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QUANTITATIVE ANALYSIS OF ELASTOMERS THROUGH THE INFRARED SPECTRA OF THEIR PYROLYZATES

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FOREWORD

This report was prepared by the Measurement and Analysis Branch and was initiated under Project No. 7360, "Materials Analysis and Evaluation Tech.," Task No. 73602, "Organic and Microanalysis", formerly RDO No. 616-17, "Identification of Molecular and Micro Structure of Aircraft Materials" and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center with Mr. F.E. Bentley acting as project engineer.

This report covers period of work from October 1953 to March 1954.

The author wishes to express his appreciation to George Rappaport of the Inland Manufacturing Division, General Motors Corporation, for his helpful suggestions and assistance during the course of this investigation.

ABSTRACT

A semi-quantitative method is described for determining polymer blends and co-polymer ratios from the infrared spectra of their pyrolyzates (distillates). The method was established through the analysis of phenolic resin blends in Buna N rubber, and by determining the percentage acrylonitrile in butadiene acrylonitrile co-polymers.

The method described here permits the semi-quantitative analysis of Buna N phenolic resin blends, which because of their physical state, cannot be analyzed by conventional methods. It also makes it possible to estimate the amount of non-combustible materials in these polymers. The method is based on the pyrolyzate technique combined with standard infrared quantitative procedures.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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INTRODUCTION

Infrared methods have been worked-out for the quantitative analysis of polymer blends and co-polymer ratios by other investigators (3). These methods are based on the fact that the polymers will dissolve in organic solvents and can be prepared free of compounding ingredients for spectroscopic investigations.

Buna N-phenolic resin blends cannot be analyzed by conventional methods because of their physical make-up. Buna N-phenolic resin blends were found to contain phenolic resin and all of the polymer blend did not dissolve in o-dichlorobenzene, the solvent commonly employed to dissolved Vulcanized rubbers. The use of standard procedures for the quantitative analysis of the polymer blend is thus prevented.

The use of the infrared spectra of pyrolyzates (distillates) for the qualitative analysis of complex organic materials was demonstrated by Harms (1), Kruse and Wallace (2). They showed that unique and reproducible, although undoubtedly complex, pyrolysis products were obtainable. These products gave distinct and reproducible infrared spectra. This fact led to the development of a semi-quantitative method for the analysis of Buna N-phenolic resin blends through the infrared spectra of their pyrolyzates. The method is based on the pyrolysis technique combined with standard infrared quantitative procedures.

Pyrolysis products of several known blends of Buna N-phenolic resin were prepared and a working curve for the estimation of unknown blends was established. The validity of the semi-quantitative pyrolysis technique was further established by determining the percentage acrylo-nitrile in Buna N elastomers. The acrylonitrile content of Buna N elastomers can be determined by conventional methods and was only included to demonstrate the general applicability of the semi-quantitative pyrolysis method.

It is particularly noteworthy that the elastomers can be separated from carbon black and inorganic materials in the rubber, leaving a clean residue. The residue from the pyrolysis of several Buna N-phenolic resin blends, containing known amounts of non-combustible materials, was collected and weighed to determine if the non-combustible ingredients could be analyzed along with the elastomer.

Although the results were somewhat high in each sample, due to a slight charring of the elastomer, the difference between the calculated and measured values were fairly constant. The pyrolysis technique, therefore, provides a semiquantitative method of determining the amount of material together with the elastomer. Furthermore, the technique isolates the inorganic materials from rubber in a form particularly suitable for spectrographic and X-ray analysis.

Apart from the longer time required to prepare the pyrolyzates the method discussed here appears to have several advantages from a qualitative aspect. These advantages are described in Appendix I.

SECTION I

SEMI-QUANTITATIVE ANALYSIS OF BUNA N-PHENOLIC RESIN BLENDS AND CO-POLYMER RATIOS

APPARATUS:

Baird infrared Recording Spectrophotometer, Model B. Sargent Micro Furnace, Combustion Assembly, Zimmerli Gage, and a Duo-Seal Vacuum Pump. The pyrolysis was performed in a combustion assembly especially constructed for this investigation. The dimensions of the combustion assembly are probably not critical. It was designed to allow reproducible conditions of pyrolysis that is, obviously, more important for quantitative studies than for qualitative analysis. No detailed investigations were made on the effect of varied pyrolysis conditions on the composition of the pyrolyzates. An attempt was made to duplicate the initial pressure, time, and temperature conditions for the preparation of each pyrolyzate. The assembly and apparatus used to prepare the pyrolyzates are shown in Figures 1, 2 and 3.

CHEMICALS:

Chloroform, Octagon Process, Inc. USP Grade: Acetone, Eastman Kodak Product "white label" quality. Both chemicals were used directly from the bottle without further purification. Dry ice was used in a cold trap in the preparation of the pyrolyzates.

PROCEDURE:

A two gram sample of rubber was placed in the combustion tube (fig. 1a), and the combustion apparatus assembled as shown in figure 2. The combustion tube was placed in the furnace, the receiving flask (fig. 1c) covered with dry ice, and the open end of the combustion assembly connected to the vacuum pump. The other tube of the assembly was connected to a Zimmerli Gage to record the pressure during the pyrolysis. The completely assembled apparatus is shown in figure 3.

The pressure in the system was reduced to 2mm of Hg. the furnace turned on, and the sample heated to a temperature of 540 to 580°C. This required about 15 minutes when the furnace was operated at 110 volts.

The pyrolysis products which formed were present in the dry ice trap and in the receiving tube leading to it. They were washed out with a 30-70% blend of acetone and chloroform. All the washings were combined and the solvent evaporated under identical conditions for each sample. The resulting tar-like pyrolyzate was placed between rocksalt plates using a 0.05 mm. spacer and the infrared spectra recorded on a Baird Model B Spectrophotometer. The spectra of the Buna N polymers blended with 0-33% phenolic resins are shown in Figures 4 and 5. Absorption bands characteristic of a-CN linkage in cured Buna N elastomers, with known amounts of acrylonitrile, are shown in figure 6.

COMPUTATION OF DATA AND RESULTS

The method used for preparing the working curves for determining the phenolic resin content of Buna N-phenolic resin blend was that employed by Dinsmore and Smith (3). It was slightly modified by using base-line absorbance ratios. This was done to minimize errors due to the inability of reproducing sample thicknesses using demountable cells. The base line technique was used to circumvent possible errors due to the overall absorption of compounding ingredients other than those originating from the Buna N rubber and phenolic resin.

A plot was made of the percent phenolic resin versus the ratio of the baseline absorbance measured at 2.95 and 4.48 microns. The absorption band at 2.95 microns is characteristic of the hydroxyl group in the phenolic resin, while the absorption band at 4.48 microns is characteristic of the nitrile linkage in the Buna N elastomer. Since the nitrile group constitutes a rather small portion of the Buna N elastomer, a gradual decrease in the intensity of the 4.48 micron band was observed when increasing amounts of phenolic resins were blended with the rubber. Conversely the 2.95 micron band increased rapidly when greater amounts of the phenolic resin were added to the rubber. This was desirable in establishing ratios of the two bands used in plotting the calibration curves.

The absorbance of the bands at 2.95 and 4.48 microns was computed according to the formula

$$A=\text{Log}_{10}\frac{I_\circ}{I}$$

The absorbance values and the percent phenolic resin blends for the samples analyzed are shown in Table I. The plot of the absorbance ratios of these bands, computed by the formula

$$R = \frac{\text{Absorbance of the 2.95 micron band}}{\text{Absorbance of the 4.48 micron band}}$$

against the percent phenolic resin blends are presented graphically in Figures 7 and 8.

The plot in Figure 7 constitutes the calibration curve for Buna N polymers blended with 0 to 16% phenolic resins. A fairly straight line relationship was obtained for this set of data in the range shown. With higher percentages of phenolic resins in Buna N rubber a straight line relationship is no longer observed. The working curve prepared from the spectra of Buna N polymers blended with 0 to 33% phenolic resins is shown in Figure 8. A similar curve was obtained from the spectra of the same pyrolyzates recorded on a Model 21, Perkin-Elmer Spectrophotometer.

None of the calibration curves prepared for the Buna N-phenolic resin blends terminated at the origin of the coordinates, but rather at an absorbance reading of 0.3 to 0.5. The intercept indicated the presence of absorption in the 2.9 micron region in the Buna N elastomers not blended with phenolic resins, which is, indeed, observed in the spectra of Buna N rubber presented in Figure 5 A.

An absorption band at 4.48 microns, characteristic of a nitrile linkage, present in Buna N polymers containing approximately 19, 27.5 and 35 percent acrylonitrile was used to construct a working curve to determine the percentage acrylonitrile in acrylonitrile butadiene co-polymers. The absorbance values for the 4.48 micron blend computed by the base-line technique, together with the known percentage range of acrylonitrile in the Buna N elastomers used in this determination are shown in Table II. A plot of the absorbance at 4.48 microns versus acrylonitrile content of Buna N elastomers is shown in Figure 9.

DISCUSSION OF RESULT

This report demonstrates that polymer blends and co-polymers will yield unique and reproducible pyrolyzates, and that their infrared spectra reflect the composition of both the polymer blends and the co-polymer ratios. No exhaustive treatment has been given to evaluate the accuracy of the quantitative results. Observation of the scattering of points on the working curves for Buna N phenolic resin blends makes it appear that the phenolic resin content of such blends can be estimated within ± 2 percent in the 0-33 percent range. An unknown sample of Vulcanized Buna N phenolic resin blend was analyzed by this method on a Baird Infrared Spectrophotometer and a Perkin-Elmer Model 21 Spectrophotometer. The results of these analyses for the phenolic resin content differed by less than one percent. The accuracy of the method is, of course, dependent on the use of essentially identical polymers and compounding ingredients in the unknown and known blends employed in preparing the working curve.

The nominal value of acrylonitrile content of several commercial Buna N polymers was used to construct the working curve shown in Figure 9. In each case the average value for the normal range of acrylonitrile content was used. This calibration curve appears at least adequate for the identifying commercial Buna N polymers of varying nitrile content. Even with a nominal value of acrylonitrile content used as standards in plotting the working curve the acrylonitrile content in the butadiene co-polymer can be estimated within ± 3 percent in the 18 to 40 percent range. The accuracy of the method described does not compare favorably with that of existing methods for the quantitative analysis of polymers. Its advantage lies in its application to systems which cannot be handled by existing methods and in its speed and convenience in determining semiquantitative results which are often sufficient for the use of rubber compounders.

SECTION II

SEMI-QUANTITATIVE DETERMINATION OF THE NON-COMBUSTIBLE MATERIALS IN BUNA N-PHENOLIC RESIN BLENDS

A quantitative analysis of the non-combustible material was conducted on several of the phenolic blended Buna N rubber samples to establish the possibility of determining the ash content along with the elastomer. In the samples analyzed the residue remaining in the combustion tube was transferred to a container and weighed. Inasmuch as the residue of the carbon black and inorganic materials retained the shape of the original rubber sample, it was easily removed by gently tapping the combustion tube. The results of these analyses are shown in Table III.

The weight percent of the non-combustible residue found in each determination was somewhat higher than the calculated values. This was expected, inasmuch as a small amount of charring occurred in the combustion tube, particularly at the ground glass connections, during pyrolysis of the sample. Of the six Buna N-phenolic resin blends determined the deviation in the differences of the calculated and measured percentages of non-combustible ash ranged from 2.7 to 3.9%. The average value of the differences in the measured and calculated ash content was 3.2%. Although the results were somewhat high in each case, the consistency of the values permits the use of a factor so that a semiquantitative estimation of the non-combustible material in the rubber can be adequately made. Although the technique does not compare favorably with existing methods of analyzing non-combustible materials in cured and compounded elastomers quantitatively, its advantage lies in the speed and convenience of determining the residue simultaneously with polymer blends or co-polymer ratios.

SECTION III

CONCLUSIONS

A semiquantitative method of determining polymeric blends and co-polymer ratios in elastomers by the infrared spectra of their pyrolyzates has been established. The applicability of the technique was established through the analysis of blends of phenolic resins in Buna N rubber, and by determining the percentage acrylonitrile in butadiene acrylonitrile co-polymers.

Although no exhaustive study was made to evaluate the accuracy of the quantitative results, the scattering of points on the working curve for Buna N-phenolic resin blends indicates that the phenolic resin content can be estimated within ±2 percent within the 0-33 percent range investigated. The calibration curve for the determination of acrylonitrile in butadiene co-polymers appears at least adequate for the differentiation of commercial Buna N co-polymers of varying nitrile content.

A semiquantitative method of determining the non-combustible materials in Buna N rubber simultaneously with the phenolic blends and co-polymer ratios was also perfected. By using a factor the total non-combustible material can be estimated within ±5 %.

Conducting the pyrolysis under reduced pressure and with controlled temperatures gives a more reproducible pyrolyzate, with less charring than those prepared at atmospheric conditions using a Bunsen burner. The technique used here partially separates the phenolic resin from the Buna N rubber permitting a more effective identification of the individual constituents in the elastomer. The technique isolates the inorganic materials from rubber in a form particularly suitable for spectrographic and X-ray analysis.

SECTION IV

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2. Kruse, P. F., and Wallace, W. B., Identification of Polymeric Materials, Anal. Chem. 25 , 1156 (1953).

3. Dinsmore, H. L., and Smith, D. C. The Analysis of Natural and Synthetic Rubber by Infrared Spectroscopy, Report No. P-2861, August 1946, Naval Research Laboratory, Washington, D. C.

4. Heigl, J. J., Bell, M. J., and White, J. U., Anal. Chem., 19, 293 (1947).

APPENDIX I

Advantages of Preparing Pyrolysis Products Under Controlled Conditions For Qualitative Analysis

The technique of preparing pyrolyzates under controlled conditions is important in the qualitative analysis of commercial mixtures and polymer blends, because the organic materials, are removed from the non-combustible residue, and in many instances, partially separated into individual constituents. The technique; therefore, allows the identification of the organic constituents present in the mixture. Pyrolyzates of Buna N-phenolic resin blends collecting in the dry ice trap were found to be richer in phenolic resin content than those collecting in other regions of the combustion assembly, making it possible to identify both the polymer blend and the base elastomer. Other commercial mixtures such as lacquers, paints, adhesives, etc., containing, in addition to carbon black and inorganic fillers, a variety of organic constituents might be sufficiently separated to allow their identification in one operation. Under conditions of reduced pressure and lower temperature a more reproducible pyrolyzate with less cracking or breaking down of the polymers into lower molecular weight components appears possible. Although more time is required to prepare the pyrolyzates under controlled conditions the partial separation of the organic materials with less charring makes this technique attractive from a qualitative aspect.

Table I

Absorbance Ratios and Percentages of Phenolic Resin Blends in Buna N Rubber

Sample No.	%Phenolic Resin	Absorbance of 2.95 Band	Absorbance of 4.48 Band	Absorbance Ratio	Calibration Curve
1	0%	0.134	0.564	0.238	Fig. 8
2	0	0.179	0.556	0.322	"
3	0	0.324	1.006	0.322	"
4	5.5	0.198	0.301	0.658	"
5	9.1	0.238	0.260	0.915	"
6	16.7	0.359	0.250	1.440	"
7	0%	0.127	0.263	0.465	Fig. 9
8	0%	0.105	0.249	0.422	"
9	5.5	0.228	0.396	0.580	"
10	5.5	0.232	0.377	0.615	"
11	9.1	0.163	0.230	0.710	"
12	9.1	0.158	0.224	0.706	"
13	16.7	0.373	0.344	1.08	"
14	16.7	0.380	0.350	1.08	"
15	33.3	0.532	0.240	2.22	"
16	33.3%	0.544	0.232	2.34	"
X		0.308	0.168	1.84	"
X		0.321	0.176	1.83	"

Table II

Absorbance Ratios and Percentages of the Acrylonitrile Constituent in Butadiene-Acrylonitrile Co-polymers

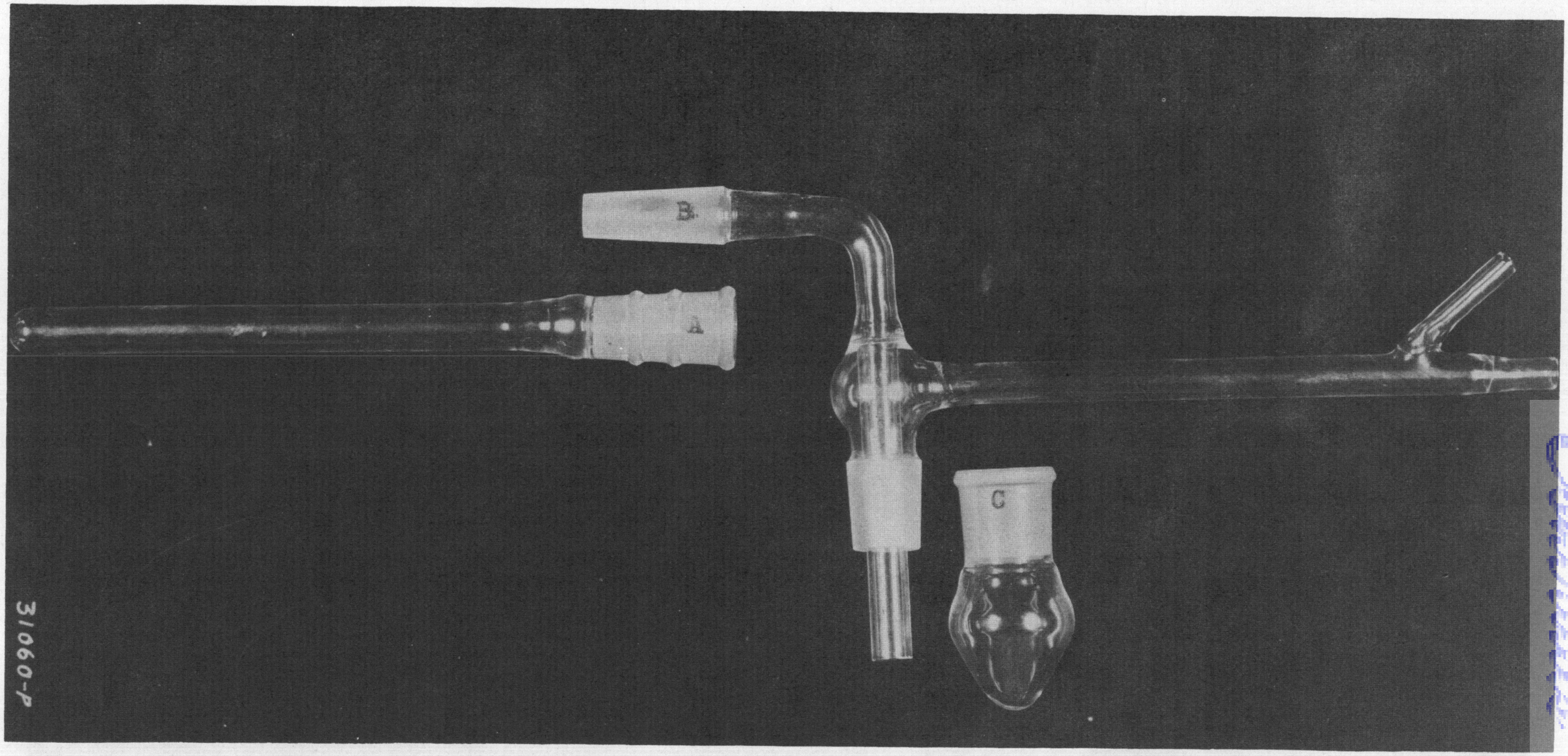
Sample No.	Type of Elastomer	Range of Acrylonitrile Given	Average Percent of Acrylonitrile	Absorbance of 4.48 Micron Band
1	Paracril 18	18-20%	19%	0.259
2	Paracril 26	26-29%	27.5%	0.537
3	Paracril 35	35%	35%	0.870

Table III

Results of the Analysis of the Residue in Buna N-Phenolic Resin Blends

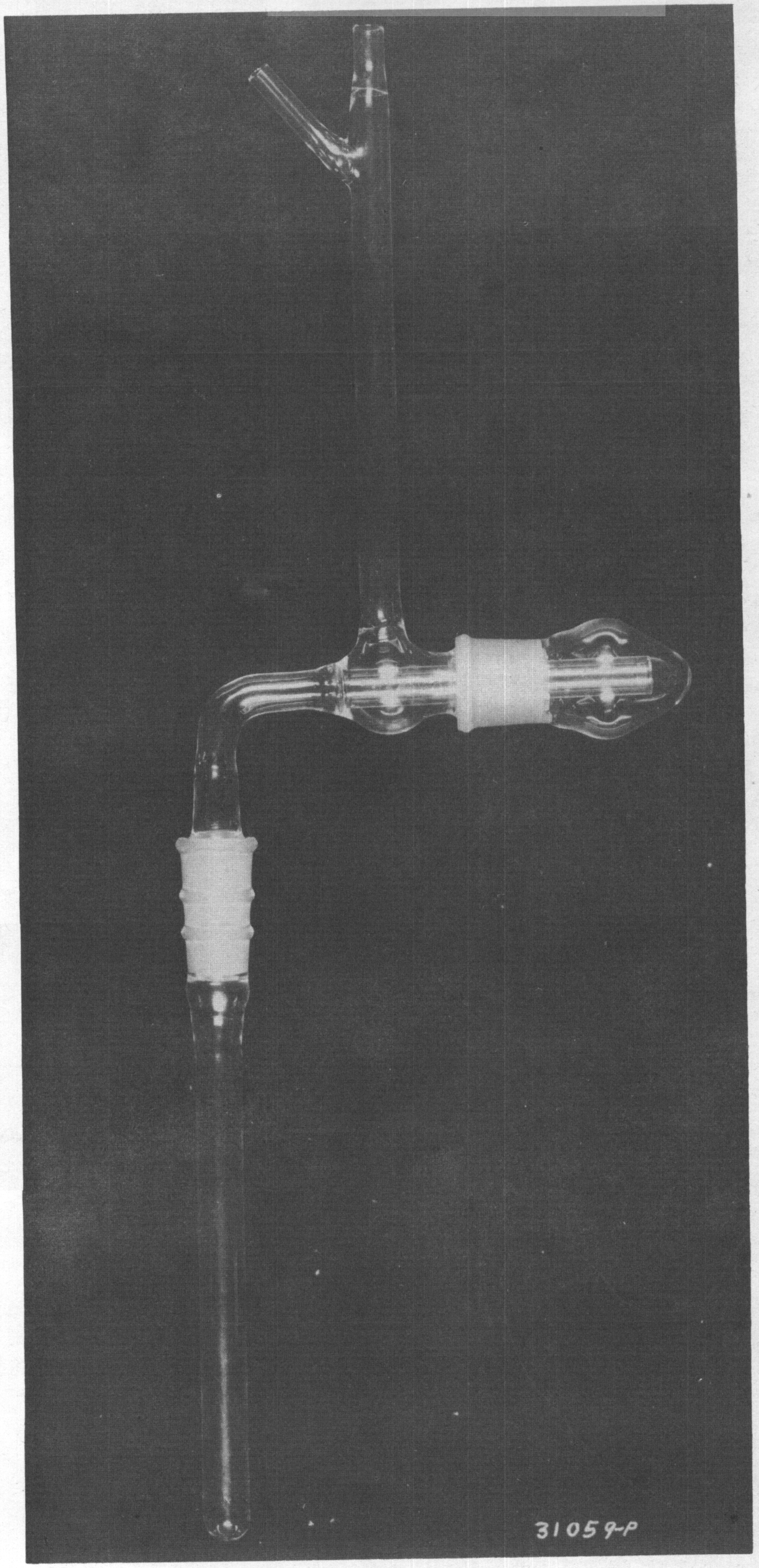
Sample No.	Calculated Wt % Residue	Wt % Residue Found	Difference +
1. -87	40.9%	43.9%	3.0%
2. -88	40.0%	43.6%	3.6%
3. -89	38.1%	41.0%	2.9%
4. -89	"	40.8%	2.7%
5. -XL	33.8%	37.1%	3.3%
6. -XL	"	37.7	3.9%
Unknown	(38.6)	41.8%	

$$\%\ \text{Residue} = \frac{\text{Wt of Residue X 100}}{\text{Wt of Rubber Sample}} - 3.2\%$$



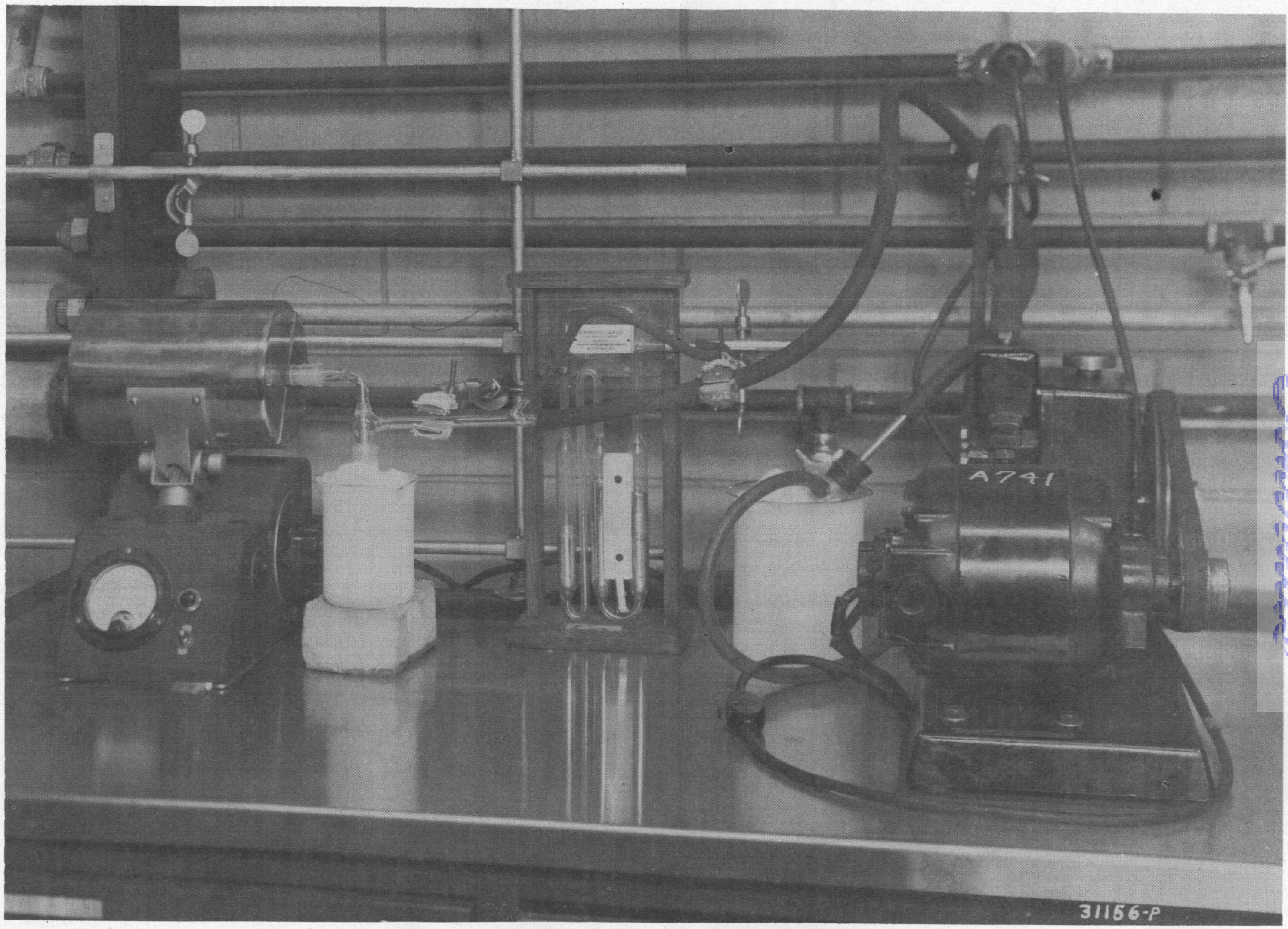
Combustion Apparatus - Dismantled
- A. Combustion tube
- B. Combustion Assembly
- C. Receiving flash

Figure 1



Assembled Combustion Apparatus

Figure 2



Combustion Apparatus Used to Prepare Pyrolyzates

Figure 3

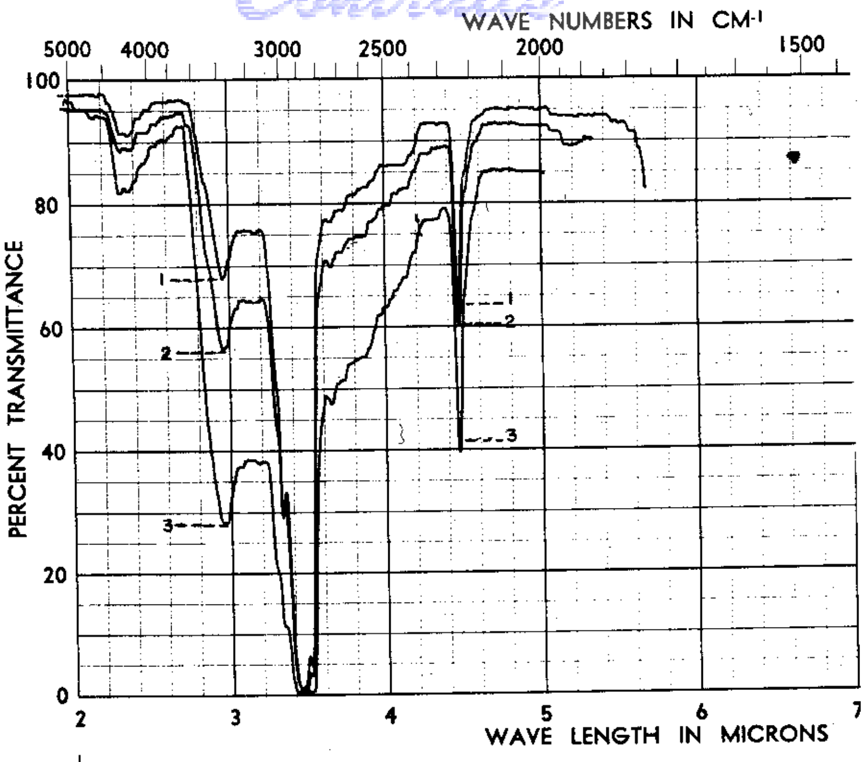


FIG. 4a. INFRARED SPECTRA OF PYROLYZATES OF BUNA-N BLENDED WITH 5.5, 9.1, and 16.7 % PHENOLIC RESIN.

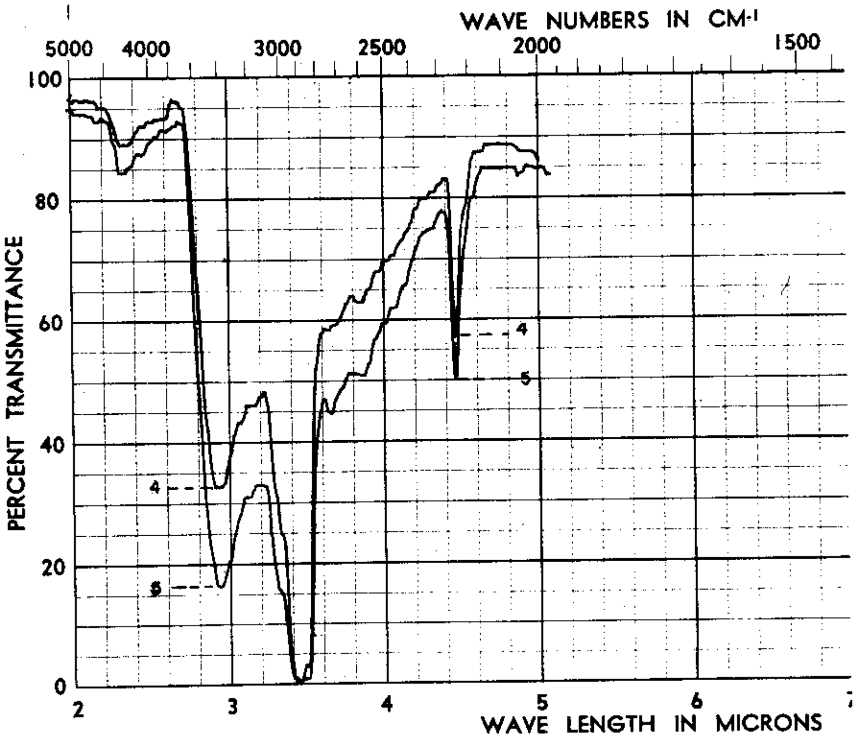


FIG. 4b. INFRARED SPECTRA OF PYROLYZATES OF BUNA-N BLENDED WITH X and 33.3 % PHENOLIC RESIN.

Figure 4

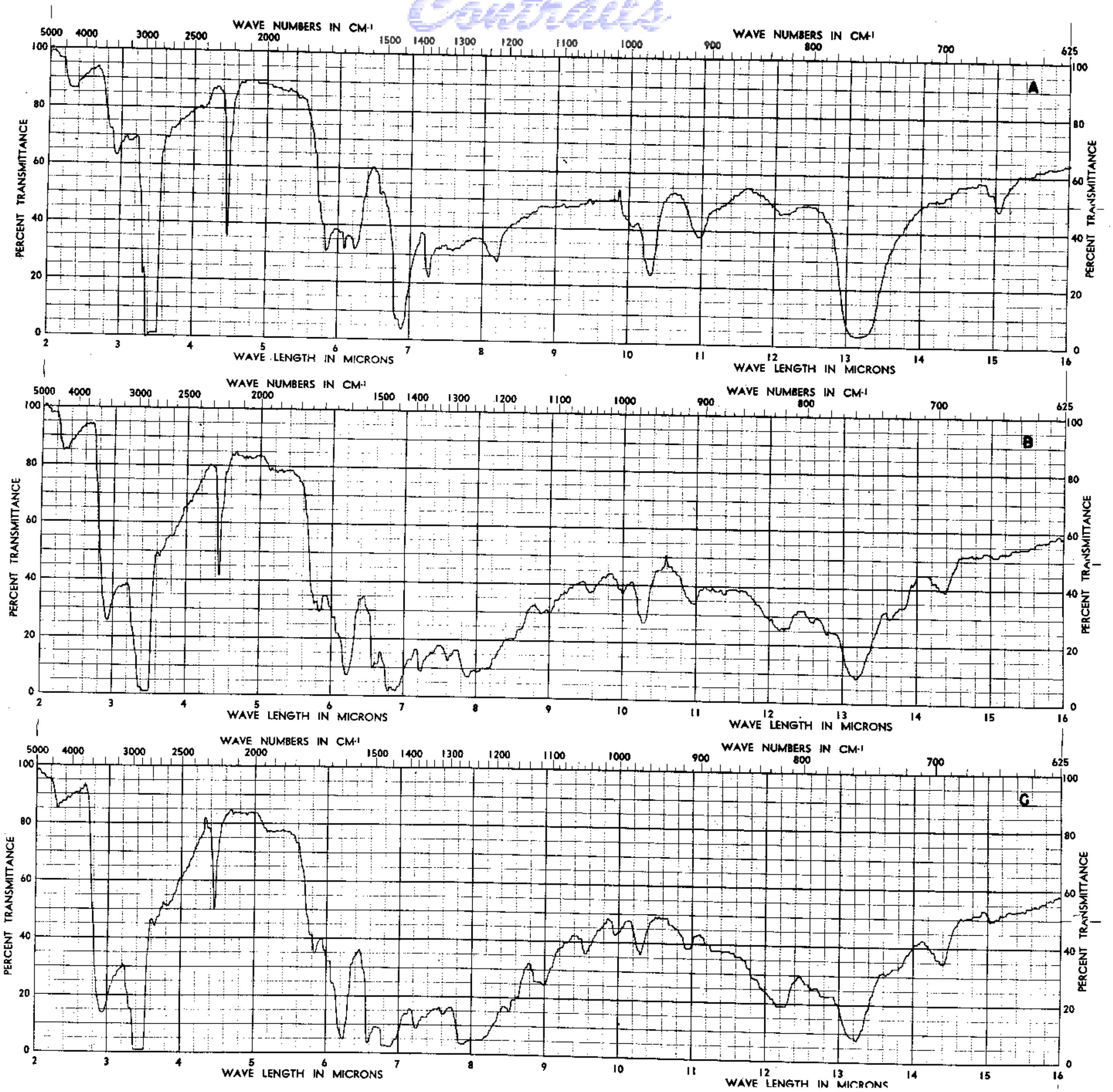


Figure 5 Buna N-Phenolic Resin Blends

A. Pyrolyzate of Buna N Rubber

B. Pyrolyzate of Buna N Rubber Blended with 16.7% Phenolic Resins

C. Pyrolyzate of Buna N Rubber Blended with 33.3% Phenolic Resins

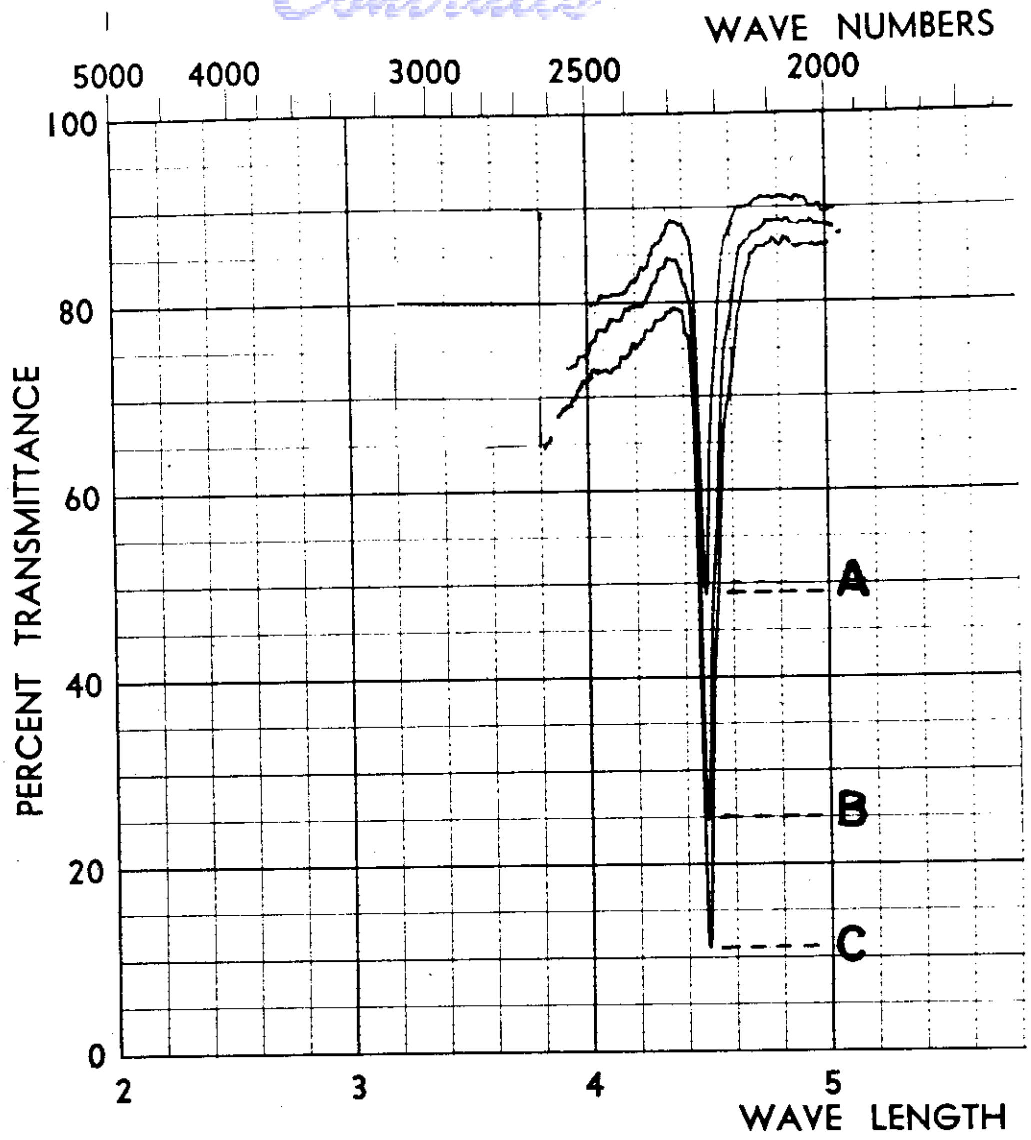
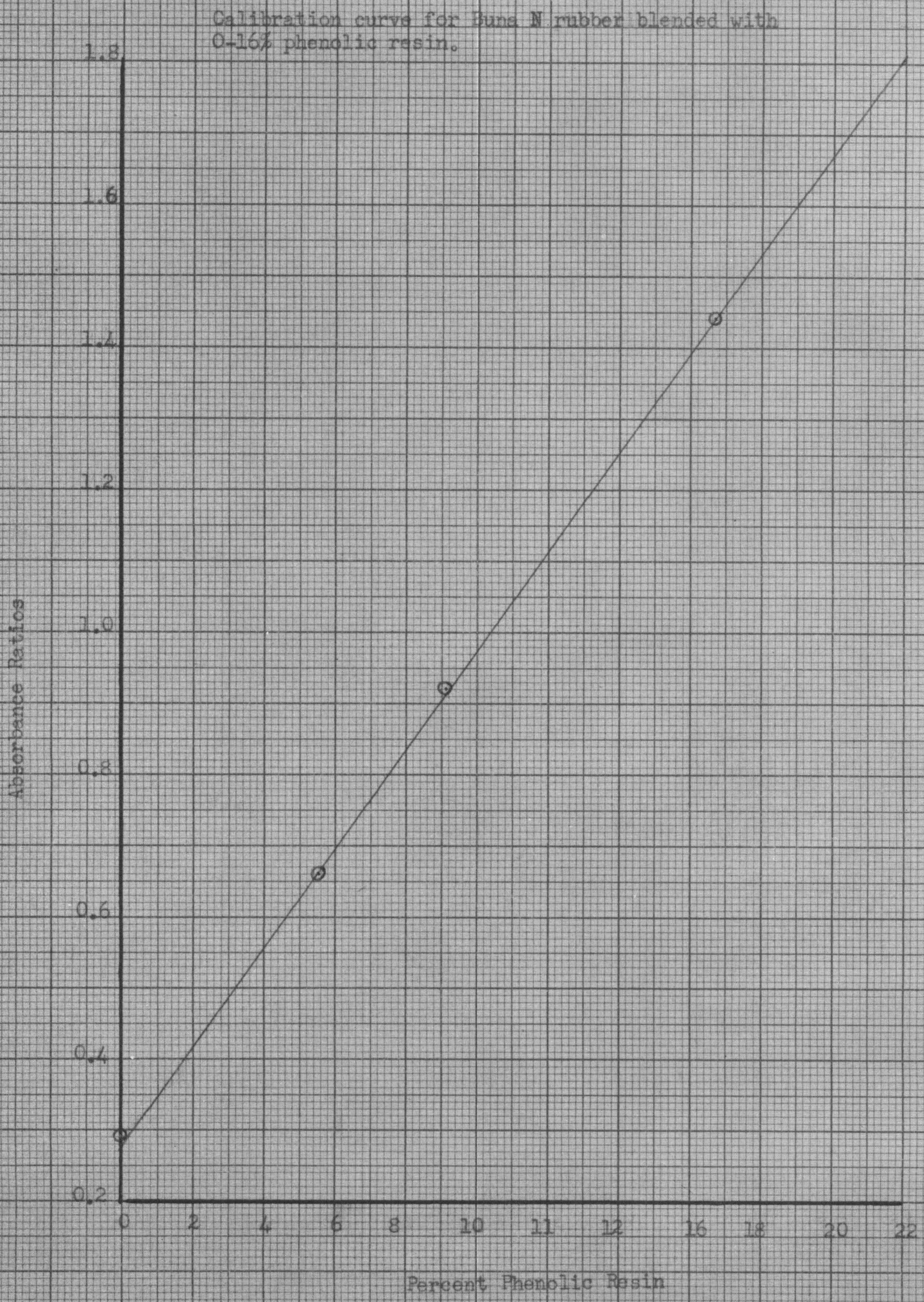


Figure 6 Pyrolyzate of Buna N rubber containing:
A - 19%; B-27.5%; C-35% Acrylonitrile.



Calibration curve for Buna N rubber blended with 0-16% phenolic resin.

Figure 7

Calibration Curve for Buna N Rubber blended with 0 to 33% phenolic resin.

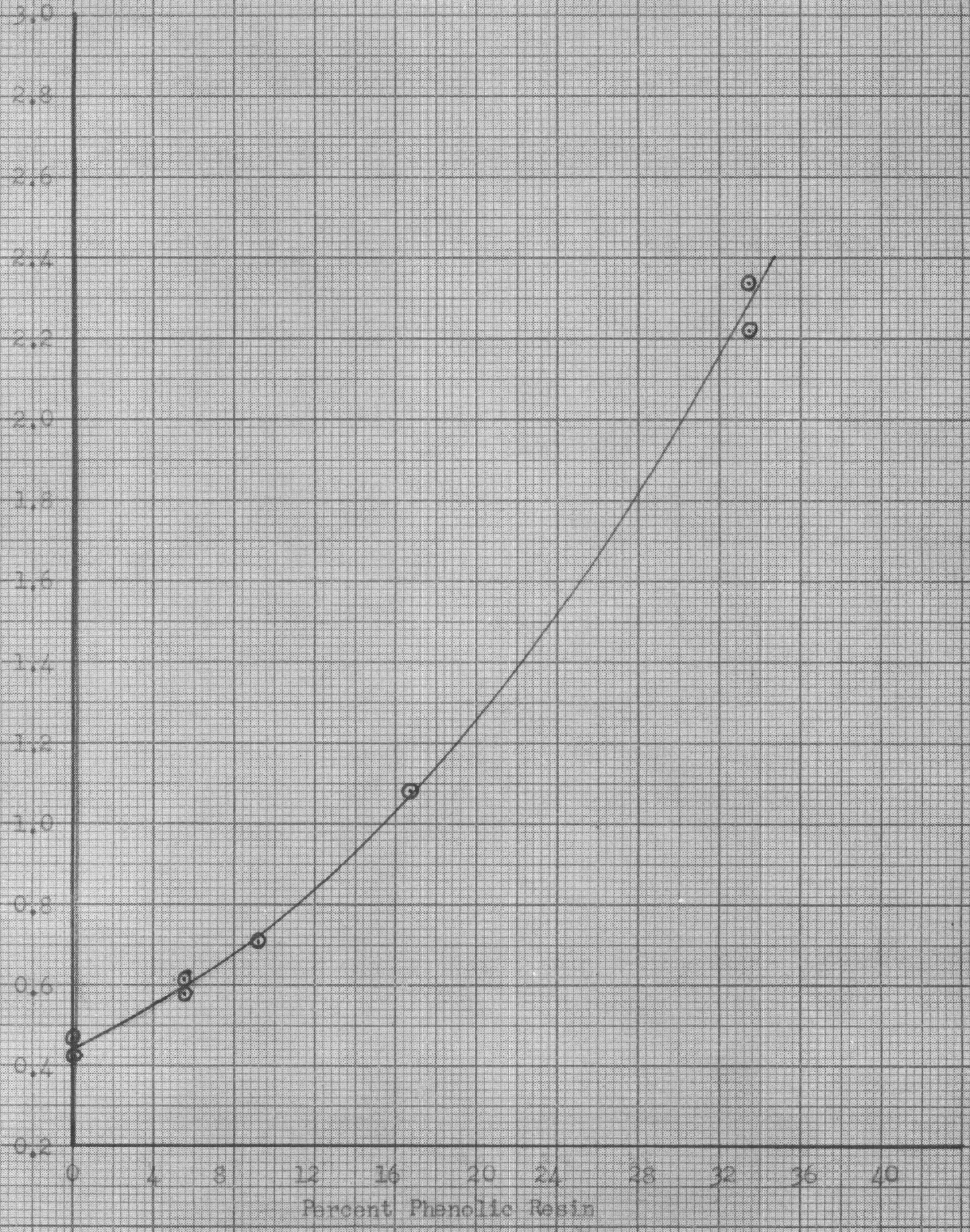


FIGURE 8.

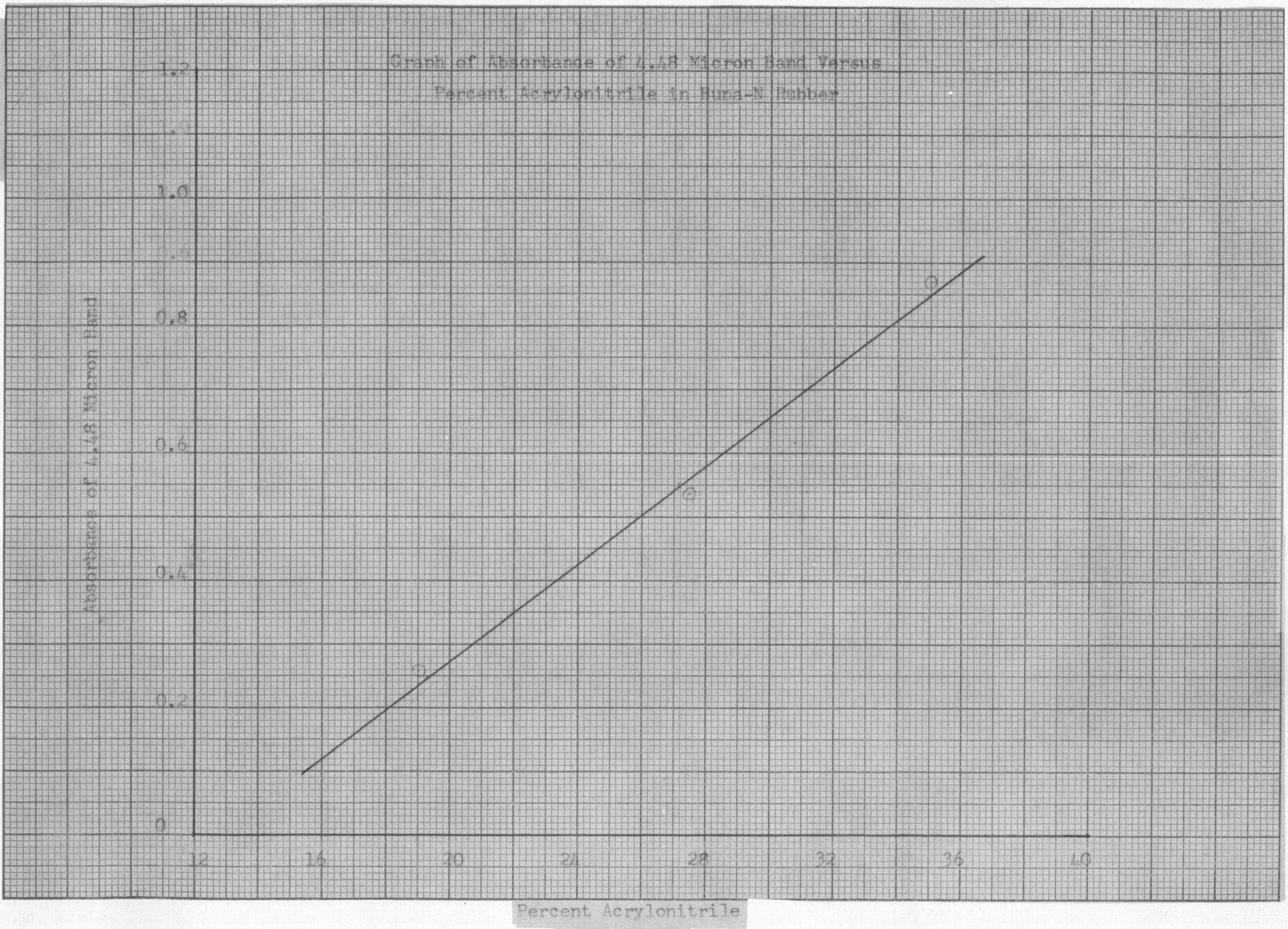

Graph of Absorbance of 4.48 Micron Band Versus
Percent Acrylonitrile in Buna-N Rubber
Absorbance of 4.48 Micron Band
1.2
1.0
0.8
0.6
0.4
0.2
0
12
16
20
24
28
32
36
40
Percent Acrylonitrile

Figure 9.