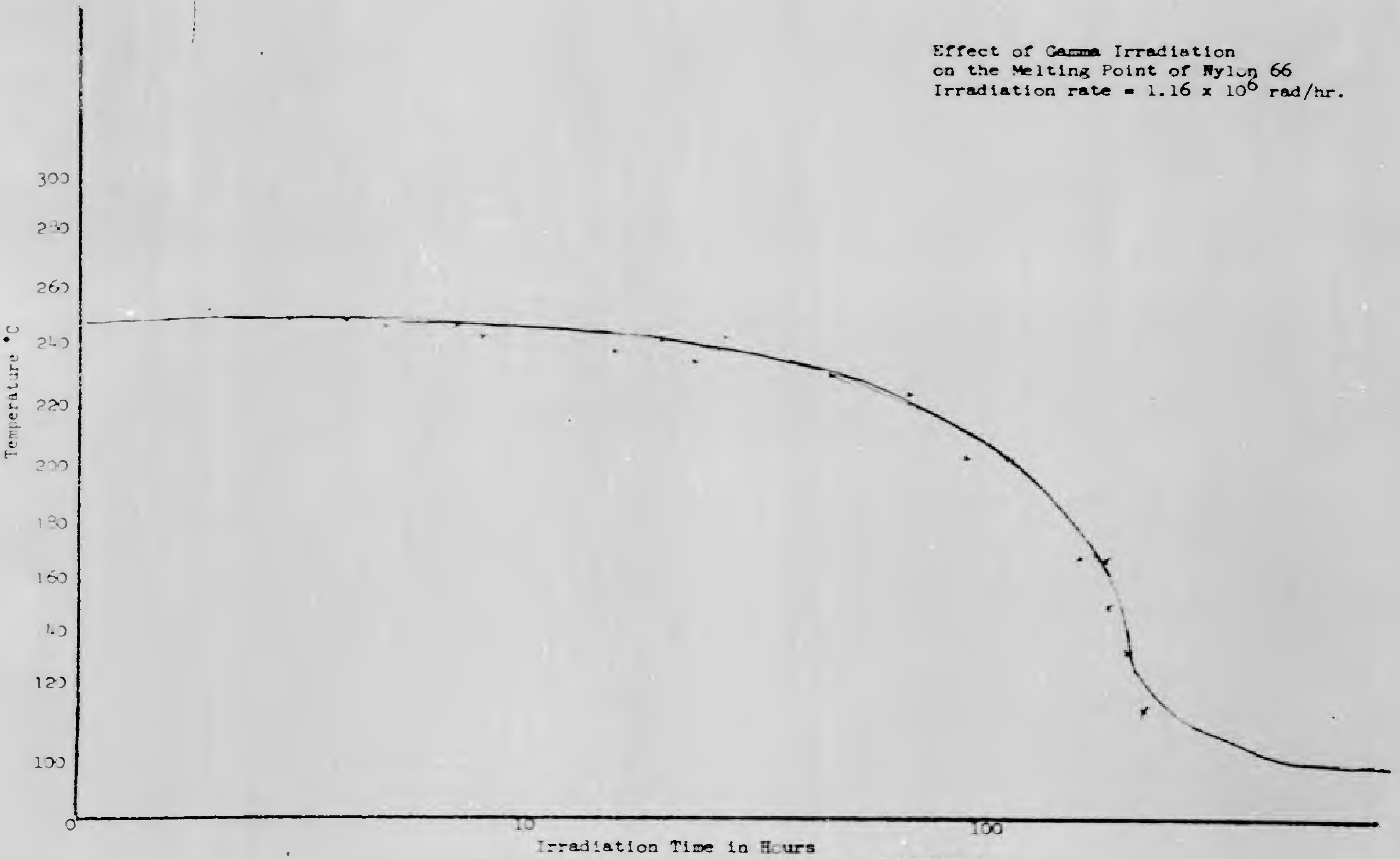
FIGURE 3



GAMMA PLUS ULTRAVIOLET IRRADIATION APPARATUS

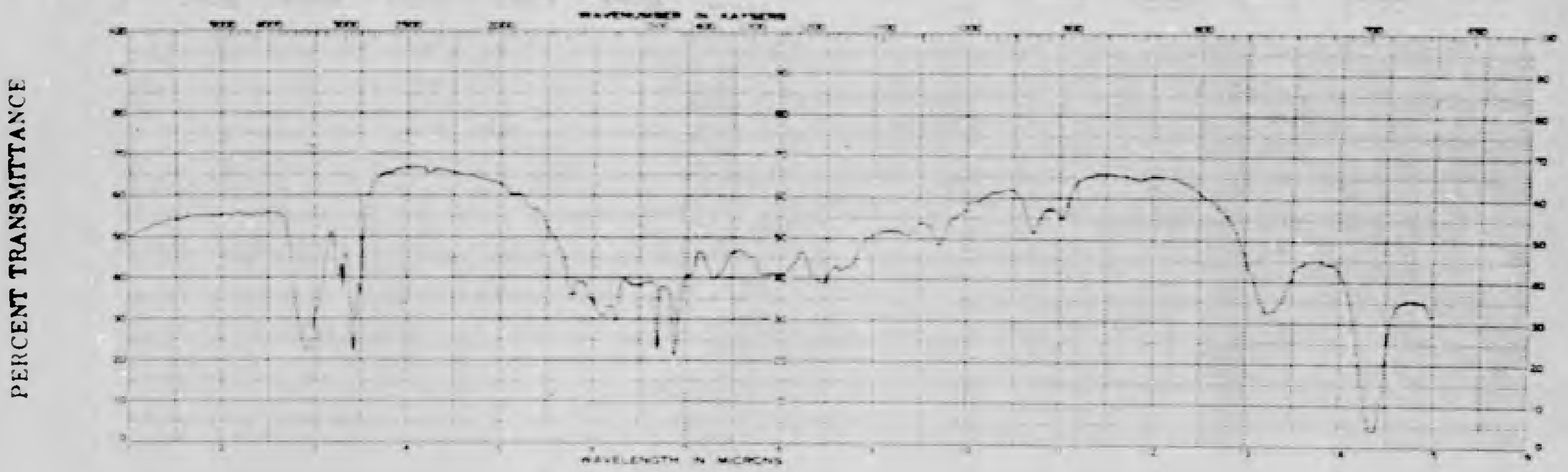
PHOTO NO: CAN-356970(L)-12-63

FIGURE 4



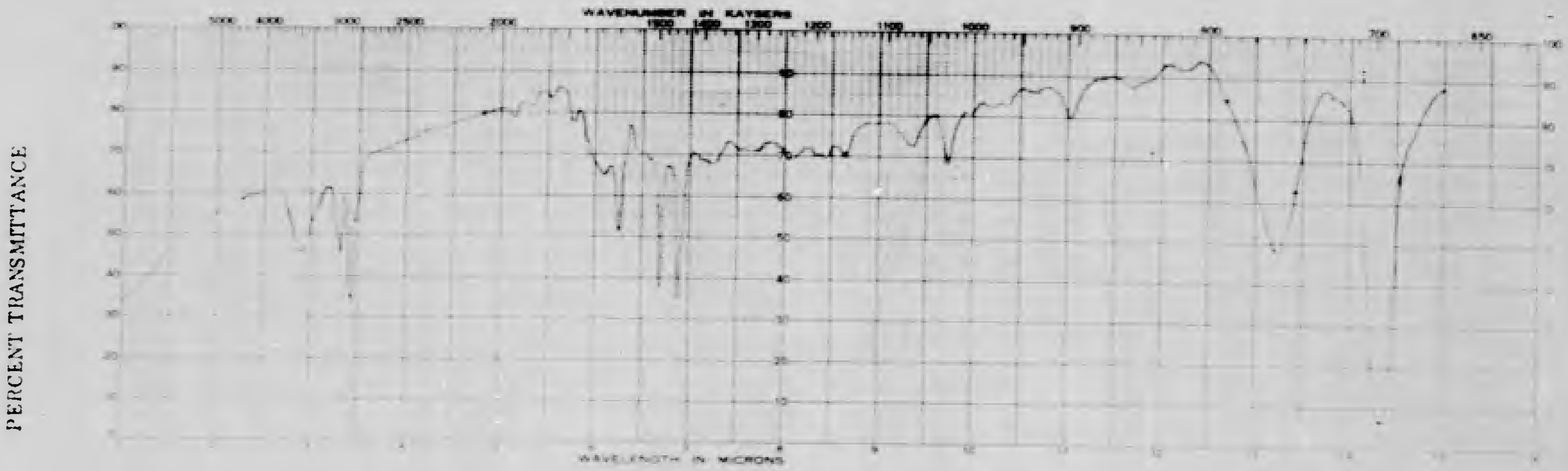
Effect of Gamma Irradiation
on the Melting Point of Nylon 66
Irradiation rate = 1.16 x 10^6 rad/hr.

FIGURE 5



IR ANALYSIS BEFORE IRRADIATION - NYLON 66 FIBER #0

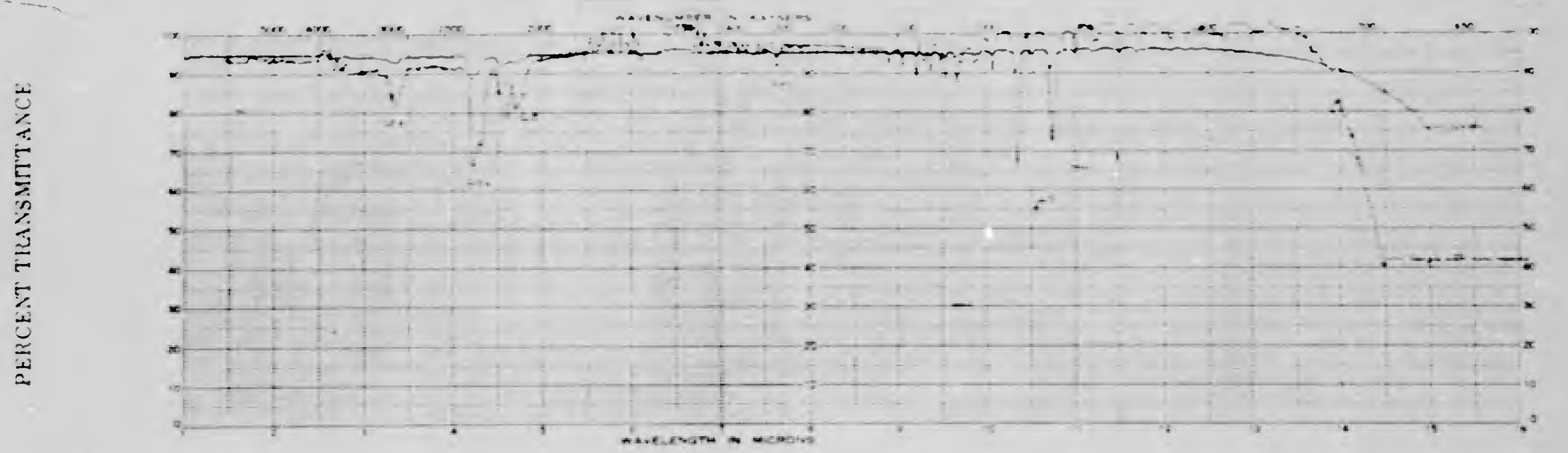
FIGURE 6a



IR ANALYSIS BEFORE IRRADIATION - NOMEX NYLON FIBER #4

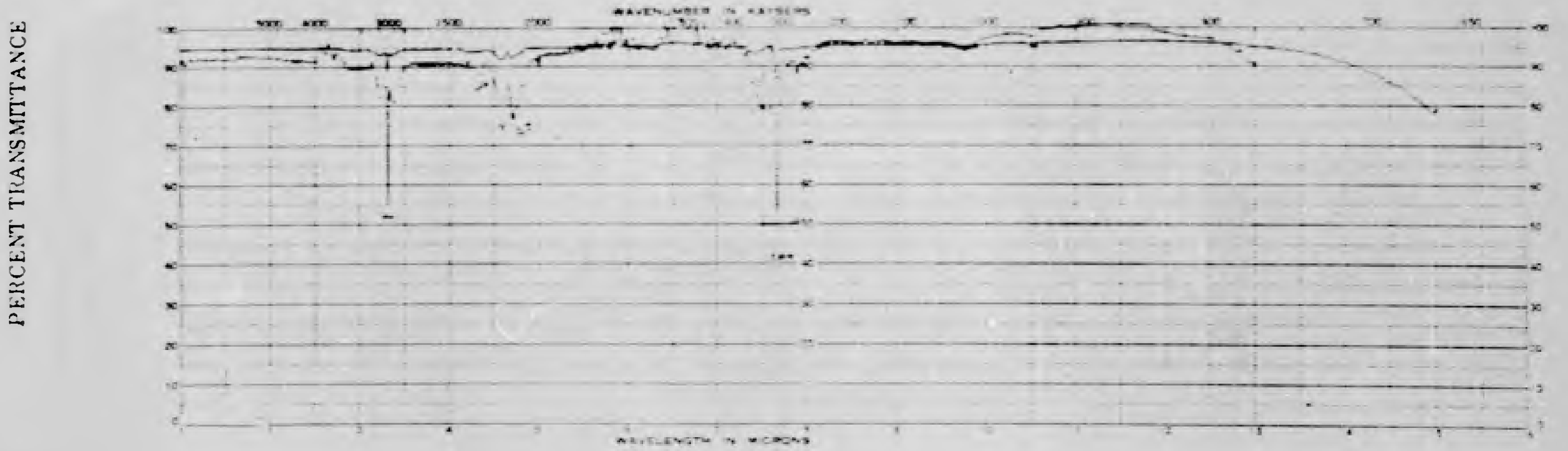
FIGURE 6b

PHOTO NO: CAN-344503(L)-5-62



IR ANALYSIS OF GASEOUS PRODUCTS OF PYROLYSIS - NYLON 66 #0

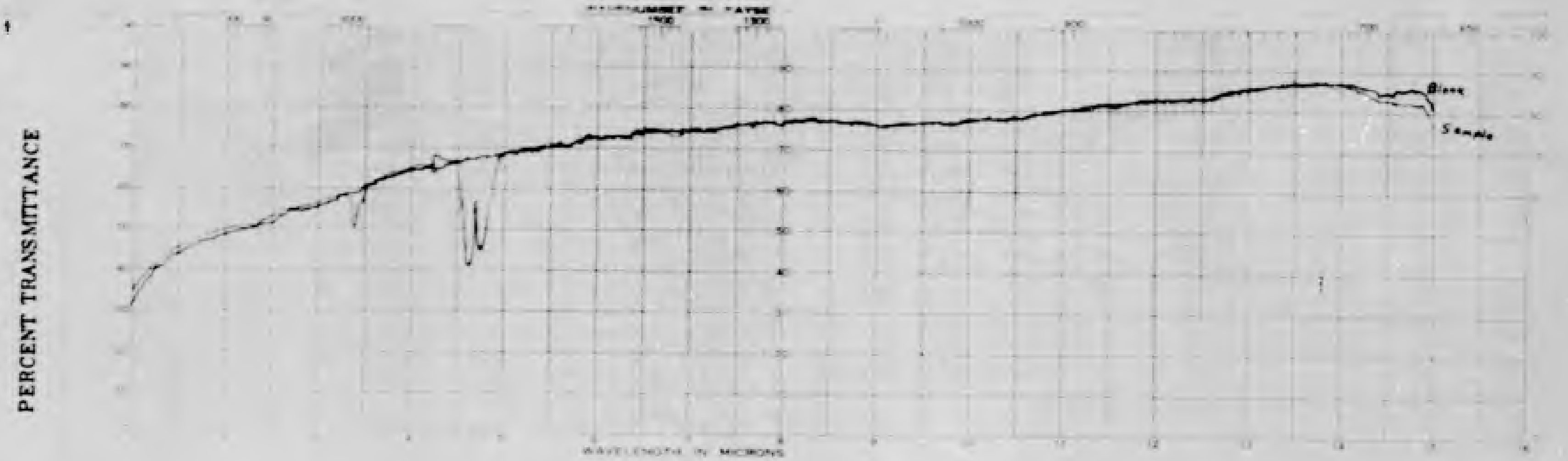
FIGURE 7a



IR ANALYSIS OF GASEOUS PRODUCTS OF PYROLYSIS - NOMEX #4

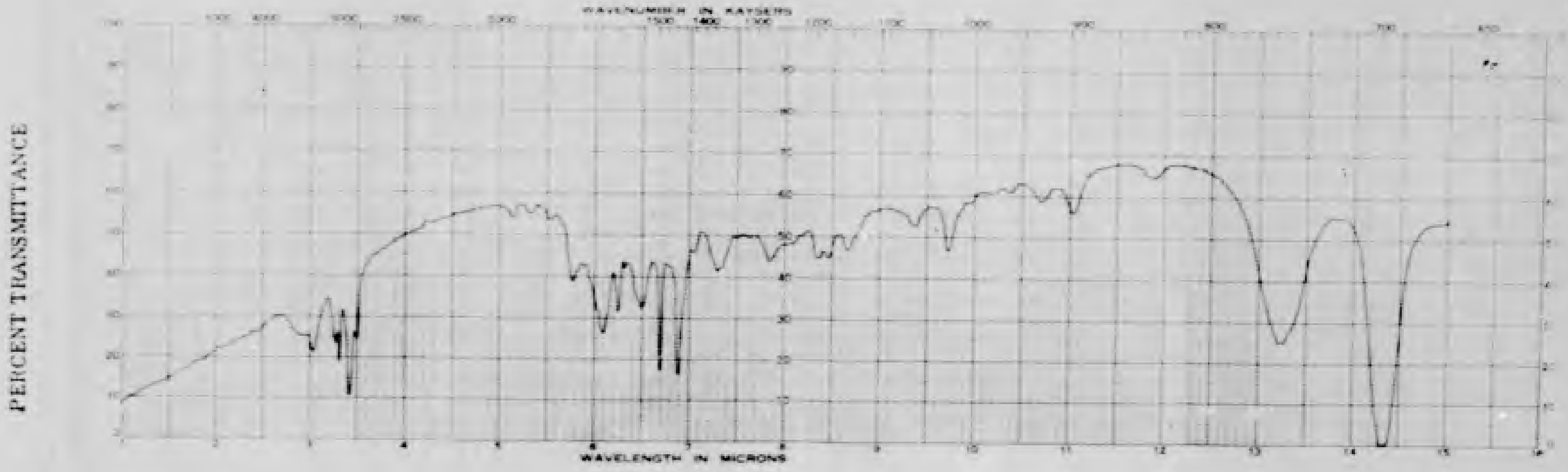
FIGURE 7b

PHOTO NO: CAN-344504(L)-5-62



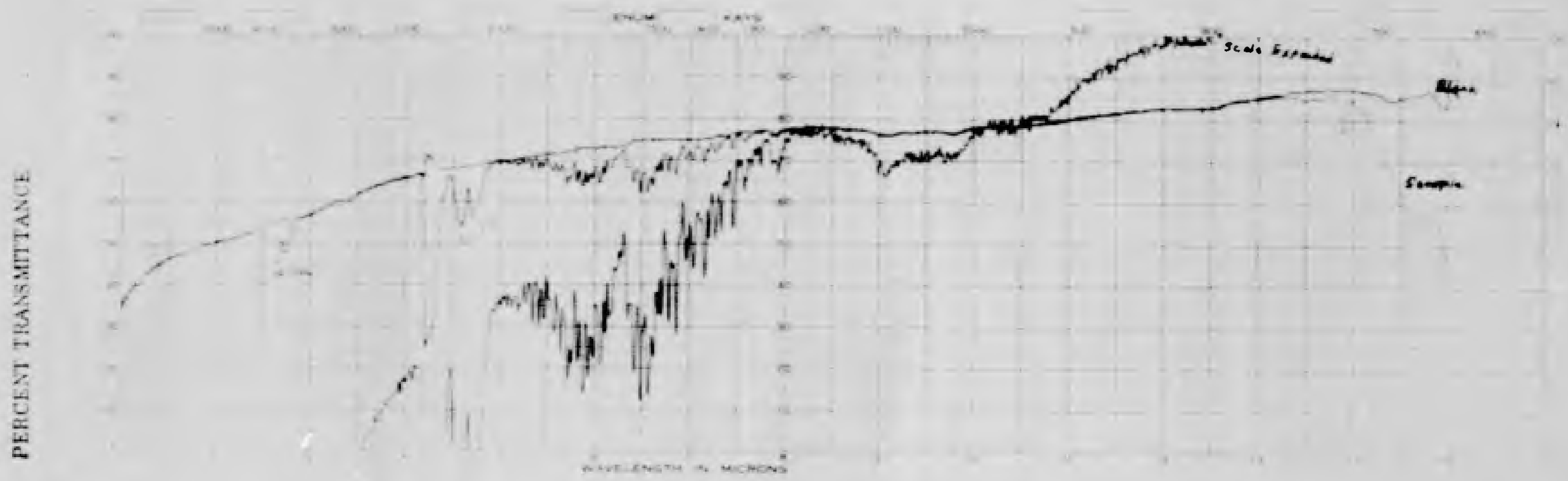
IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^8, RADS GAMMA IRRADIATION IN AIR OF FIBER #0

FIGURE 8a



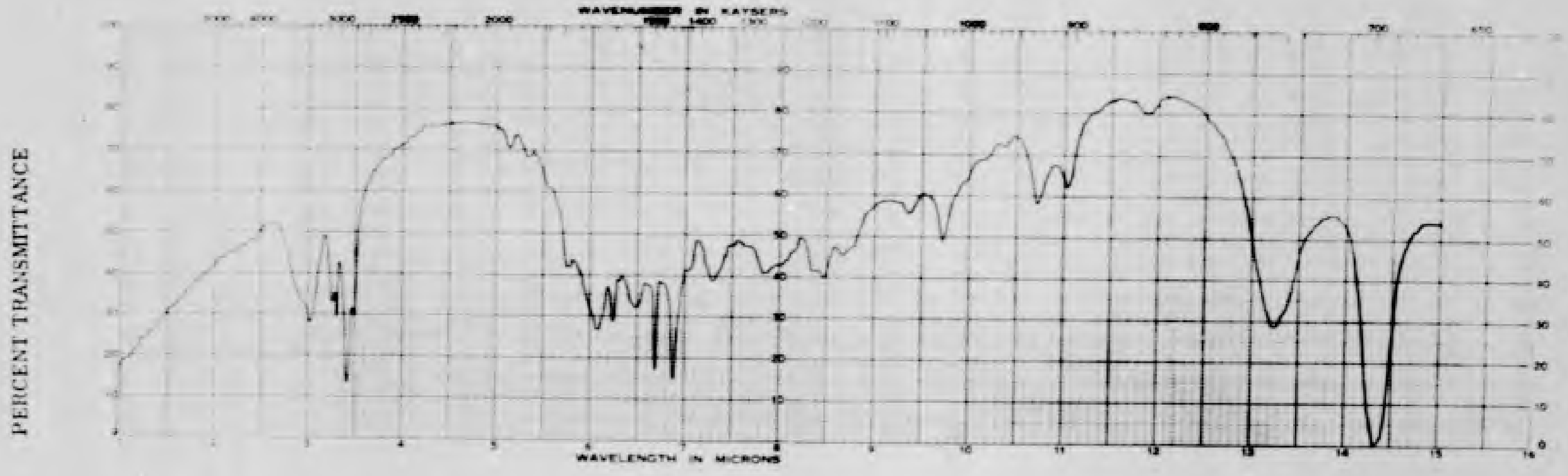
IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN AIR OF FIBER #0 FIGURE 8b

PHOTO NO: CAN-352547(L)-5-63



IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^6 RADS GAMMA IRRADIATION IN NITROGEN OF FIBER #0

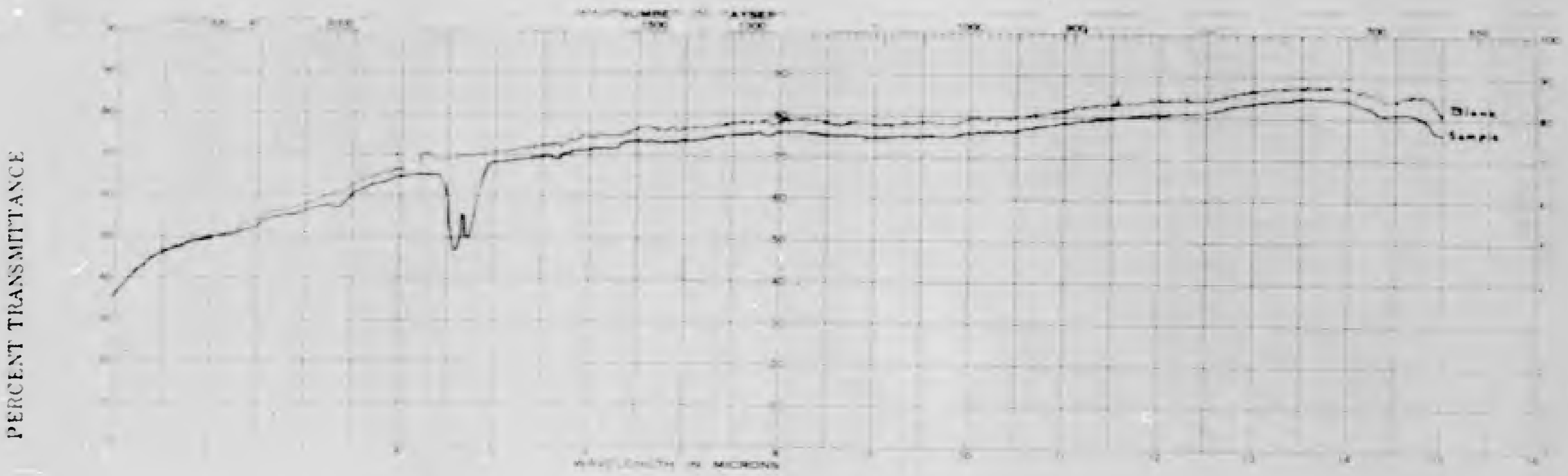
FIGURE 9a



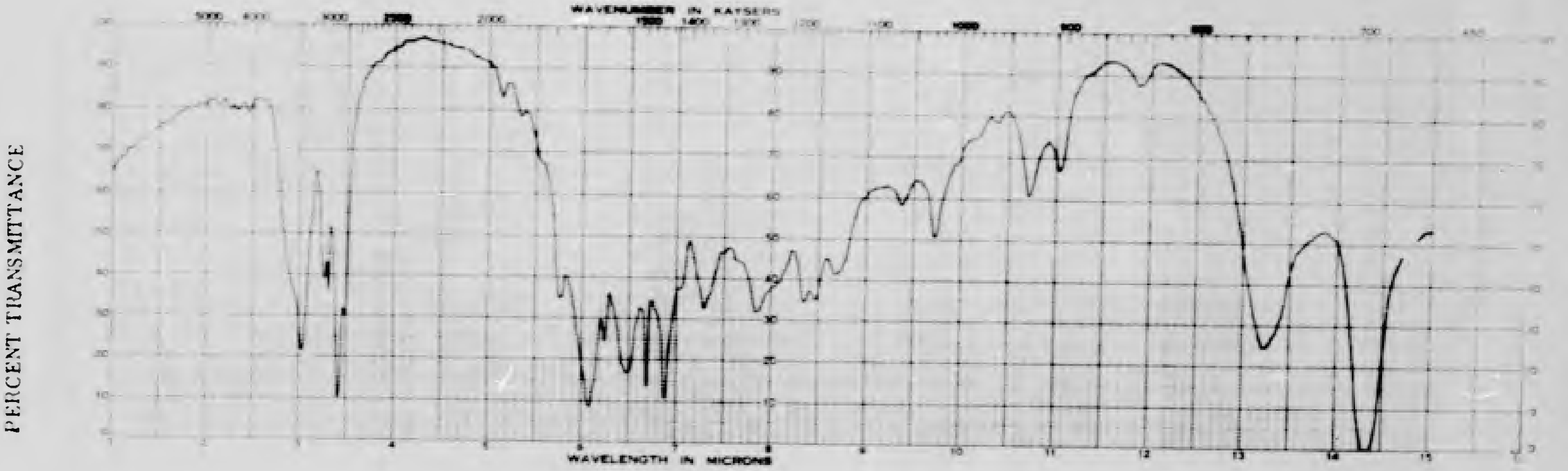
IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN NITROGEN OF FIBER #0

FIGURE 9b

PHOTO NO: CAN-352548(L)-5-63

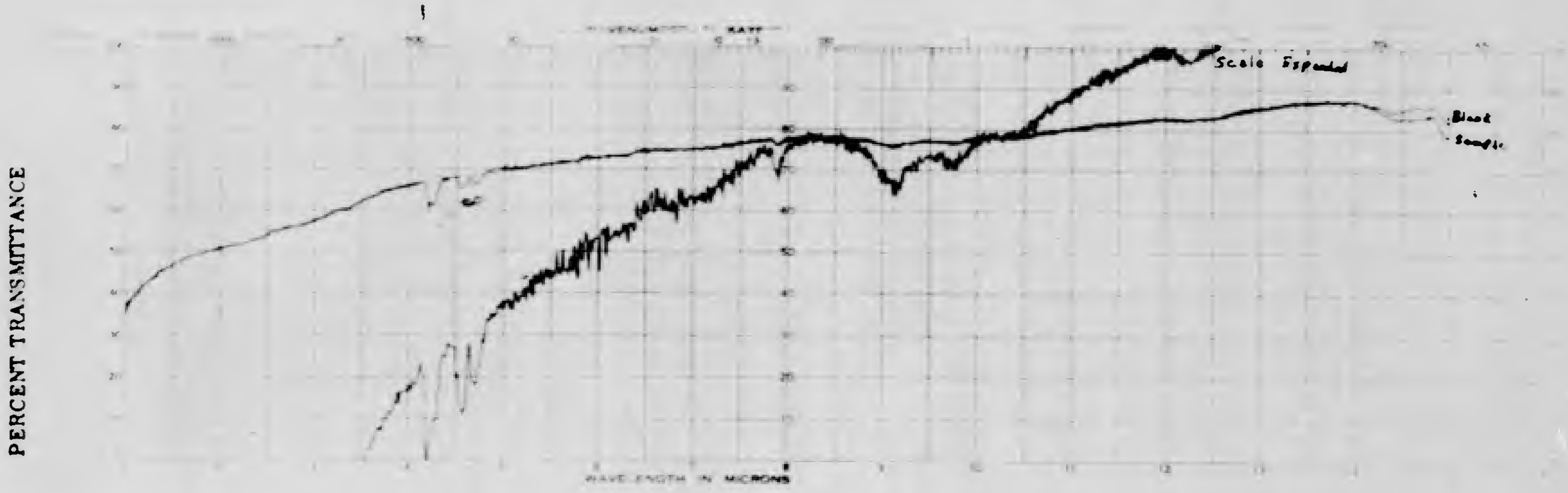


IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN A VACUUM OF FIBER #0
FIGURE 10a



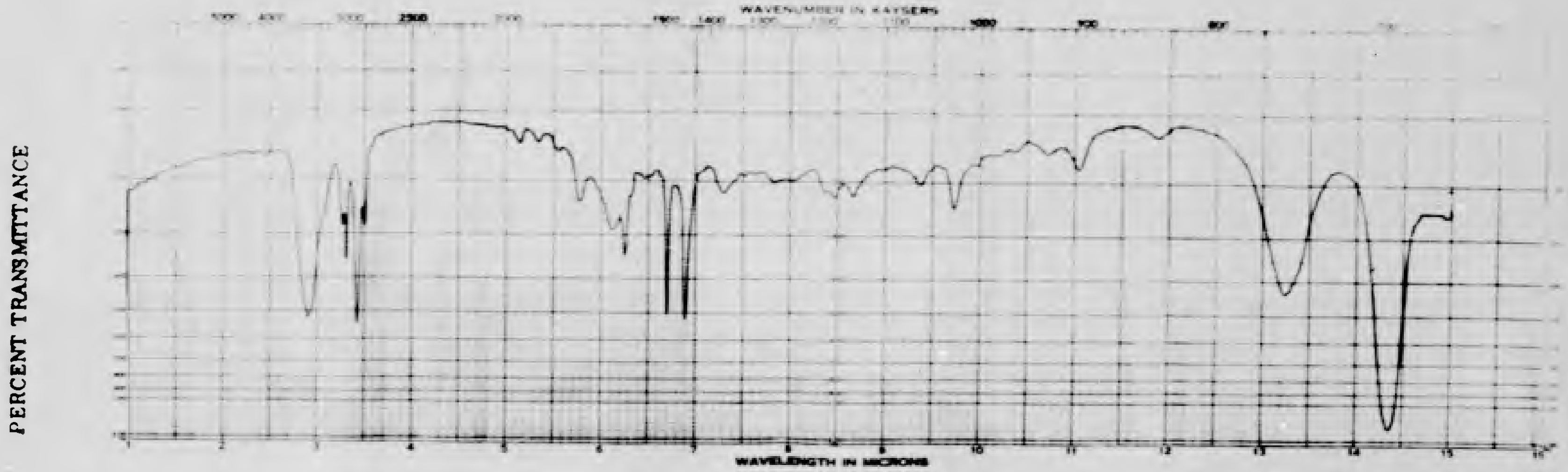
IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN A VACUUM OF FIBER #0
FIGURE 10b

PHOTO NO: CAN-352549(L)-5-63



IR ANALYSIS OF GASEOUS PRODUCTS AFTER 6.04 x 10^{-2} WATTS UV IRRADIATION OF FIBER #0 IN AIR

FIGURE 11a

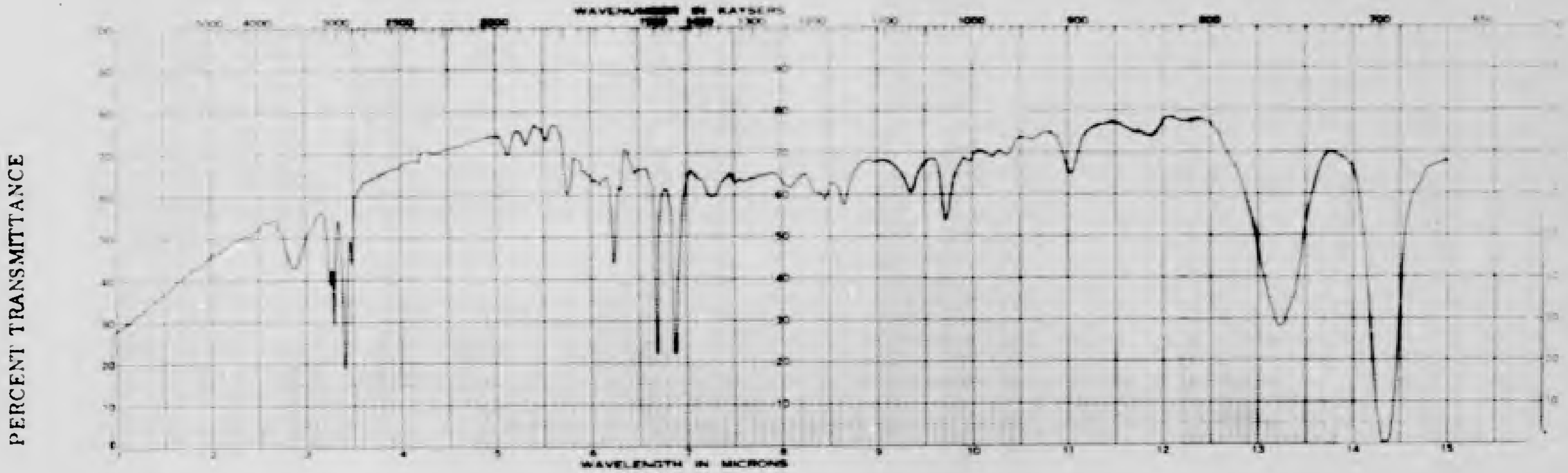


IR ANALYSIS OF THE RESIDUE AFTER 6.04 x 10^{-2} WATTS UV IRRADIATION OF FIBER #0 IN AIR

FIGURE 11b

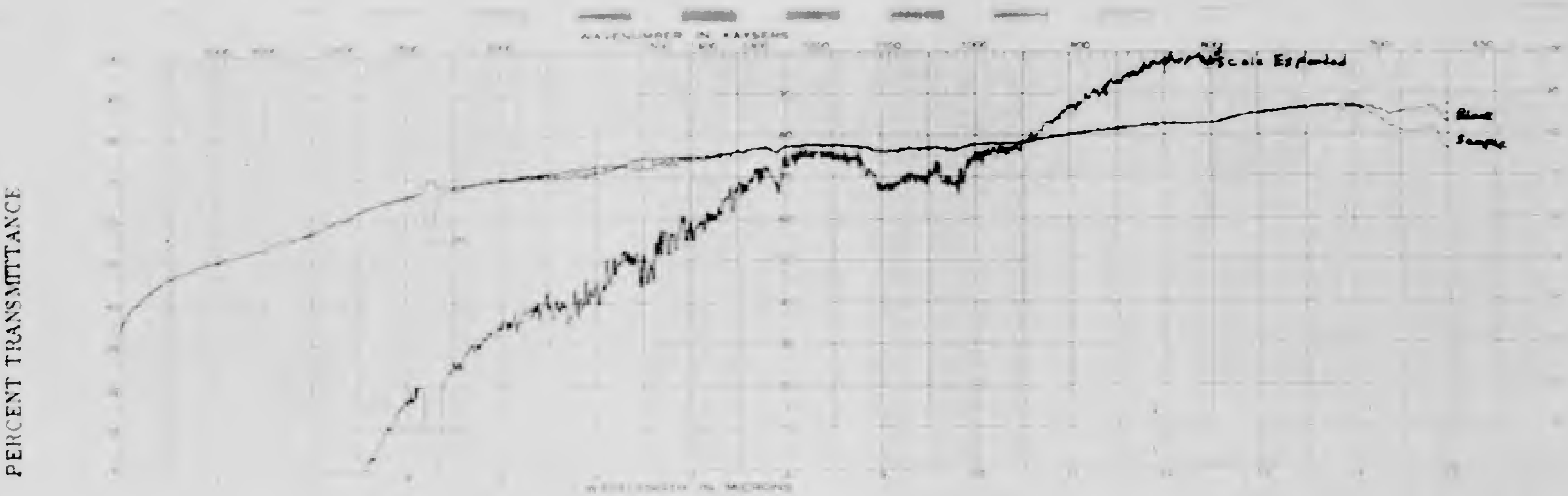
PHOTO NO: CAN-352550(L)-5-63

IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN AIR OF FIBER #4
FIGURE 12a

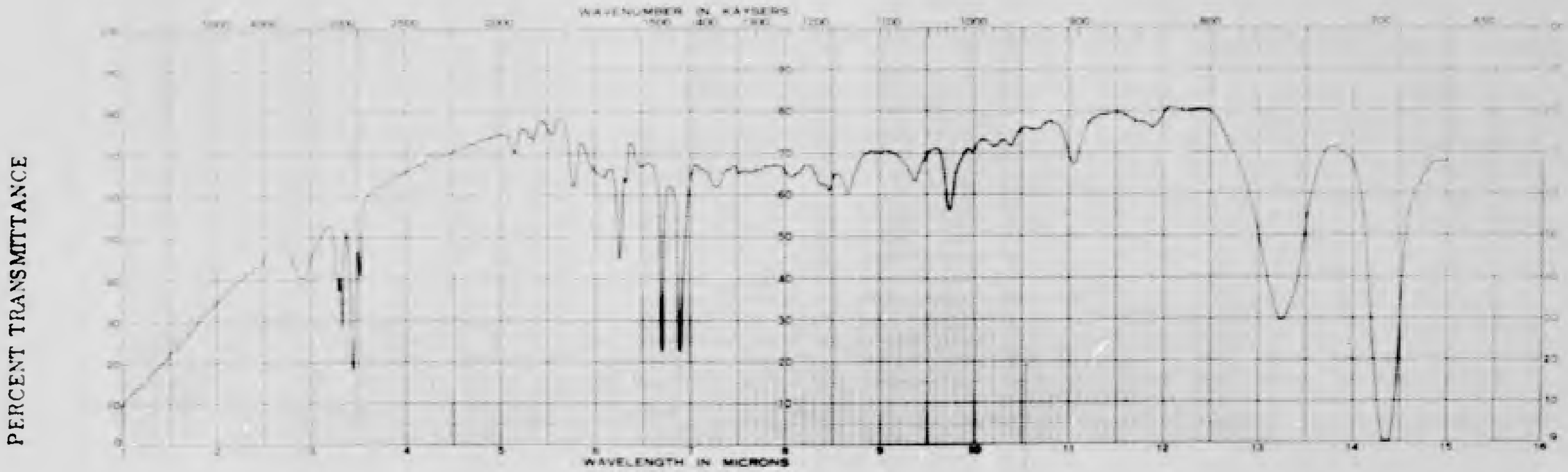


IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN AIR OF FIBER #4
FIGURE 12b

PHOTO NO: CAN-352551(L)-5-63

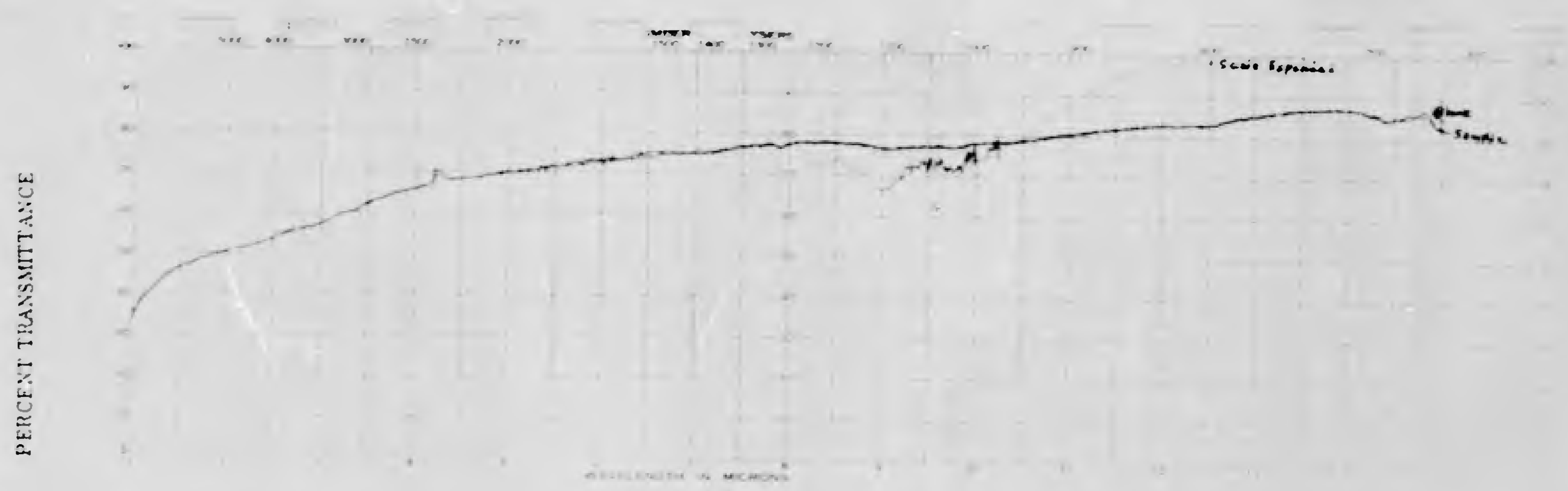


IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN NITROGEN OF FIBER #4
FIGURE 13a



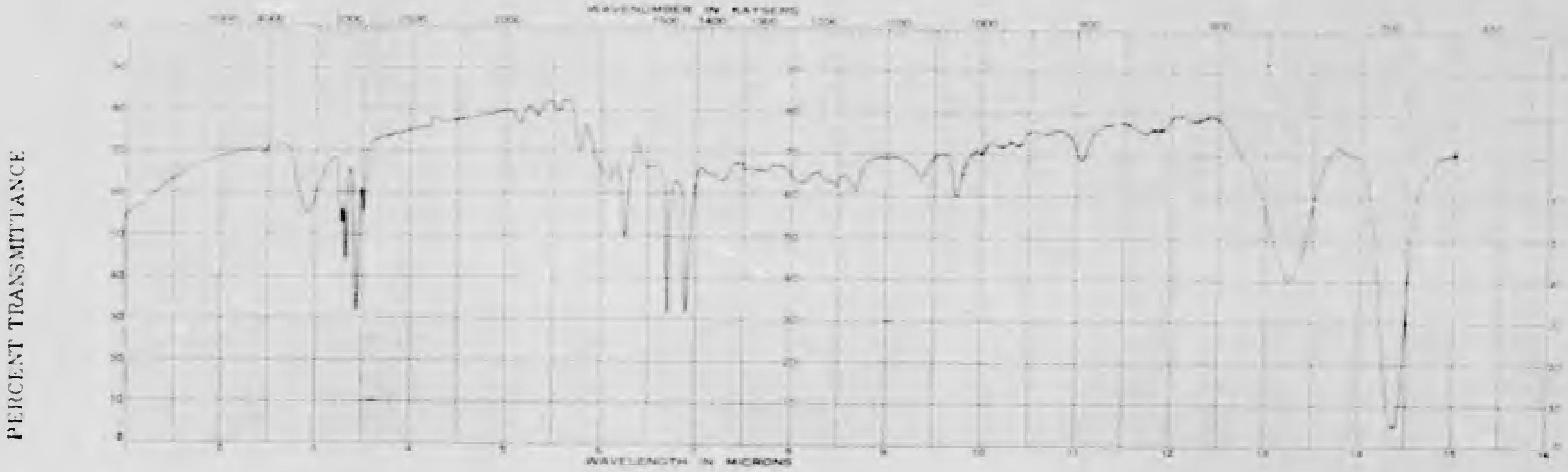
IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN NITROGEN OF FIBER #4
FIGURE 13b

PHOTO NO: CAN-352552(L)-5-63



IR ANALYSIS OF GASEOUS PRODUCTS AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN A VACUUM OF FIBER #4

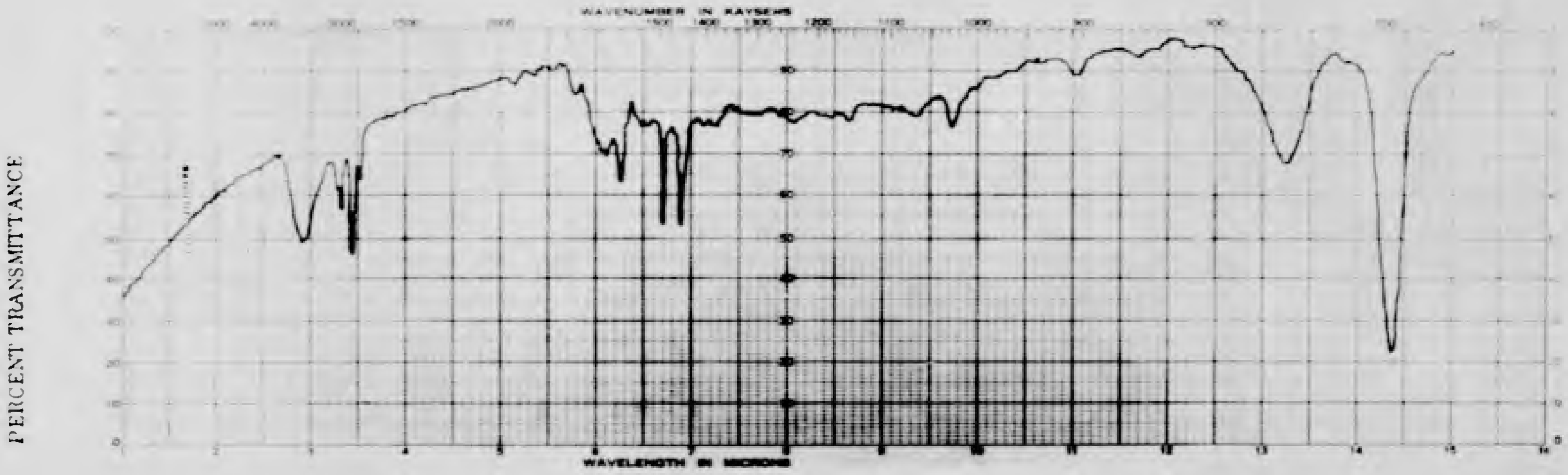
FIGURE 14a



IR ANALYSIS OF THE RESIDUE AFTER 1.72 x 10^8 RADS GAMMA IRRADIATION IN A VACUUM OF FIBER #4

FIGURE 14b

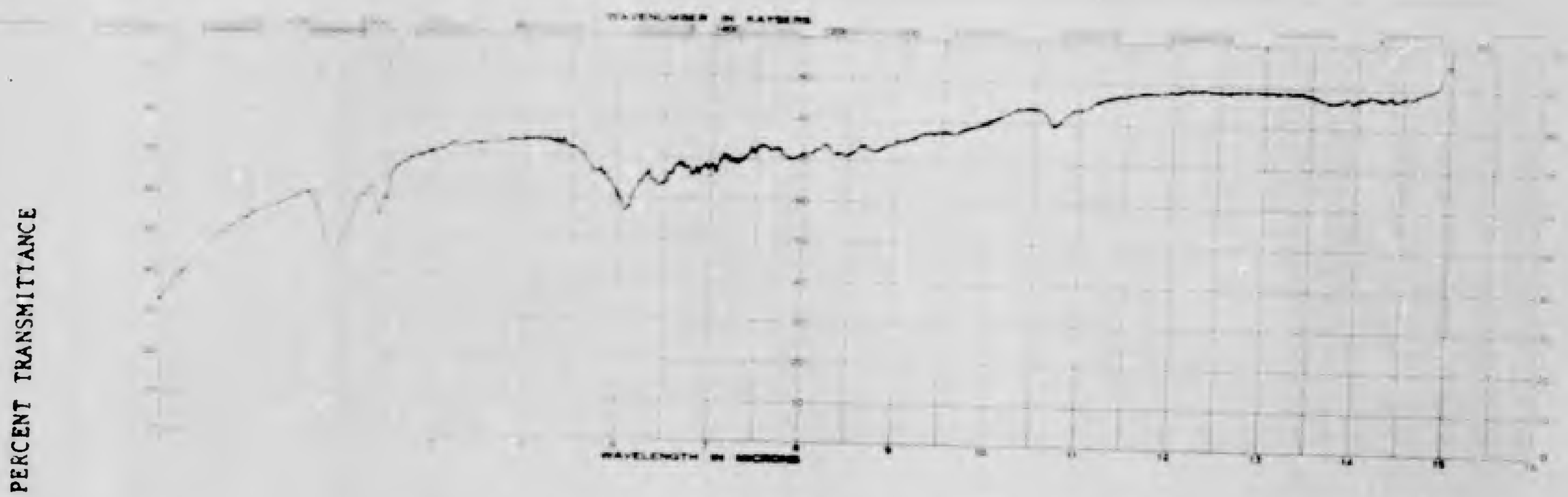
PHOTO NO: CAN-352553(L)-5-63



IR ANALYSIS OF THE RESIDUE AFTER 6.04 x 10^{-2} WATTS OF UV IRRADIATION OF FIBER #4

FIGURE 15

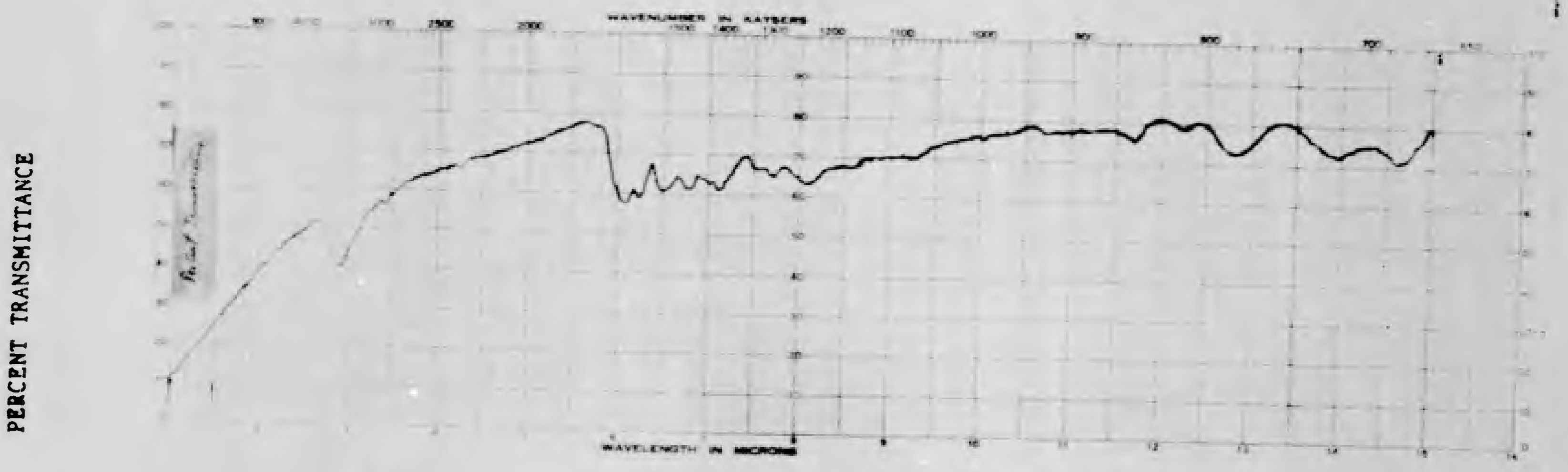
PHOTO NO: CAN-352554(L)-5-63



IR ANALYSIS OF RESIDUE AFTER 1.72 x 10^8 RADS OF GAMMA IRRADIATION CONCURRENTLY WITH 1.2 x 10^{-2} WATTS OF UV IRRADIATION OF FIBER #0

PHOTO NO: CAN-357588(L)-1-64

FIGURE 16a



IR ANALYSIS OF RESIDUE AFTER 1.72 x 10^8 RADS OF GAMMA IRRADIATION CONCURRENTLY WITH 1.2 x 10^{-2} WATTS OF UV IRRADIATION OF FIBER #4

PHOTO NO: CAN-357589(L)-1-64

FIGURE 16b

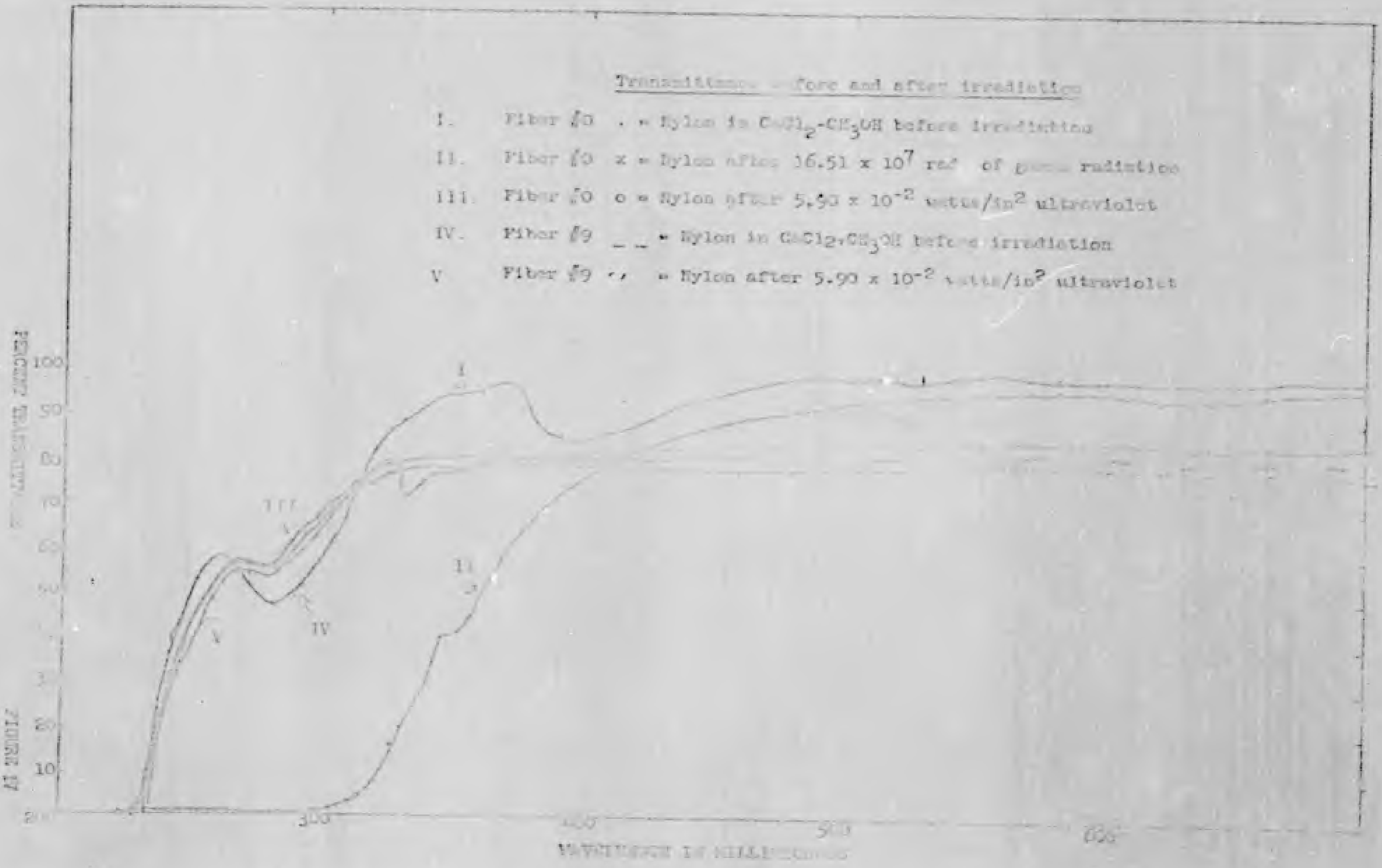

Transmittance before and after irradiation

FIGURE 17

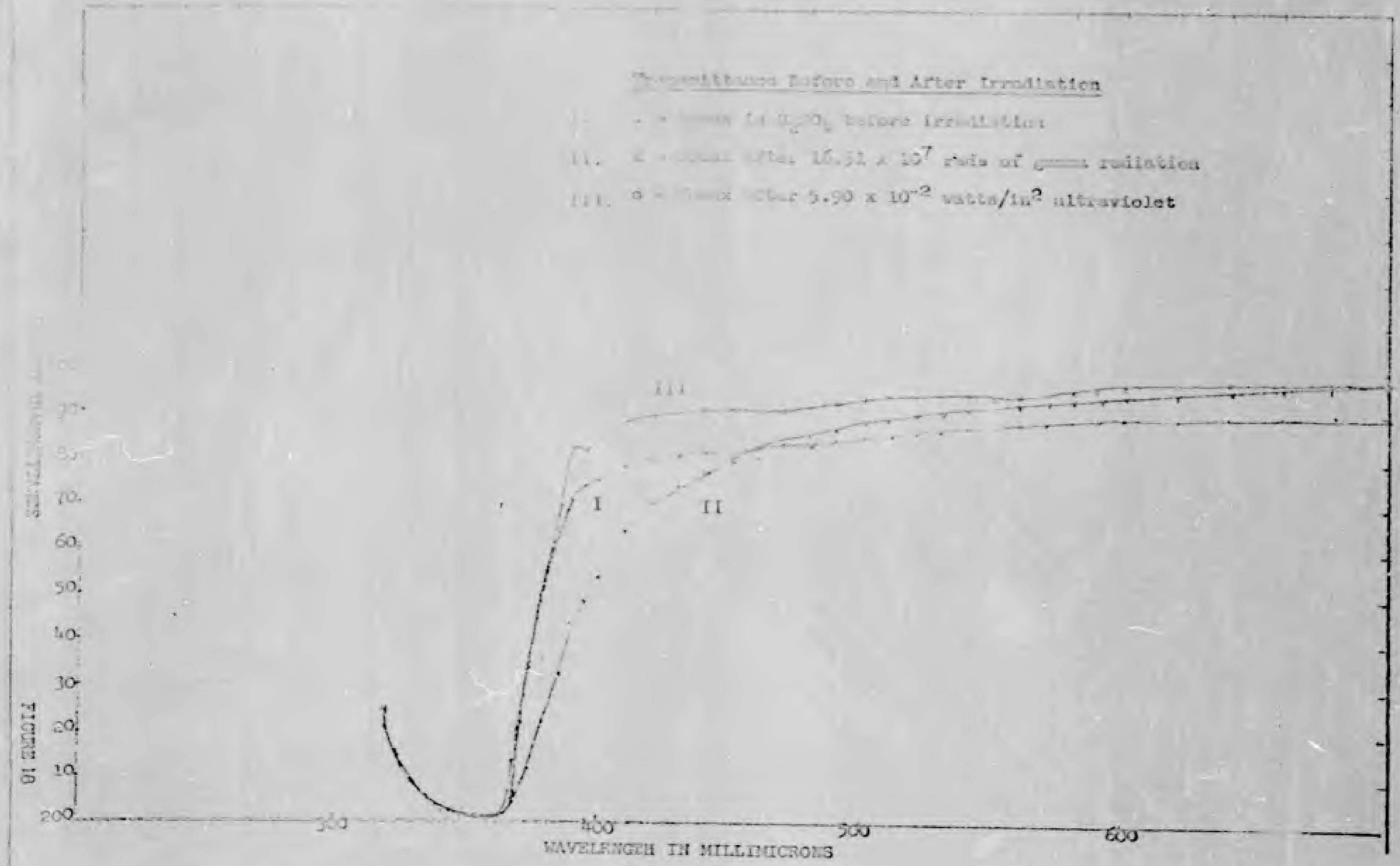
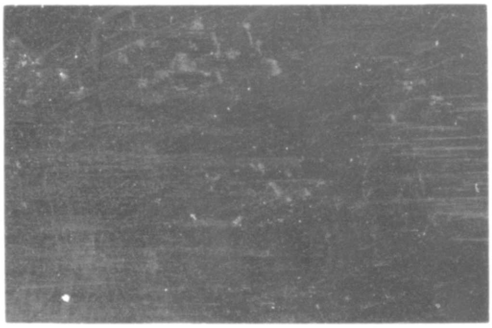
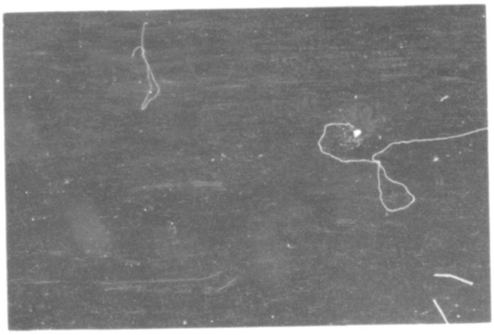

Transmittance Before and After Irradiation
I. – = [illegible] in [illegible] before irradiation
II. x = [illegible] after 16.51 x 10^7 rads of gamma radiation
III. o = [illegible] after 5.90 x 10^-2 watts/in^2 ultraviolet
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
200
300
400
500
600
I
II
III
WAVELENGTH IN MILLIMICRONS

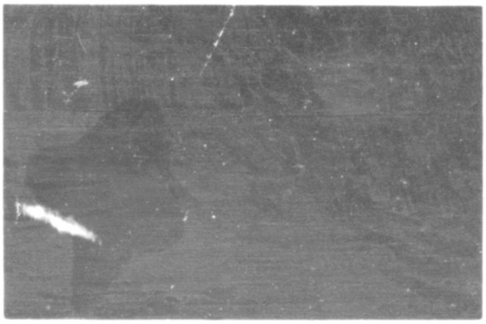
FIGURE 18



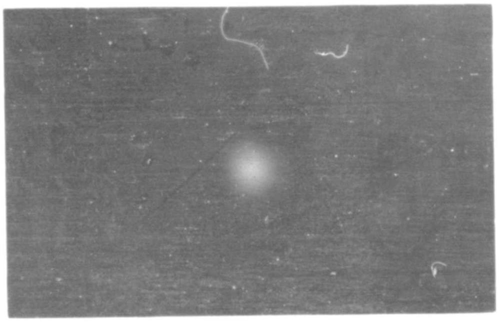
Nylon 66 - Before Irradiation
Figure 19a



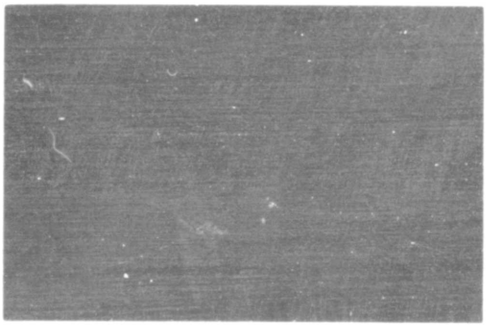
Nylon 66 - After 2.08 x 10^7 Rads Gamma Irradiation
Figure 19b



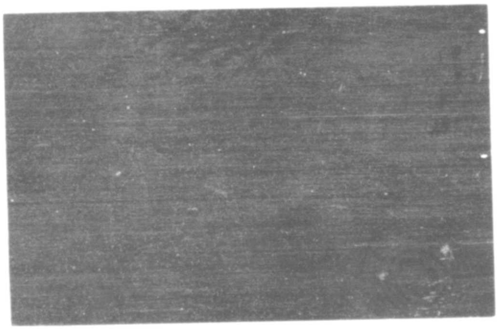
Nomex Nylon - Before Irradiation
Figure 19c



Nomex Nylon - After 8.9 x 10^7 Rads Gamma
Figure 19d



Nylon 6 - Before Irradiation
Figure 19e



Nylon 6 - After 2.08 x 10^7 Rads Gamma Irradiation
Figure 19f

Table 1

Viscosity Data for Solutions of Nylon (Fiber #0) in $CuCl_2CH_3OH$1/

Specimen	η_r	$\ln \eta_r / c$	$[\eta]$
Solvent	1.00		
#0 nylon unirradiated	1.80	0.588	0.65
#0 nylon after			
6.04×10^{-2} - in air	1.59	0.464	0.50
watts UV - in vacuum	1.53	0.425	0.46
#0 nylon after			
4.7×10^{-3} watts UV - in air	1.46	0.378	0.40
6.88×10^{6} rad - in nitrogen	1.58	0.457	0.49
#0 nylon after			
1.2×10^{-2} watts UV - in air	1.18	0.166	0.17
1.72×10^{-8} rad - in nitrogen	1.16	0.148	0.15
#0 nylon after			
1.72×10^{8} rad - in air	1.08	0.077	0.078

1/ η_r = relative viscosity (3,4)*

$\ln \eta_r / c$ = inherent viscosity

$[\eta] = \frac{3(\eta_r^{1/3} - 1)}{c}$ = intrinsic viscosity (1)*

$c = 1$

* ( ) Bibliography references

DATA ON SOME NYLONS BEFORE AND AFTER IRRADIATION

TEST CONDITION	AS RECEIVED			GAMMA IN RADS AFTER 1.72×10^8			UV IN WATTS 6.04×10^{-2}			UV IN WATTS + GAMMA IN RADS 4.7×10^{-3} — 5.58×10^6			UV IN WATTS + GAMMA IN RADS 1.2×10^{-2} — 1.72×10^8			THERMAL 2 HRS. 260°C		
Fiber	Tensile Strength lbs	Relative Viscosity η_r	Melting Point °C	Tensile Strength Retained %	Relative Viscosity η_r	Melting Point °C	Tensile Strength Retained %	Relative Viscosity η_r	Melting Point °C	Tensile Strength Retained %	Relative Viscosity η_r	Melting Point °C	Tensile Strength Retained %	Relative Viscosity r	Melting Point °C	Tensile Strength Retained %	Relative Viscosity r	Melting Point °C
Nylon 66 (Fiber 30)																		
Air	3.67	1.80	256-260	33	1.08		78	1.59	251-254	68	1.46		0	1.18		insol formless mass		
Nitrogen										91	1.58	246-248	27	1.16	210-216			
Vacuum																		
Nylon 66 (Fiber 29) Sunlight Resistant																		
Air	3.52	1.74	256-260	39		210-214	90	1.64	254-259	83	1.52		13	1.25				
Nitrogen								1.69		88	1.65		24	--	225-230			
Vacuum								1.60										
Nylon 6 (Fiber 32)																		
Air	2.14	1.75	214-222	30		170-182	87	1.71	208-212	82	1.42		7					
Nitrogen							87	1.74		95	1.67	206-210	27	1.86				
Vacuum								1.75				--			--			
Nomex (Fiber 34) A more heat resistant nylon																		
Air	2.50	2.78	--	98	2.68	Does not melt	92	2.55	Does not melt	103	2.66	Does not melt	94	2.65	Does not melt	94	insol	Does not melt
Nitrogen					2.67					109	2.75		96	2.15		96	insol	
Vacuum					2.67											97	insol	

TABLE 2

UNCLASSIFIED

UNCLASSIFIED