Navy Department - Office of Naval Research

NAVAL RESEARCH LABORATORY
Washington, D.C.

* * *

Chemistry Division - Chemical Spectroscopy Section

20 August 1946

FR-2861

THE ANALYSIS OF NATURAL AND SYNTHETIC RUBBER BY INFRARED SPECTROSCOPY

By

H.L. Dinsmore and D.C. Smith

- Report No. P-2861-

Distribution Unlimited

Approved for Public Release

* * *

Approved by:

D.C. Smith, Head, Chemical Spectroscopy Section
Peter King, Head, High Polymers Section

Dr. P. Borgstrom
Superintendent, Chemistry Division

Commodore H. A. Schade, USN
Director, Naval Research Laboratory

Preliminary pages . . . a - f
Numbered pages 55
Appendices. . . . . A,B,C
Plates. 50
Tables 19
Bibliography 54-55
Distribution . . . . . g

NRL Problem P-97

ABSTRACT

This report describes an investigation of the applicability of infrared spectroscopic methods for determination of the elastomer composition of industrial rubber products. The investigation has comprised several distinct phases, which can be divided roughly as: (1) development and evaluation of generally feasible techniques for obtaining a valid spectrum of the elastomer content of any rubber specimen, and (2) development and evaluation of detailed analytical procedures for certain representative cases. The groundwork phase has been more extensive than required by the special applications subsequently considered, in order that other applications in general would not be limited by sample preparation problems; and in the second phase, the emphasis also has been to apply methods which would be equally useful in any of the numerous analogous analytical applications. The special cases here considered are: (a) the qualitative analysis of elastomer mixtures, (b) the quantitative analysis of Natural GR-S mixtures, and (c) determination of the nitrile content of Buan-N copolymers. Dependable routine procedures have been presented for these determinations and give in practice an accuracy of ±1%. These methods can be extended to analogous problems with a minimum of alteration, and this same order of accuracy can be expected in general.

TABLE OF CONTENTS

Text	Page No.
ABSTRACT	b
GENERAL INTRODUCTION TO REPORT	1
A. Authorization	1
B. Statement of Problem	1
C. Known Facts Bearing on the Problem	2
D. Considerations in the Present Investigation	4
E. Evaluation of Previous Work	5
F. Method of Attack.	6
PART I - THE INFRARED SPECTRA OF NATURAL AND SYNTHETIC RUBBER FROM PURE GUM SAMPLES	7
INTRODUCTION	7
A. Statement of Objective	7
B. Previous Related Work	7
C. Special Considerations.	8
D. Scope and Method of Investigation	8
EXPERIMENTAL	8
A. Description of Samples	8
B. Details of Sample Preparation Methods	9
C. Details of Spectroscopic Investigation	11
DISCUSSION OF RESULTS	13
A. Spectral Characteristics and Reproducibility	13
B. Effects of Impurities	14
C. Suitability of Sample Preparation Method.	14
D. Spectrometer Requirements	15
SUMMARY AND CONCLUSIONS	15
PART II - INFRARED SPECTRA OF NATURAL AND SYNTHETIC RUBBER FROM COMPOUNDED AND CURED SAMPLES	17
INTRODUCTION	17
A. Statement of Objective	17
B. Previous Related Work	17
C. Special Considerations.	18
D. Scope and Method of Investigation	19

PLATES

	NO.
Spectra of Vulcanized GR-I	26 to 28
Spectrum of Vulcanized Neoprene-GN	29
Spectra of Vulcanized Neoprene-E	30 and 31
Spectrum of Vulcanized Neoprene-ILS	32
Spectra of Vulcanized GR-S	33 and 34
Spectra of Vulcanized Chemigum-N-1	35 to 37
Spectrum of Vulcanized Hycar-OR-15	38
Spectrum of Vulcanized Hycar-OR-25	39
Spectrum of Vulcanized Perbunan-35	40
Spectrum of Vulcanized Butaprene-NF	41
Spectra of Vulcanized Thiokol-FA	42 and 43
Spectrum of Vulcanized Thiokol-ST	44
Spectrum of Vulcanized Thiokol-RD	45
Spectra of Pure Elastomers	46
Spectrum of o-Dichlorobenzene	47
Working Curves for Natural/GR-S Analysis	48
Additional Working Curves for GR-S Determination	49
Working Curves for Acrylonitrile Determination	50

15. The only generally feasible means of spectroscopic examination of rubber specimens therefore must involve separation of the rubber content from compounding ingredients. Aside from the necessary elimination of opaque materials, isolation of the rubber hydrocarbon from all foreign ingredients favors the validity of the final results by virtue of their independence of the variable non-rubber composition of the total specimen. Study of the isolated rubber content thus affords the greatest possibilities for development of dependable and widely useful analytical procedures. The potential reliability of the method here is essentially dependent upon the general adequacy of a given procedure for accomplishing separation of the total rubber content of specimens of completely unspecified composition. This is obviously requisite to determination or study of all elastomers that may be present in the specimen.

16. A basic problem involved in the present development of methods of spectroscopic analysis of rubber, therefore, was seen to be the development of satisfactory means of sample preparation by which the rubber content of any specimen might be isolated for spectroscopic study. Separation by a three-step process appeared most promising: (1) Extraction of all organic additives and impurities by a solvent not dissolving the rubber polymer; (2) complete solution of the extracted rubber content in a solvent inert to the remaining filler; (3) separation of filler and opaque solids from the solution of rubber hydrocarbon. The isolated rubber hydrocarbon could then be studied spectroscopically as a transparent film, following evaporation of the solvent.

17. These operations require that no step involve solvents which could alter the rubber polymer chemically by reaction and that no materials be introduced which could not be removed subsequently. It was believed that extraction of all organic impurities would present no problem, but that inert and complete physical solution of the rubber content might prove difficult in all but a few cases, since solvent resistance is characteristic of most cured elastomers. A second serious problem was believed to be the removal of dispersed particles of filler or solid pigment from the rubber hydrocarbon solution. Because of minute particle size, carbon blacks in particular remain dispersed as permanent colloidal suspensions. It was necessary that generally feasible procedures be found first for these operations in order that schemes of analysis might subsequently be developed based only upon the characteristic spectral differences of the different elastomers.

E. Evaluation of Previous Work

18. At the beginning of the present investigation a survey of related infrared work showed that all previously reported studies were of little use to the present problem. The most complete investigation having a similar objective was that of Barnes and co-workers (1)(2), in which the spectra of several polymers were obtained and a method was devloped for the analysis of tires and tubes composed of Buna-S and natural blends. The analytical method, as presented, yielded satisfactory results for its authors' purpose and indicated the applicability of infrared methods. The accuracy of the results did not appear nearly as good as might be expected, however, and sufficient data to allow complete evaluation of the method were not presented. Furthermore, except for the two polymers involved in the example analysis, the spectra presented were obtained only from uncured samples, and the general applicability of the analytical method for vulcanizates of other elastomers was not investigated.

19. Other numerous but less extensive investigations (4)(15)(16)(17) have not been concerned with analytical applications and, except for natural rubber, have been confined to uncured polymers. These investigations have not contributed at all to the problem of sample preparation, and, in general, it is impossible to evaluate the validity of the spectra given because of questionable sample purity, measurement technique, or instrumental accuracy.

20. It was believed, therefore, that an investigation of much wider scope and of much greater thoroughness and detail was required. It was also believed that while the basic procedures of some previous work might prove satisfactory, the present investigation should be made entirely independent and should be of extent an character required to make a conclusive evaluation of the applicability of infrared methods. In addition, it was intended that specific analyses which might be developed should be presented in sufficient detail to enable their adoption in routine analytical work without further developmental or research work. While it was realized that the number of possibly useful analyses could not be exploited here, development of a generally feasible method of spectroscopic investigation was considered a necessary objective, and study of a sufficiently representative variety of applications was desired to insure minimization of work required to make further specific extensions.

F. Method of Attack

21. Because of the extensive nature of the present investigation, comprising both a necessary groundwork for sample preparation on the one hand and development and evaluation of various analytical schemes on the other, it was considered best that the experimental work be divided into three parts in order to separate roughly some of the many variables involved.

22. Part I concerns the determination of the true rubber hydrocarbon spectrum for each elastomer by using pure gum samples under conditions involving minimum possibility of structural change through sample preparation. Such reference spectra are required to determine the theoretical possibility of spectroscopic identification and analysis of the various elastomers. In addition, they are required as standards for comparison in subsequent parts of the investigation.

23. Part II concerns the development of reliable sample preparation techniques and their application to the determination of the rubber hydrocarbon spectrum of each elastomer from compounded and cured specimens representative of industrial rubber products. This is required to evaluate the applicability of infrared analysis to practical methods of characterization for commercial products.

24. Part III concerns the application of the results of Parts I and II to the detailed development of methods of analysis of two or more elastomers compounded and cured in a single sample. This phase of the problem involves determination of the optimum procedure and accuracy of quantitative analysis in a number of specific cases of practical importance.

25. Because of the interdependence of the various phases of the problem the separate parts, as described above, were carried out consecutively and independently. For the reader's convenience the results of each part are presented separately. Although the experimental details have been fully presented, repetition has been avoided as much as possible by using some cross-references. Except for these details and a full understanding of the considerations involved, the separate parts of the report may be read independently.

TABLE I (Conti)

Chemical Class	Representative Specimen
(b) Isobutylene-Isoprene Copolymer	(3) GR-I
(c) Chloroprene Polymers	(4) Neoprene-GN
	(5) Neoprene-ILS
(d) Butadiene-Styrene Copolymer	(6) GR-S
(e) Butadiene-Acrylonitrile Copolymers	(7) Chemigum-N-1
	(8) Hycar-OR-15
	(9) Hycar-OR-25
	(10) Perbunan-35
	(11) Butaprene-NF
(f) Ethylene Polysulfide Polymers	(12) Thiokol-FA
(g) Mixed Copolymer of Butadiene, Acrylonitrile, and di-isopropylidene ketone.	(13) Thiokol-RD

All samples were obtained from the NRL High Polymer Section. Although no information is available as to exact composition of these specimens, the minimum purity specifications of each are 97% rubber hydrogarbon. The remaining 3% is chiefly antioxidant.

B. Details of Sample Preparation Methods

(1) Extraction of Impurities

32. Extraction of the specimen by ethyl alcohol was employed for removal of antioxidant and other minor impurities. Choice of extraction solvent was greatly limited by the tendency of nearly all uncured elastomers to dissolve or swell (forming gels) in such solvents as chloroform, benzene, or acetone. Ethyl alcohol (commercial grade, 95%) achieved adequate purification without significant solution or swelling of any elastomers. The standard A.S.T.M. Rubber Extraction Assembly was used (8). This assembly, shown in Plate I, consists of 400 ml. extraction flask (A.S.T.M.), siphon cup, and water-cooled metal-coil codenser. Heat was furnished by a hot-plate.

33. Approximately two grams of sample were used for each preparation. In order to facilitate extraction and solution, the sample was cut (with scissors) into thin strips (approx. 1 mm thick). Because of the tackiness of gum rubber these were placed on a filter paper in parallel rows sufficiently separated so that when the paper was rolled the strips of rubber were not in contact but were spearated by a layer of paper. The sample thus prepared was placed in the siphon cup and was extracted continuously for approximately 24 hours with two or three 80 ml. portions of (ethyl) alcohol. The progress of extraction was followed by noting the coloration of the successive portions of solvent. Extracted material was often indicated also by precipitation when the solvent was cooled to room temperature. As spectra were accumulated the data showed that extraction for more than twenty-four hours was unnecessary.

(2) Solution of Polymer

34. The major problem in Part I was that of accomplishing solution of the various gum elastomers at room temperature, the greatest difficulties being

encountered with Neoprenes and Buna-N's. The results of examination of a number of solvents are presented briefly in Table II and more fully in Table IV. The conclusions reached will be considered below. The source and quality of all solvents investigated in Part I are tabulated in Table III. No purification of any of these solvents except p-cymene was considered necessary. Despite distillation before use, p-cymene was subject to significant oxidation, with the result that non-volatile impurities were deposited in the rubber. This solvent, however, was used only with tube reclaim (because of the requirement here of a higher-boiling solvent). A more detailed description of the troubles encountered will be given later.

35. Ethylene dichloride proved to be a satisfactory solvent for every class of gum rubber studied. Methyl ethyl ketone was particularly effective for Buna-N types. Natural rubber, Thiokol-FA, Butyl Rubber (GR-I), and Buna-S (GR-S) dissolved readily in any of several solvents (see Table II). The two Neoprene types dissolved adequately only in ethylene dichloride. 40 to 60 ml. of solvent per gram of rubber were generally sufficient for complete solution. The solutions obtained were transparent and exhibited light color characteristic of the various elastomers (see Table IV).

36. Specimens of the more soluble elastomers - Natural rubber, Butyl, Buna-S, and Thiokol-FA - were completely dissolved in satisfactory solvents at room temperature simply by 6 to 8 hours' mechanical shaking. Satisfactory solution of Buna-N's, Neoprenes, and Thiokol-ID, however, was not achieved in this manner. Because of the tendency of these elastomers (particularly Buna-N's) to form a gel structure with the solvent, excessive quantities of solvent and very long shaking were required before appreciable homogeneous solution was obtained, and even then complete solution of the specimen was seldom achieved. Separation of the thin solution from the gelled residue generally was possible.

37. Solution was accomplished far more rapidly and effectively in a Waring Blendor. In this operation, rapidly revolving blades cut the rubber into minute bits, simultaneiously stirring these vigorously with the solvent. First the specimen was placed in the solvent and allowed to soften and swell for a minimum of two hours. The mixture was then blenderized for 20 minutes, or until the solution was homogeneous and clear. Since considerable heat was generated during blenderization, continuous operation was limited to 15 minutes in order to keep the solvent below the boiling point. In this manner homogeneous solution of all samples studied was rapidly obtained in a minimum quantity of ethylene dichloride or other satisfactory solvents. Blenderization was particularly effective in reducing gels to homogeneous and surprisingly thin solutions without use of additional solvent. [The Waring Blendor, Central Scientific #17233, with #17244 (small size) glass jar is shown in Plate 2.] In order to avoid contamination of sample and loss of solvent the rubber gaskets of the jar were replaced by gaskets of felt between outer ones of lead and the screw cap of the jar was fitted with a lead gasket in place of the paraffin-coated cardboard.

38. Tube reclaim was treated as an exception to the other gum samples since it contained a mineral filler and also was considerably less soluble. It was extracted by a 32/68 blend of acetone/chloroform, and was dissolved by refluxing with a 20/80 blend of xylene/p-cymene, a procedure recommended by Barnes (2). The red iron oxide filler was removed by centrifuging. A thorough investigation of preparation methods for compounded specimens was not considered at this point.

(3) Removal of Excess Solvent

39. Vacuum distillation was employed for concentrating the polymer solutions for film spreading. Because of the tacky, viscous character of gum rubber cements and corresponding difficulty of sample removal from a flask of standard design, a specially designed, jointed flask (shown in Plate 3) was employed. The wide mouth of the flask permitted removal of nearly all the sample with a spatula as well as thorough cleaning of the flask with a bottle brush. To avoid contamination no grease was used to seal the joint, inasmuch as the volatile solvents employed distilled rapidly at 50°C with only moderate vacuum. Later it was found that solvent evaporation could be accomplished even more conveniently by placing the solutions in shallow dishes on a hot water bathprovided with a strong air draft (e.g., an A.S.T.M. gum bath). This method allowed simultaneous evaporation of several samples. Frequent stirring (by hand) adequately eliminated gel formation due to localized evaporation at the surface. Solvent removal was stopped when the concentrate was sufficiently syrupy to hold its shape when spread as a film. In the case of elastomers which tended to form gels easily (particularly Buna-N's) concentration had to be stopped short of this point, since films of gelled samples were neither homogeneous nor clear. From such insufficiently concentrated solutions films of suitable thickness were obtained by repeated spreading of films on top of each other.

(4) Film Preparation

40. Films of uniform thickness were readily obtained by evaporation of the remaining solvent from a layer of the concentrate spread between parallel spacers placed at opposite edges of a (flat) rocksalt plate. The syrupy sample was spread as a flat, even layer by a razor blade drawn along the spacers. A second razor blade was used to hold the spacers in place. Diagrams of these operations are given in Plate 4. All films studied were spread on rocksalt or potassium bromide plates in this manner. Films of every elastomer except Thiokol-FA were solid after final solvent evaporation. Films of the latter remained a very viscous liquid but satisfactorily held their shape. Determination of the appropriate film thickness for useful spectral measurements was made by trial preparation of films of several thicknesses and subsequent spectroscopic inspection. The recommendation by Barnes that the absorption of the strong band between 6.8 and 7.0 common to all rubber spectra be between 80 and 90% served as a useful check measurement, inasmuch as this band proved to be one of the strongest absorptions in all the rubber spectra. In the present work, use of three sets of spacers - 0.05, 0.10 and 0.20 mm - enabled suitable films to be obtained in all cases.

C. Details of Spectroscopic Investigation

(1) Design and Operation of Spectrographic Equipment

41. All spectroscopic work was done using a large recording spectrometer of high resolving power, built at the University of Oklahoma. The monochromator consists of interchangeable 6" sixty-degree NaCl and KBr prisms in Littrow-Wadsworth mounting. A Nernst Glower is used as the source of radiation and a thermocouple as the receiver. The arrangement of source, potics and receiver are shown in Plate 5. The thermocouple output is amplified by a D.C. amplifier of the type described in reference (21) and in turn operates a Leeds & Northrup

"Speedomax" recorder, which records the energy spectrum as a continuous ink trace on a decimally ruled chart. Angular prism position is registered in arbitrary numbers by a veeder counter and can readily be converted to wavelength (in microns) by calibration data. Chart and prism movement are exactly synchronized, the chart being driven by the prism drive motor through selsyn coupling. The two prisms afford high resolving power over a range from 2 to 23 mu. The resolution obtainable between 2 and 14 mu with the rocksalt prism is indicated by the spectra of ammonia, stibine, and HCl given in Plate 6.

42. In the operation of this spectrometer each wavelength region must be scanned successively (under identical conditions) with and without the sample in the radiation path in order that relative absorption may be measured, e.g., as percentage transmission. Spectra as recorded consisted therefore of a pair of traces measuring the energy transmitted by the sample and by a "blank", plus several measured points indicating zero energy. From these a percentage transmission spectrum was obtained by measuring corresponding ordinates point-by-point over the veeder number range. After conversion of veeder numbers to wavelength, spectra were replotted to a linear wavelength scale as percentage transmission vs. wavelength. Standard ruled charts (of the National Bureau of Standards) were used for final expression of the data. Under normal operating conditions the accuracy of wavelength measurement of the spectrometer (and of the calibration data) is considered better than 0.005 mu over the 2 to 15 mu range, and a reproducibility of intensity measurement within 1/100 full scale is possible.

(2) Data Obtained

43. A complete detailed summary of all sample preparations and allied spectroscopic studies made in Part I is given in Table IV. Since all pertinent features are adequately described there and are tabulated conviently for evaluation, only the scope and general character of the data obtained are considered at this point.

44. Satisfactory spectra were obtained of every elastomer studied in Part I (para. 31). Complete spectra from 2 to 14 mu were obtained with NaCl prism for all samples satisfactorily prepared. Spectra from 14 to 23 mu were obtained with KBr prism for only Natural Rubber and Neoprene. As no appreciably strong absorption was found beyond 14 mu and as the spectra from 2 to 14 mu were sufficient for characterization, no further work was done beyond 14 mu.

45. Thirty sample preparations were made and nearly forty spectra were obtained. Aside from ten preparations which were unsatisfactory as a result of incomplete solution or complete gelation of the sample or as a result of impurities introduced in the p-cymene preparations, twenty preparations were entirely suitable and afforded adequate study of the thirteen elastomers. For nearly all preparations duplicate films and spectra were obtained in order to determine the reproducibility of film spreading and actual spectral measurement. In some cases duplicate sample preparations and spectra were made in order to determine the reproducibility of the over-all sample preparation and measurement method. In other cases, variations in the sample preparation were made, for example, in the solvent or solution technique employed, in order to determine the validity of the final spectrum, i.e., the influence, if any, of the specific preparation method employed on the spectral features obtained.

46. All spectra obtained of each elastomer were checked for reproducibility by direct comparison of the recorder records. This was done without sacrifice of accuracy because of the close similarity of the records, and the reproducibility of operating conditions. For close comparison of the different elastomers, one representative spectrum of each of the thirteen samples was replotted on standard charts. These reference spectra are shown in Plates 7 to 19.

DISCUSSION OF RESULTS

A. Spectral Characteristics and Reproducibility

47. Comparison of the spectra of the thirteen elastomers given in Plates 7 to 19 establishes two fundamental results. First, the spectra of the seven basic classes of rubber are all significantly different from each other. Second, the spectra of various synthetics representative of the same basic copolymer class are nearly identical. A third important general feature of all these spectra is their simplicity. Fewer than ten prominent bands are present between 2 and 14 mu in any of the spectra. The prominent bands are well isolated and complex weaker structure is largely absent.

48. The characteristic uniqueness of the spectra of Natural rubber, Butyl, Neoprene, Buna-S, Buna-N, Thiokol-FA, and Thiokol-RD is evident by comparison of Plates 7, 10, 11, 13, 14, 19, 45 and 46. These qualitative differences correspond to basic differences in copolymer structure and furnish an adequate basis for spectroscopic characterization of each class. Critical examination of these spectra further shows that one or more prominent bands in each can be found sufficiently isolated from all others to enable its detection in any binary blend of elastomers. The close similarity of the spectra of rubber types representative of a particular copolymer class is seen by comparison of the five Buna-N spectra (Plates 14 to 18), or by comparison of Neoprene-GN and -ILS, (Plates 11 and 12). The minor differences which exist are quantitative rather than qualitative, and correspond to different proportions of the components comprising the same basic copolymer structure. Spectroscopic distinction between such elastomers is correspondingly less obvious, requiring comparison both of band intensities and positions.

49. Excellent spectral reproducibility was obtained for all duplicate films of a given sample preparation. This factor was best evaluated when the films studied were of nearly equal thickness. In all such cases, differences in absorption were closely consistent throughout the spectrum and showed that film spreading and spectral measurement were reproducible within the accuracy of experimental error. In all cases where duplicate preparations were made of an elastomer the spectra also exhibited this same close consistency of absorption throughout the wavelength range. This showed that nearly perfect reproducibility of spectra was obtainable with a satisfactory over-all method of preparation and measurement. Finally, equivalent results were obtained in all cases involving alternative (but adequate) preparation methods. For example, samples of an elastomer dissolved at room temperature by shaking or at higher temperatures by blenderization or refluxing gave equivalent spectra; the same was true of all preparations employing different solvents. This showed that such factors were without significant influence on the spectral characteristics.

50. Although all these variables were not spearately checked in the case of every elastomer studied, in none of the cases studied did any exception to nearly exact spectral reproducibility occur which could not be attributed defi

nitely to a faulty step in the preparation or measurements and thus be eliminated by appropriate adjustments. In view of this complete consistency of spectral results, the reliability and reproducibility of the general over-all method of study were considered very satisfactory, and the validity of the individual spectra, as dependent only upon the elastomer itself was believed well established. A more exhaustive check of this nature with each elastomer was not believed desirable at this point since repeat preparation in Part II of each elastomer (as the vulcanizate) would furnish not only a further check on spectral validity and reproducibility with respect to sample preparation but a check with respect to specific sample origin as well.

51. It should be emphasized, however, that the reproducibility obtained above requires careful experimental work. First, the use of badly fogged (opaque) or badly scratched sample plates will result in errors due to the scattering of radiation unless this effect of scattered light is compensated by a proper correction, which in general, is difficult to determine. Similarly, low transparency of the rubber film also results in errors which cannot easily be corrected. Although good films are not hard to prepare, some skill is required, and the average worker requires some practice before best results are obtained. Occlusion of air bubbles in the film must be avoided and uniformity of thickness must be maintained. And in all cases the spreading of a good film is dependent upon the adequacy of the sample preparation. Gelling of the sample, for instance, results in a much less transparent film which will scatter radiation and, in addition, makes preading a film of uniform thickness virtually impossible.

B. Effects of Impurities

52. Only two types of absorptions were encountered which were not reproducible and were obviously of foreign origin. These could be identified either with (1) slight oxidation of the rubber hydrocarbon, or (2) impurities introduced by the p-cymene in the Tube Reclaim preparations.

53. Slight oxidation of some samples was evident by weak hydroxyl absorption near 3.0 mu and by weak carbonyl absorption between 5.8 and 6.0 mu. The latter absorption generally appeared as unresolved broadening of the 6.0 mu C=C band on the short wavelength side. Both 3.0 mu and 5.8 to 6.0 mu absorptions were most pronounced in Tube Reclaim spectra. Since in all cases absorption due to oxidation was so weak as to affect in no way the characteristic features of the spectra, special precautions to avoid this slight oxidation were considered unnecessary.

54. The use of p-cymene as solvent resulted in additional bands throughout the 2 to 14 mu region, particularly at 5.02, 6.60, 9.81 and 12.20 mu. None of these absorptions masked the elastomer spectrum to such an extent as to make characterization difficult. Since spectra of Tube Reclaim were obtained in which these bands were absent, their foreign nature was unquestionable. Subsequent work has shown these bands to have their origin in oxidation products of the p-cymene. These formed whenever p-cymene was maintained at reflux temperature for ten hours or longer, despite previous purification of the p-cymene by percolation through activated silica gel or by distillation over dry calcium oxide.

C. Suitability of Sample Preparation Method

55. The spectral reproducibility that has been obtained leaves no question

concerning the purity of the elastomers studied following preparation, since variable weak bands have not been obtained in the spectra of extracted samples. The importance of extraction was investigated for Neoprene-GN and -ILS and for Hycar OR-15 and -25 by preparing in an otherwise identical manner extracted and unextracted specimens of each. Only a few additional, weak bands were found for the unextracted preparations, and it is likely that the effects of extraction were roughly equivalent for the other gum samples.

56. The other important function of the preparation method is that of obtaining a thin, transparent film of the purified polymer; and for this the procedures of solution, solvent removal, and film spreading have been entirely satisfactory. Suitable volatile solvents for each gum elastomer have been found, ethylene dichloride being effective for all thirteen types. Because of their tendency to persist as gels, Buna-N's, Neoprenes, and Thiokol-RD require blenderization for complete solution. (Blenderization furnishes a generally adequate solution technique, uniform in application for all gum rubber studied.)

57. While an extensive study of preparation methods was not pursued for development of an optimum general procedure, the success of the techniques employed in this work leaves little to be desired. In addition, the procedures employed (except for film spreading) are significantly free of exacting demands of special skill and experience on the part of the investigator and thus favor routine application.

D. Spectrometer Requirements

58. By comparison of the spectra of the various elastomers (in Plates 7 to 22) with the spectra of ammonia and HCl, given in Plate 6, to indicate the resolving power of the spectrometer, it is evident that the high resolution of this spectrometer was not necessary in the present study. Because of the general simplicity of rubber spectra, a small commercial spectrometer would be entirely adequate for complete spectroscopic examination of rubber and most rubber mixtures.

SUMMARY AND CONCLUSIONS

59. A relatively simple method for the preparation of uncured rubber for spectroscopic study has been developed and each step of the method has been presented in detail. The method has been applied successfully to thirteen elastomers representative of seven common classes of rubber.

60. Spectra of the thirteen elastomers studied have been obtained in the 2 - 14 mu region, and the validity and reproducibility of the spectra have been established. The spectra obtained have been of nearly pure gum samples preparaed under mild conditions and are considered representative of the pure rubber hydrocarbon.

61. On the basis of the experimental evidence the following conclusions have been established:

(a) The 2 to 14 mu spectrum of each basic class of elastomer is unique: At least one well-isolated absorption band in each spectrum can be used to identify that elastomer in a binary blend with any other. This constitutues an adequate basis for the characterization of elastomer content by infrared analysis,

(b) Different rubbers under a particular copolymer class possess qualitatively identical spectra. Variation in the copolymer components produces quantitative differences in the spectrum. This constitutes a spectroscopic basis for determination of copolymer composition.

PART II - INFRARED SPECTRA OF NATURAL AND SYNTHETIC RUBBER FROM COMPOUNDED AND CURED SAMPLES

INTRODUCTION

A. Statement of Objective

62. In view of the results obtained in Part I with pure gum elastomers it can be seen that the applicability of infrared analysis to commercial rubber products will depend: (1) upon the development of adequate techniques for obtaining the elastomer spectrum of compounded and cured mixes, and (2) upon the characteristics and reliability of the spectrum so obtained. As mentioned previously (para. 15), isolation of the elastomer content is required of any spectroscopic method practicable in the general case because of the necessity of removing opaque fillers and because of the advantages gained in making the data independent of the non-rubber composition. This important problem of purification and preparation of typical rubber vulcanizates for spectroscopic examination constitutes the main objective of Part II. In this connection the particular objective desired was development of a single method of study which would be applicable in general to cured and compounded rubber of unspecified composition..

63. Since the reproducibility and uniqueness of the spectra of each elastomer, however obtained, determine the ultimate applicability of the experimental method, separate investigation of several factors was required in Part II in addition to development of the necessary experimental techniques. These factors included:

(a) the overall spectral reproducibility obtainable by application of a particular procedure of sample preparation and measurement;

(b) the equivalence of spectra obtained under different conditions of sample preparation;

(c) the reproducibility of spectral features of the elastomer under different conditions of cure and compounding of the original specimen.

With respect to this last variation the spectrum of the pure gum elastomer constituted the final reference for evaluation of spectral validity. For this important comparison the spectra from Part I were employed in Part II. Satisfactory spectral correspondence and development of a reliable preparation method of sufficient scope will then assure application of the methods to analysis of blends of elastomers. The individual details and accuracy of special applications of this nature are to be considered in Part III.

B. Previous Related Work

64. Aside from scattered spectroscopic studies of vulcanized natural rubber (generally with specimens containing no filler) the work directed by Barnes (2) is the only study of a cured synthetic or of rubber reinforced with a "filler" in the usual manner. The particular objective in this case was the analysis of tires and tubes containing Buna-S and natural rubber. Separation of

the rubber content of the compounded specimen was accomplished by solution of the rubber by refluxing in a moderately high-boiling solvent (83% p-cymene, 17% xylene), and carbon black was removed by simple filtration following 6:1 dilution of the solution with hexane containing 15% benzene. These techniques apparently were applied only to vulcanizates of natural rubber and Buna-S compounded with a carbon black filler.

65. In the absence of experimental work with other cured synthetics and other types of fillers, two features of the Barnes procedure merit particular consideration:

(1) The solvent: Since Buna-S is one of the more soluble synthetics, the solvent employed might be ineffective in dissolving other types of cured rubber, particularly Buna-N, Thiokol, and Neoprene. Accordingly, solution of blends of other elastomers by this solvent might be highly selective.

(2) The filtration: No explanation for rapid coagulation and settling of colloidally dispersed carbon black simply by dilution seems reasonable except by occlusion of carbon particles to rubber thrown out of solution by the hexane (a very poor solvent for rubber). If this were the case, such treatment would unquestionalby be selective with blends of elastomers of different solubility.

66. On the basis of the work reported (2), evaluation of these factors and of the over-all method was impossible, both in the specific example studied and in ascertaining the general adequacy of the method to other rubber compositions. Accordingly, an entirely original and thorough investigation of much greater scope and detail was definitely necessary in order that procedures might be developed of the range and effectiveness needed for a general method of analysis. Conclusive evaluation of the methods developed was considered essential in order that subsequent specific applications might be made without further preparatory work.

C. Special Considerations

67. Curing and the presence of compounding ingredients increase both the experimental difficulties of examining finished rubber specimens and the difficulty of studying spearately the importance of individual factors to the spectroscopic results. In order that the rubber hydrocarbon may be studied at all, solution of the polymer is essential, being requisite both to filler removal and to film preparation. Because of the low solubility of most cured elastomers and because of the colloidal nature of carbon black fillers, difficulties were anticipated in development of generally adequate techniques for these operations. However, purification of the rubber from organic impurities was expected to be feasible by the usual methods of solvent extraction; and the techniques of solvent removal and film preparation from Part I were considered suitable for Part II.

68. With a suitable preparation method of sufficient scope, application of the method to analysis of rubber composition still depends ultimately upon the correspondence of the spectra obtained of the elastomer with respect to differences in cure and sample preparation treatments. While variations in the extraction, solution and filler removal operations permit to some extent individual evaluation, the uncertain effects on the elastomer spectrum of the original cure and its possible alteration by solution, etc., remain superimposed and do not permit separate and regulated study. Accordingly, it was realized that the

accuracy of the method of study and the reliability of the results could be established adequately only by the consistency of the spectra obtained through numerous duplicate and varied preparations of each specimen. Much more exhaustive repetition of work was believed necessary in Part II, therefore, in order that, regardless of the degree of correspondence between the cured and the gum elastomer spectra, the significance, reproducibility, and scope of the method of study itself might be established.

D. Scope and Method of Investigation

69. The investigation in Part II comprised preparation and spectroscopic study of eighteen compounded specimens (para. 70). These included representative finished specimens of all elastomers studied in Part I (para. 31). Fillers included five carbon blacks, an iron oxide, and a kaolin clay; and a variety of mixes and types of cure were used. The specimens studied in Part II adequately represented finished industrial products in composition and hence in accompanying difficulty of preparation and study. The procedure employed for isolation and spectroscopic study of the rubber hydrocarbon was as follows:

(a) Preliminary Milling and cutting of the specimen.

(b) Extraction of plasticizers, antioxidants, accelerators, and other organic additives and impurities.

(c) Solution of the rubber hydrocarbon content of the extracted specimen by refluxing with a suitable solvent.

(d) Removal of Dispersed Solid Matter from the solution by centrifugation or by a suitable filtration technique.

(e) Removal of Excess Solvent to obtain a syrupy concentrate of the rubber hydrocarbon.

(f) Film Spreading (exactly as in Part I), and evaporation of remaining solvent in vacuum oven.

(g) Spectroscopic Study (exactly as in Part I). These operations will be presented in detail in the following sections.

EXPERIMENTAL

A. Description of Samples

70. The specimens studied in Part II are listed below in Table V according to chemical class of the elastomer.

TABLE V

ELASTOMERS STUDIED AS CURED AND COMPOUNDED SPECIMENS

Chemical Class	Representative Specimen (*)	Filler
(a) Natural Rubber	(1) Vulcanized Natural Rubber (F-2-1)	(none)
	(2) Vulcanized Natural Rubber (F-4)	F.T.
	(3) Revulcanized Tube Reclaim	Red Iron Oxide

TABLE V (Cont.)

Chemical Class	Representative Specimen (*)	Filler
(b) Isobutylene--Isoprene Copolymer	(4) GR-I (F-1002)	F.T.
	(5) GR-I (F-1010-1)	a Kaolin clay
(c) Chloroprene Polymers	(6) Neoprene-E (F-206)	M.T.
	(7) Neoprene-GN (F-210-2)	F.T.
	(8) Neoprene-ILS (F-207)	M.T.
(d) Butadiene-Styrene Copolymer	(9) GR-S (F-602)	(none)
	(10) GR-S (F-606)	S.R.F.
(e) Butadiene-Acrylo--nitrile Copolymers	(11) Chemigum-M-1 (F-1003)	S.R.F.
	(12) Hycar-OR-15 (F-407)	M.T.
	(13) Hycar-OR-25 (F-402)	S.R.F.
	(14) Hycar-OR-25 (F-416)	S.R.F.
	(15) Perbunan-35 (F-1302)	M.T.
	(16) Butaprene-NF (F-205)	F.T.
(g) Ethylene Polysulfide Polymers	(17) Thiokol-FA (F-804)	S.R.F.
	(18) Thiokol-ST (F-801)	S.R.F.
(h) (Copolymer of Butadiene Acrylonitrile, and di-isopropylidine ketone)	(19) Thiokol-ND (F-803)	S.R.F.

* Compounding formula; see Tables VI, VII.
F.T., M.T., S.R.F. designate carbon blacks; see Table VII.

All cured specimens were obtained from the NRL High Polymer Section, and were compounded at NRL from the same gum stocks used in Part I. Details of the composition and cure of each specimen are presented in Table VI. A glossary of the compounding materials used is given in Table VII.

B. Details of Sample Preparation Methods

(1) Milling and Cutting

71. In order to facilitate extraction and solution of the rubber, the specimen first was shredded by several passes through a standard roll mill (at room temperature) and then was finely chopped in a Wiley Laboratory Mill to pass through a #20 mesh screen. Shredding on the roll mill made the finer cutting operation considerably easier. Although absence of tackiness is requisite to use of the Wiley Mill, all cured samples were satisfactorily free of tack. The Wiley Mill, Internediate Model, American Instrument Co. #5-2120, is shown in Plate 20. Approximately ten minutes were required for cutting twenty grams of rubber.

(2) Extraction

72. Extraction of the specimen by a 68/32 chloroform/acetone blend was

employed for removal of all soluble non-rubber ingredients (accelerators, anti-oxidants, plasticizers, waxes, etc.). The low solubility of all cured elastomers permitted use of these solvents without significant solution or swelling of the rubber. This extraction solvent was considered adequate on the basis of A.S.T.M. specifications (8). The identical apparatus described in Part I, para. 32, and shown in Plate 1, was employed.

73. Approximately four grams of sample were used in each preparation. The milled sample was placed loosely in a porous thimble and covered by a wad of cotton to prevent sample from washing out. The thimble was then placed in a siphon cup and the sample extracted continuously for approximately twenty-four hours with two or three 80 ml. portions of solvent. Absence of color transmitted to a fresh portion of solvent after two hours was considered evidence of complete extraction. As spectra were accumulated the data confirmed this opinion and were consistent in showing extraction for more than twenty-four hours to be unnecessary. No extracted material ever appeared as a precipitate. Generally, used solvent was recovered by simple distillation over dry calcium oxide and used a second time. Collection of more than 90% of the distillation assured no significant change in the porportions of the blend.

(3) Solution

74. By far the largest part of the work in Part II was concerned with obtaining adequate solution of all the cured elastomers listed in para. 70. The greatest difficulties here were encountered with Buna-N types, Neoprene-ILS, and Thiokol-ID. Preliminary tests showed that refluxing in solvents boiling well over 120°C was requisite to solution in all cases. However no solvents boiling above 190°C were considered because of the difficulty of removing such solvents for film preparation and because of the possibility of sample decomposition with severe heating. Likewise the general inertness of the solvent itself at reflux temperature was a necessary requirement for maintaining sample purity. The results of examination of a number of solvents are tabulated in Table VIII and in more detail in Table X. The source and quality of all solvents investigated are tabulated in Table IX. All solvents except C.P. grade pyridine and aromatics (used as diluents) were distilled before use to eliminate any possibility of non-volatile impurities. Despite distillation, p-cymene and the three ketones employed as solvents were subject to significant oxidation during use with the result that non-volatile materials were deposited in the rubber. Attempts to eliminate this decomposition by distillation of the solvent over dry calcium oxide (to remove peroxides) or by percolation through silica gel resulted in no permanent improvement. The remaining solvents were satisfactory with respect to inertness during use, except as noted below.

75. Ortho-dichlorobenzene proved to be a satisfactory solvent for every cured elastomer studied. Only this solvent adequately dissolved Neoprene-ILS, Thiokol-ID, and the five Buna-N types; it was fully as effective as the other solvents studied for the remaining elastomers. In addition, the technical grade of o-dichlorobenzene proved to be entirely free of harmful impurities and was characterized by complete inertness during use. Tetrachloroethane successfully dissolved all cured elastomers except Neoprene-ILS, Thiokol-RD, and Buna-N's. This solvent was of satisfactory inertness during use, and the commercial grade proved to be free of harmful impurities. Traces of free hydrochloric acid, which were found to persist on refluxing, required use of an all-glass reflux assembly but were entirely without effect on the dissolved polymer

and the spectroscopic results. Pyridine gave partial solution of Neoprene-ILS, Thiokol-TD, and the five Buna-N's, but complete solution was never obtained with this solvent. Extensive work was not done with this solvent because of its odor and because of the superiority of other solvents. It is likely that the remaining elastomers could be dissolved effectively by pyridine. Para-cymene effectively dissolved all cured elastomers except Buna-N's and Thiokol-RD. This solvent, however, was so readily oxidized during prolonged refluxing that all but a few preparations were seriously contaminated by gums, and the spectra were of little use. Nitropropane and three high boiling ketones (See Table IX) were investigated as solvents for Buna-N rubber. The former proved ineffective and was not investigated further. All three ketones were greatly oxidized during refluxing and contaminated the sample to such an extent that no determination of their effectiveness as solvents was possible in any case. Considerable oxidation of the rubber occurred in every case as evidenced by the brittleness of undissolved sample.

76. Solution was effected by placing the sample in refluxing solvent for 24 to 36 hours. 200 ml. of o-dichlorobenzene or tetrachloroethane was more than sufficient solvent for 4-gram specimens of natural rubber, Neoprene-GN and -E, Butyl, Buna-S, and Thiokol-FA and -ST. For complete solution of 4-gram specimens of the Buna-N's, Neoprene-ILS, and Thiokol-RD more than 300 ml. of solvent (o-dichlorobenzene) were usually necessary. In these three cases solution was most effectively accomplished by successive application of the solvent in two or three 150 ml portions. Before application of fresh solvent the previous saturated solution was separated from undissolved sample either by filtration through a coarse paper or by decantation after an hour of settling. Blenderization (para. 37) decreased the time required for solution but was never essential and was seldom employed, as the cured specimens showed no permanent gelling tendencies. Although dispersion of the filler throughout the solution generally prevented visual observation of the progress of solution, tests with successive applications of solvent showed that absence of appreciable undispersed residue after an hour of settling was sufficient evidence of complete solution of the polymer. After filler removal all solutions containing appreciable rubber were clear and varied in color from yellow to dark amber, depending upon the identity and concentration of dissolved rubber hydrocarbon. Although the flask and condenser assembly used for extraction (para. 32) was employed in much of the work, an all-glass reflux assembly was considered more desirable for maintaining sample purity. A simple and effective glass condenser was designed to replace the metal one without necessitating use of a different type of flask. The glass condenser and reflux assembly is shown in Plate 21 and is described in Appendix A. Use of the glass condenser was essential in work with pyridine, tetachloroethane, and p-cymene, each of which reacted with the metal condenser.

(b) Removal of Filler

77. In the present investigation the "fillers" encountered included five carbon blacks and two inorganic materials - an iron oxide and a Kaolin clay. Because of the much finer division of carbon blacks compared to inorganic fillers, these two broad classes differ in general behavior, and a different method was needed for removal of each.

(a) Inorganic Fillers

78. In the two cases studied centrifugation was entirely adequate for complete removal of suspended iron oxide and clay. Approximately 50 ml quanti-

ties of "solution" were centrifuged at ca. 1000G's for 30 to 40 minutes. The clear solution was then decanted from the packed residue in the tube. Although specimens containing other inorganic filler were not available for study, these two fillers studied are comparable in density and particle size to nearly all inorganic fillers used with rubber, and the results are believed typical of this general class.

(b) Carbon Blacks

79. Removal of carbon blacks was unusually difficult because of the much finer division and colloidal dispersion of the particles, and centrifugation was found not at all effective. The procedure developed by Barnes (2) (para. 65) also was checked carefully but was found to be unreliable (see Appendix B). After unsuccessful tests with Bentonite, Fuller's Earth, and silica gel, a successful filtration procedure using "Celite" Analytical Filter Aid was developed. Although a theoretical basis for this method was not considered and the optimum conditions were probably not determined, the procedure developed was rapid and entirely dependable, accomplishing complete removal of colloidal carbon in every case investigated. The procedure given below proved most effective.

80. The "solution" of rubber and colloidal carbon is diluted with benzene to ca. 350 m. total volume. Into one volume of this solution 1/4 to 1/2 volume of "Celite" (Johns Manville) is stirred, and a small portion of the slurry is poured into a moderately fine filter paper (e.g., Whatman #41), in a 60° long-stem funnel. If the filtrate is completely clear, the entire quantity of slurry is poured into the funnel and filtered. On the other hand, if the drops of filtrate have a black cast, the contents of the funnel are returned immediately to the original container, more "Celite" is added (with stirring), and a second trial filtration is made. Generally, sufficient "Celite" will have been added after two or three trial filtrations, and the filtration is then completed as above. Use of a great excess of "Celite" is not harmful but is undesirable in that it causes greater hold-up of solution. Practically all of this solution can be recovered by washing the used "Celite" with fresh solvent and combining the filtrates. For most effective recovery, the "Celite" is stirred into two volumes of hot benzene and this slurry filtered as before. A second "washing" treatment generally yielded colorless filtrate and was never worthwhile.

81. A number of variations were purposely made - omission of the benzene dilution, filtration of some solutions at room temperature and others at 100°C, slow or rapid addition of the "Celite" - to determine the optimum conditions. None of these factors had any appreciable influence on either the efficiency or the rate of the filtration. Successive filtrations with moderate amounts of "Celite" also was tried, but proved less satisfactory. The great advantage of the trial-filtration procedure lies in the fact that solutions containing much carbon black filter with increasing slowness as the pores of the filter paper become clogged, whereas carbon-freed solutions filter rapidly. Aside from the end results of complete carbon removal, all work has been consistent in showing that the details of the method have entirely no bearing on the spectroscopic results. Extensive work with solutions containing two elastomers - a series of natural and GR-S blends and a series of natural and Buna-N blends - has shown conclusively that no selectivity in solution hold-up is exhibited when such solutions are filtered with excess "Celite". In this respect, the "washing" operation is in no way essential to the validity of the results.

(5) Removal of Solvent

82. Vacuum distillation was employed for removal of solvent in order to concentrate the polymer for film preparation. The conventional Claisen-type flask was used rather than the jointed flask used in Part I (para. 39), since a better vacuum and correspondingly lower distillation temperature were possible. The same arrangement shown in Plate 3 was used. Heating was accomplished by immersion of the flask in a beaker of oil or hot water on a hot plate. By utilization of the vacuum of a water aspirator all solvents used distilled rapidly below 110°C. Distillation was stopped when the sample was sufficiently viscous for film spreading. Because of the slowness of evaporation of the solvents used in Part II, an unnecessary excess of residual solvent was undesirable. The viscous concentrate was most easily and completely poured from the flask to a smaller container by dilution with a few ml. of benzene. No difficulty of sample removal was encountered because of the comparatively non-tacky character of cured rubber concentrates. The volatility of the benzene enabled restoration of the desired concentration by a few minutes evaporation in a vacuum oven.

(6) Film Spreading

83. Spreading and testing of films for spectroscopic study was done exactly as in Part I, para. 40. Evaporation of residual solvent required less than one hour in an 80°C vacuum oven, or less than four hours at room temperature. Even after complete evaporation of the solvent,,films of natural rubber and of Thiokol-FA and -ST remained sticky. This was true of all preparations of these elastomers regardless of the solvent used. However, these films did not flow appreciably in eight hours and permitted accurate spectroscopic measurements. Films of Buna-S, Buna-N's, Butyl, Neoprenes, and Thiokol-RD were solid and were nearly free of tackiness.

C. Details of Spectroscopic Investigation.

(1) Spectrometer - Design and Operation.

84. All spectra in Part II were obtained using the same spectrometer described in Part I (para. 41) under identical conditions of operation (para. 42).

(2) Data Obtained.

85. A complete and detailed summary of all sample preparations and allied spectroscopic measurements made in Part II is presented in Table X. Since the results as tabulated there conveniently afford individual evaluation of preparation features, only the scope and general nature of the measurements made and data obtained are considered in the following paragraphs.

86. Satisfactory spectra were obtained of every specimen studied in Part II (para. 70). All specimens which were suitably prepared were studied from 2 to 14 mu (with NaCl prism) and the spectrum obtained. One sample representative of each class of elastomer was studied between 14 and 23 mu (with KBr prism) and the spectrum obtained. As no appreciable absorption was found in the latter region, no further work was done there.

87. In all, over fifty sample preparations were made and nearly sixty spectra were obtained. While a number of preparations were unsatisfactory as a result of inadequate solution of the polymer or serious contamination by im-

purities, several satisfactory preparations and spectra were made of each sample in order to establish the individual importance of the major variables involved to the spectral reproducibility obtainable with the over-all method. These studies were as follows:

(a) Spectra were obtained of every elastomer from o-dichlorobenzene preparations; most of these were checked by a duplicate preparation.
(b) Spectra were obtained of all elastomers except Neoprene-ILS, some Buna-N's and Thiokol-RD from preparations in tetrachloroethane.
(c) Spectra were obtained of all elastomers except some Buna-N's and Thiokol-RD from p-cymene preparations, although most of these showed contamination of the sample.
(d) A few spectra were obtained of Buna-N's, Neoprene-ILS, and Thiokol-RD from preparations in pyridine, and some (unsatisfactory) work was done with still other solvents.

88. All spectra obtained of each elastomer were checked for reproducibility by direct comparison of the recorder records (para. 46). One or more representative spectra of each elastomer then were plotted on standard charts to enable close examination of individual features and accurate comparison with the pure gum spectrum of Part I. The 23 spectra plotted in Part II are shown in Plates 22 to 45.

DISCUSSION OF RESULTS

A. Spectral Characteristics

(1) Reproducibility and Validity of Spectra.

89. The high degree of spectral reproducibility obtained for gum samples in Part I would hardly be expected in this work with compounded and cured samples, for here any variations in the relatively severe treatment of the rubber, especially during vulcanization, would be expected to result in slightly different and permanent effects. However, the spectra obtained of preparations of finished rubbers showed much better reproducibility than had been anticipated, and, in fact, equalled that obtained for gum specimens.

90. The spectral reproducibility for duplicate films of a satisfactory sample preparation had already been established in previous work and was confirmed here. Duplicate sample preparations of any sample also yielded equivalent results and thereby established the excellence of the over-all reproducibility of the method of study. An indication of the validity of the spectral results was given by the spectral equivalence obtained with variations in the sample preparation procedure, particularly the solvent. As shown in the summary of experimental work (Table X), extensive duplication and use of alternative solvents was made whenever possible for nearly all samples studied in order that the results might be completely evaluated. The close correspondence of all spectra of each specimen, regardless of the particular method of preparation, left no question concerning the independence of the results from specific preparation features, provided the over-all method was adequate for study of the polymer.

91. The greatest significance which can be attached to the results, however is shown by comparison of the spectra with those obtained for pure gum elastomers in Part I. Nearly exact identity of the corresponding spectra was obtained without exception! This fact alone is adequate evidence of the validity of all results obtained both in Part I and in Part II of the investigation. The effects of compounding and curing, and of the sample preparation itself clearly have been eliminated in the spectral results. Unquestionably then, the spectra obtained are only those of the rubber hydrocarbons.

92. Both the reproducibility of the polymer spectra for finished rubber samples and their identity with those for pure gum rubber are of utmost importance for spectroscopic applications. Except for experiment error, these factors will determine the degree to which the ultimate accuracy obtainable in infrared analysis will be reached. Since the spectra of the finished rubber and the gum elastomer are virtually identical, favorable conditions for accurate results are assured in all cases where the experimental methods apply. This range of application includes at least all the types of rubber encountered in the course of the present investigation.

93. Complete identity of spectra determined with an uncured and a cured elastomer was somewhat surprising even though the spectrum of only the rubber hydrocarbon was obtained. Changes in the molecular structure of the polymer certainly occur during vulcanization, and it seems most unlikely that these changes would be completely reversed during preparation of the sample for spectroscopic study. Therefore, certain differences in the spectra would be expected. Some minor differences were found and will be discussed below, but the explanation of the great similarity of the spectra probably derives from the very nature of the infrared absorption of a polymer on the one hand, and of the vulcanization process on the other. Since the absorptions due to vibrations of a large molecule as a whole contribute negligibly to the total absorption, the spectrum of a polymer is always determined more by the structure of the smaller recurring units than by the total size or gross configuration of the chain. For example, straight chain hydrocarbons of from 15 to 20 carbon atoms have nearly identical spectra. Since the chains of the rubber polymers are much longer, virtually no effect of molecular weight is obtained in the spectroscopic results. This was shown in the course of the experimental work on some of the more insoluble elastomers where spectra obtained of successive fractions of the rubber were identical within the accuracy of measurements. Vulcanization of an elastomer likewise introduces almost negligible change in the average recurring-unit configuration. Since the number of cross-linkages formed in establishing the three-dimensional configuration of the vulcanizate is comparatively small, the majority of structural units are unaltered. The net result of curing after redissolving the rubber apparently consists, then, mainly of changes which involve relatively few of the recurring units of the polymer and therefore does not alter the rubber spectrum to any appreciable extent.

(2) Spectral Differences.

94. It is of interest now to consider the nature and probably analytical importance of certain differences more or less consistent between the gum and cured elastomer spectra. When the gum and the cured elastomer spectra are compared, the most obvious dissimilarity noticed is the region from 5.6 to 6.1 mu. While this region is largely transparent for the gum elastomer spectra, nearly all cured elastomers show considerable broad absorption here. This absorption

is largely unresolved and varies greatly in appearance, even for duplicate preparations of the same specimen. The nature of this spectral region and the non-reproducibility mentioned establish this absorption as not fundamental to the polymer but due to carbonyl structures resulting from oxidation of the polymer. This conclusion is supported also by rather strong hydroxyl absorption at 3.0 mu (also foreign to all pure elastomers). While the variable character of such absorption renders the 3.0 mu and 5.6 to 6.0 mu regions worthless for reliable measurement, neither region is valuable for elastomer identification. However, since no other spectral regions are affected in any way by mild oxidation of the polymer, the analytical usefulness of the spectra is unimpaired by this factor.

95. A second difference fairly prominent in many of the cured rubber spectra is a great increase of general background absorption between 7 and 15 mu. This effect appears as appreciably lower transmission between distinct bands than in the pure gum elastomer spectrum and thus results in poorer definition of the bands themselves. This general absorption is undoubtedly consistent with the greater molecular size of the cured elastomer, since the analogous effect is observed in comparison of spectra of successive members of homologous series of simpler hydrocarbons: the lower members show sharp, steep bands with high transmission in-between, while the higher members show lower transmission throughout and thus less sharpness of band structure. In the cured rubber spectra this absorption beyond 7 mu is highly variable, not only with respect to the elastomer but also with respect to the several preparations of the same specimen. In view of the probable dependence on curing, it is to be expected that such absorption would not be reproducible with sample preparation, particularly with regard to solution at high temperatures. The effects discussed above are well illustrated by comparison of the several spectra of natural rubber (Plates 7 to 9, and 22 to 25), which, in fact, comprise the worst case encountered. The variable background absorption beyond 7 mu does not affect, qualitatively, the characteristic features or general appearance of the elastomer spectrum, but may lead to false ideas concerning the relative strengths of bands in well separated spectral regions. While the effect, then, is of no consequence to qualitative characterization of rubber, it clearly cannot be neglected when quantitative measurements are desired. This fact must be evaluated experimentally for the specific case in question, and thus will be considered further in Part III.

96. Finally, the absence of certain weak bands in the spectra of cured GR-I, Chemigum, and Butaprene should be pointed out. For the latter two elastomers the gum spectra, (Plates 14 and 18), show a weak (though sharp) band at 6.45 mu, which does not appear in the cured elastomer spectra. In view of the weakness of this band, the presence of a trace of impurity in the gum sample is a reasonable explanation. The fact that soaps absorb very strongly in this region (6) supports this conclusion, since this type of impurity is likely to be present in gum rubber (after emulsion polymerization) and is moreover not particularly soluble in (and hence readily extracted by) alcohol. Either the use of better extraction solvents for the cured specimens or reactions of the soap during curing (6) are adequate explanation of the absence of the band in cured rubber spectra. In the case of GR-I, the extra band in the gum rubber spectrum (Plate 10) is somewhat stronger and comes at 6.50 mu. A similar explanation may hold in this case, since no cured GR-I spectra show this absorption. Minor differences of this nature are of no consequence in spectral analysis of rubber, since weak bands of uncertain origin are generally avoided in selection of bands for characterization.

(3) Impurities

97. No additional bands or inconcsistent spectra were encountered except in cases of contamination of the rubber by impurities from the solvent. This occurred only in preparations involving pyridine, p-cymene and highboiling ketones. For pyridine some of the spectra obtained possessed impurity bands between 4.5 and 5.0 mu; but aside from this region, the spectrum of the elastomer was correct. For p-cymene and the three ketones, an impurity spectrum was obtained featuring strong bands at 5.82, 6.60, 9.81 and 12.22 mu. While the p-cymene in Part II gave a stronger impurity spectrum than in Part I for Tube Reclaim (para. 54), the elastomer spectrum was always easily distinguishable. However, for all the ketone preparations, the impurity spectrum was much stronger and was characterized by such strong general absorption through the entire 5 to 14 mu region that nothing characteristic of the rubber was distinguishable. The explanation of this impurity spectrum as due to oxidation products of the solvent (i.e. gums) deposited in the rubber is supported by all the experimental evidence. The extensive formation of gums was clearly observable as great darkening of the solvent and eventually precipitation when p-cymene was refluxed alone for more than ten hours. The gums obtained here gave the same spectrum as given by the contaminated rubber preparations. During all rubber preparations which gave the impurity spectrum, this same behavior of the solvent was observed. In all cases oxidation of the rubber accompanied oxidation of the solvent, as shown by the brittleness of that part of the specimen not dissolved.

B. Suitability of Sample Preparation Method.

98. The experimental results obtained through isolation of the rubber hydrocarbon as described leave little to be desired from the spectroscopist's viewpoint. The consistent spectral reproducibility, the near identity of spectra of the cured and uncured elastomer, and the spectral independence from exact conditions of sample preparation, all favor this type of method. For these reasons, isolation of the rubber hydrocarbon is preferred whenever possible, and when possible, assures accurate and reliable results. The specific method developed in this investigation for accomplishing this result applied to finished rubber of all common commercial types and can be executed uniformly for all specimens.

99. The limitation of the solvent is largely the limitation of the method, and whenever a suitable solvent can be found which will adequately dissolve the elastomer, the method is feasible. Of the solvents investigated, o-dichlorobenzen proved very satisfactory and most widely useful. This solvent alone extends the method to all elastomers studied during this work, and would likely prove adequate in an even more general case. It is possible, however, that in exceptional cases, such as highly cross-linked polymers, some other solvent would be required. While failure to find any solvent would prevent sample preparation and spectroscopic study, this situation has not been encountered and is considered very unlikely in work with commercial products.

100. The other important step in the method- the separation of filler from rubber solution - has long been recognized as a difficult task, especially in the case of colloidal carbon blacks. Although the theory of the "Celite" filter-aid technique used here has not been considered, the empirical results obtained in over fifty preparations with a variety of blacks have established beyond doubt the effectiveness and general reliability of this procedure. Blacks of various particle size, surface area, and pH values have all been completely removed,

although the work involved has been greater in some cases than in others. Aside from its general adequacy, the method is significant in the comparative unimportance of following closely a set procedure. The fact that no selectivity is exhibited when solutions of mixed elastomers are treated is of the greatest value in assuring this method dependable general application. In this respect the only limitation to the filler removal method is the amount of experimental work which can be tolerated.

101. In addition to the possibility of limitations imposed by the solvent and the work involved in separation of the filler, the analyst might also reject or criticize the over-all method because of its length. It must be remembered, however, that isolation of rubber hydrocarbon can hardly be considered a single-step process. Although the time factor is not to be minimized here, the method was developed with emphasis on reliability and accuracy rather than speed. In the general case, this over-all method is considered feasible, not unnecessarily laborious, and wholly essential to the present purpose. In view of its dependability and wide range of usefulness, the method is considered, in fact, surprisingly free either of exacting specified procedures or of requirements of skill and experience on the part of the worker. As pointed out previously, considerable latitude is allowable in nearly all of the operations of sample preparation without impairing their effectiveness or influencing the spectral results. Accordingly, the method developed here should be very well adapted to routine applications. Although simplification of the procedure might well be possible in certain cases, such changes should not be made before they have been fully evaluated.

102. A total time of approximately five days is required for sample preparation of a finished rubber by the methods of Part II. However, the major time-consuming operations - extraction, solution, and filtration - are of such a nature as to permit simultaneous treatment of six or eight samples in little more time than is required by one sample. In the course of this investigation, preparations of 6 or 8 samples were done in six man-hours per sample. This figure could be reduced further on a production basis.

SUMMARY AND CONCLUSIONS

103. A reliable method has been developed for preparation of finished rubber specimens, enabling separation of the elastomer content for spectroscopic examination. Each step of the method has been presented in detail, and each operation has been carefully evaluated, both as to effectiveness and as to influence on the ultimate spectral results. The method has been applied successfully to a variety of typical reinforced vulcanizates of fifteen commercially important elastomers, and one specific procedure has been found which is entirely adequate for all these cases.

104. Spectra of the fifteen cured elastomers have been obtained in the 2 to 14 mu region. Very good spectral reproducibility for the over-all method of study has been obtained both for duplicate and for varied sample preparations. The validity of the spectra has been established by their close agreement with the spectra of pure gum elastomers in Part I.

105. On the basis of the experimental evidence it is concluded that:

(a) an adequate method has been developed for obtaining a valid spectrum of the polymer content of any typical compounded and cured natural or synthetic rubber specimen; and

(b) the elastomer spectrum, when obtained by the prescribed method, is characterized almost entirely by the type (chemical structure) of polymer and not by its past history (cure, compounding, specific preparation treatment).

These fundamental results, and the spectral uniqueness of the different classes of elastomers (summarized in Part I), provide a sound experimental basis for spectroscopic analysis of typical rubber products. A few specific cases are to be considered in Part III.

PART III - ANALYTICAL APPLICATIONS

IDENTIFICATION AND QUALITATIVE ANALYSIS

A. Basis of Method

106. The basis for analysis of rubber by infrared spectroscopy lies in the following results established in Parts I and II (para. 61, para. 105):

(1) each class of elastomer possesses a characteristically different spectrum;

(2) this spectrum is virtually unaffected by sample preparation treatments or by previous compounding and curing;

(3) completely adequate experimental methods have been developed for obtaining the polymer spectrum of rubber specimens of all common types.

Because of the spectral reproducibility of the elastomers and general reliability of the experimental methods, the degree of spectral selectivity alone need be considered for characterization of rubber in the general case. The distinguishing features of the various elastomer spectra will now be considered in some detail in their application to analysis.

107. The uniqueness of over-all spectral characteristics for each elastomer is shown in Plate 46. Identification of a rubber specimen containing a single elastomer thus is always feasible simply by comparison of the spectrum with reference spectra. The following absorptions characterize the individual elastomers: Natural and Neoprene are distinguished from all other classes by a broad band at 12 mu and are differentiated from one another by the exact position of this band, by a strong band (in Natural) at 7.25 mu, by the strength and position of the 6 mu band, and by the appearance of the 9 mu region; Butyl is distinguished by a strong, unique band at 8.13 mu and by a strong doublet at 7.20, 7.30 mu; Buna-N and Buna-S are characterized by strong bands at 10.3 and 10.9 mu (common to butadiene polymers), and Buna-S is readily identified by unique bands at 6.23, 6.70 and 14.3 mu, while Buna-N is identified by a sharp band at 4.47 mu; Thiokol-FA and -ST possess identical spectra, characterized by a group of strong bands at 8.36, 9.64, 9.98, 9.32 and 9.68 mu; Thiokol-RD possesses typical Buna-N bands at 4.47, 10.25 and 10.86 mu, but is readily set apart by a strong, unique band at 5.86 mu and by a doublet at 7.25, 7.38 mu. These results are presented compactly for reference in Table XI.

108. While identification of a singly occurring elastomer is always unambiguous, exact spectral correspondence may not always be found because of significant differences in polymerization or in copolymer proportions. For example, the Buna-N band at 4.47 mu may be weak or strong compared to the butadiene absorption at 10.3-9 mu, depending upon the acrylonitrile/butadiene ratio of the copolymer. Similarly, the relative strengths of the 10.3 and 10.9 mu bands will vary with the ratio of 1:4 - to 1:2 - addition of the polymer.

109. The interpretation of differences of this type illustrates an import-

ant point not heretofore considered - namely, the value of structural interpretation of the spectral absorptions. Much can be learned from examination of the spectrum with a quantitative viewpoint when the absorptions are correlated with particular structural groups or units, such as phenyl, vinyl, internal double bond, tertiary carbon, etc., since it may then be possible to identify the elastomer more specifically as a particular type, rather than as to chemical class alone. Thus, high-acrylonitrile Buna-N may be differentiated from low-acrylonitrile Buna-N. Also, sodium polymers and emulsion polymers are readily distinguished, since the former is predominantly a 1:2- polymer, while the latter is largely 1:4- structure. Finally, questionable bands may often be attributed to impurities (e.g., to oxidation) on the basis of structural interpretation. Accordingly, structural explanation of prominent bands should be employed as a desirable supplement to empirical comparison of gross spectral features in arriving at a more specific characterization of the sample. The structural explanation of the bands found in elastomer spectra is considered in detail in Appendix C.

110. The qualitative analysis of a mixture of elastomers imposes the more severe requirement of recognizing the characteristic absorptions of one elastomer in the presence of the others. While it follows from paragraph 107 that the major component can easily be identified, the detection of elastomers present in minor amounts (or assurance of their absence) depends upon the degree of spectral differences - namely, the isolation of the bands and their relative strengths. The limiting concentration of a minor component which can be detected introduces, then, a quantitative aspect which must be evaluated for each case to be considered. For example, the 4.47 mu band, which identifies any acrylonitrile copolymer, occurs in a region otherwise entirely transparent for the rubber spectra (Plate 46), and accordingly, one percent of a nitrile rubber can readily be detected in any sample. A different example is afforded by Thiokol-FA, which possesses a series of unusually strong bands between 7.5 and 10.5 mu. While other elastomers absorb somewhat in this region, the great strength of the characteristic Thiokol spectrum readily enables identification of a few percent of Thiokol in any mixture.

111. In general practice, however, it is believed that the presence of several different elastomers in a single sample is rarely encountered and that binary mixtures embrace practically all the important cases. For all binary combinations of the elastomers considered here the specificity and strength of the characteristic bands allow detection of a concentra tion as low as 5% in nearly all cases. A mixture of Natural with Neoprene may be an exception, but the limiting concentration of Neoprene detectable is certainly less than 10% in this most difficult case.

112. Although differentiation between chemically similar elastomers of different quantitative composition is feasible to some extent (para. 109), the infrared spectrum is generally of very limited value in this respect, since such differences would not be readily obvious in the spectrum of a mixture. The case of greatest practical importance is that of Natural and Reclaimed Natural. Here such close spectral correspondence exists that no differentiation is possible, since Reclaim is distinguished only by a general background absorption and vagueness of bands entirely comparable to the general effect of vulcanization (para. 95).

B. Experimental Procedure

(1) Sample Preparation.

113. For accomplishing isolation of the entire polymer content of a rubber

specimen, the appropriate methods of Part I or Part II are employed, as required by the state of cure, purity, and filler content of the sample. The critical step in the preparation is that of obtaining nearly complete solution of the rubber. Ethylene dichloride accompanied by blenderization (para. 37) should be used for gum samples; o-dichlorobenzene under reflux (para. 76) should be used for cured rubber, and samples of low solubility should receive successive solution treatments if necessary. Normal precautions should be exercised throughout for achieving and maintaining purity of the polymer; and particular attention should be paid to obtaining a homogeneous concentrate of the polymer and clear even films for spectroscopic measurement. Preparation of a set of films of four different thicknesses, as described in para. 40, is recommended in order that useful spectral measurements may be made at all wavelengths.

(2) Spectral Examination.

114. For reliable results in qualitative analysis of polymer content it is desirable to obtain the complete spectrum from 4.5 to 14 mu. While some useful information can be obtained from the 3 to 4 mu region, its use is not essential for the present purposes and, in addition, requires considerably more resolving power than is obtained with most prism spectrometers. A film thickness which gives 85 to 90% absorption for the strong band around 6.8 to 7.0 mu should be studies over the complete range. The major component or components will absorb appreciably for this film thickness and thus will be easily identified. Spectral regions of low absorption may then be examined with a film of greater thickness so that elastomers present in trace quantities may be detected or definitely ruled out.

115. Identification of the elastomers present in the sample is made by systematic examination of the spectra thus obtained. For this purpose those wavelengths characterized by one or more elastomers are listed in Table XII. Certain of these wavelengths (marked *) provide unambiguous identification of a single elastomer, and examination of these positions first will make the remaining wavelengths more specific. The typical analysis given in Table XIII illustrates this procedure. In addition to searching for individual bands, direct comparison of the over-all spectrum with reference spectra of each elastomer not definitely ruled out is essential. Since definite intensity relationships as well as wavelengths characterize each pure elastomer spectrum, much can be learned by comparison of gross spectral features. The spectra given in Plates 7 to 19 may be used for reference, in which case the spectrum for analysis must be plotted on a similar scale. It is probably advisable, however, to prepare a similar set of reference spectra with the particular spectrograph to be used in the analysis. Not only will this eliminate spectral differences due to differences in resolving power, but if standard conditions of the instrument operation are adopted the recorder records may be used as such for comparison and thus the tedious procedure of replotting the data on standard forms be avoided.

116. While the procedure given above is adequate in any case, the applications encountered in practice may often permit making considerable short-cuts, such as recording only selected short regions instead of the complete spectrum. This will depend upon some previous knowledge of the sample, upon the accuracy and completeness of results desired, and largely upon the experience of the analyst.

C. Experimental Results and Conclusions.

117. A series of Natural/Buna-S blends and a series of Natural/Buna-N

blends were examined. These samples were compounded with carbon black and were cured in a typical manner. In all cases the component elastomers were easily identified in the lowest concentration considered (10%). Since the spectral differences involved in these two mixtures are of the same order of magnitude as those involved in other mixtures, similar results would be obtained in other cases, except possibly Neoprene/Natural (para. 111).

118. The Natural/Buna-N analyses established an important experimental result concerning sample preparation adequacy. Since natural rubber and Buna-N are at opposite extremes of solubility, it might be expected that after partial solution of a blend, particularly one low in Buna-N, only Natural would be detected in the dissolved fraction. However, Buna-N was clearly evident in every case. Apparently, lower molecular weight fractions of the Buna-N existed in appreciable proportions and were readily dissolved in the first solution treatment. Since this would very likely happen in any case, reliable qualitative analysis probably never requires complete solution of the polymer content. Although the desirability of effecting complete solution whould not be minimized, these results indicate the probable dependability of qualitative work even when solution difficulties are encountered.

119. It is concluded that in general any binary mixture of elastomers composed of basically different unit structures can be qualitatively analyzed by infrared spectroscopy. A conservative estimate of the limiting concentration required for detection is put at about 5%.

QUANTITATIVE ANALYSIS OF NATURAL/GR-S MIXTURES

A. Basis of Method

120. Since molecular absorption is an unalterable and additive property (para. 9), any feasible qualitative differentiation theoretically can be made quantitative whenever the requisite spectral reproducibility can be achieved by the experimental procedure. The adequacy of the methods of Part II in this respect and the permanence of spectral features of the elastomers have already been established (para. 105). There remains to consider, however, the spectroscopic problems pertaining to quantitative work. Although only one analysis, that of Natural/GR-S blends, is considered in detail and is experimentally confirmed here, analogous procedures may be used and similar results obtained for most other binary combinations of the elastomers considered in this report. In this respect it should be said that the choice of Natural/GR-S as an example analysis was determined entirely by the industrial importance of this blend and not because this particular determination was considered more easily adaptable to quantitative treatment than numerous other analyses.

121. Determination of the concentration of a material from its spectral absorption generally involves the following steps:

(a) selection of a sensitive and reliable spectroscopic measure of the component, and determination of an unambiguous relationship (or function) between the measured absorption and concentration;

(b) construction of a "working curve" expressing this function for a series of accurately known concentrations;

(c) subsequent analysis of samples by applying the functional values obtained to this working curve.

If this is done for each component of a mixture, complete quantitative determination of the composition is achieved. Because of the use of previously determined reference data, this working curve analysis requires the utmost spectral reproducibility of the over-all experimental method. The results of Part II (para. 105) show the sole and necessary condition for this to be complete solution of only the elastomer content of the sample. Since this can be accomplished for all the fifteen cured elastomers considered in this report by the method presented in Part II, sample preparation presents in general no limitations to quantitative accuracy (para. 99). Possible limitations relate, therefore, almost entirely to spectral features peculiar to the sample, that is, to special characteristics of the sample which would be reflected in its spectrum. For example, the extent of duplication, or reproducibility, obtained in manufacture of a particular copolymer sets an ultimate limit to the reliability of its determination using a given set of reference data. Such factors must be evaluated for each specific case in questions, and only the problems pertaining to Natural/GR-S blends will be considered at this point.

122. Empirical comparison of the spectra of Natural and GR-S (Plates 7 and 13) indicates that Natural can be detected in the mixture by the bands at 7.25 and 11.95 mu and that GR-S can be detected by several bands, such as those at 6.70, 10.35, and 14.30 mu. These bands are listed below with the associated structures (according to Appendix C):

Elastomer	Wavelength (mu)	Absorption due to:
Natural	7.25	$-CH_3$ (methyl group)
	11.95	$-(CH_3)C = CH -$ (isoprene linkage)
GR-S	6.70	$-C_6H_5$ (phenyl group)
	10.35	$-CH = CH -$ (1:4-addition butadiene linkage)
	10.95	$>C = CH_2$ (1:2-addition butadiene linkage)
	14.3	$-C_6H_5$ (phenyl group)

While either of the bands listed for Natural is characteristic of this elastomer, the 7.25 mu band is preferable for analysis, since the $-CH_3$ structure should be invariant upon vulcanization, etc., while changes may occur in the double bond content and hence in the intensity of the 11.95 mu band. For GR-S, a butadiene-styrene (Buna-S) copolymer, the structural origins of the bands to be used for analysis are of even greater importance. The 10.35 and 10.95 bands are due to 1:4 - and 1:2 - modes of addition respectively, and since these may vary with polymerization conditions, use of either of these bands alone to determine the entire elastomer would be unreliable. A more satisfactory band is that at 6.70 mu, due to the pheny ring. While the relative strength of this band will depend upon the styrene content of the copolymer and therefore will vary for Buna-S in general, for GR-S the styrene content has been fixed and maintained as nearly as possible at the same value by all manufacturers. For this reason (and to the extent that it is true) the phenyl band may be used alone for GR-S determination. The 7.25 mu band (for Natural) and the 6.70 mu band (for GR-S), then, appear to be the

most satisfactory ones for quantitative analysis. In addition to the considerations above, these bands are definitely preferable to those at longer wavelengths because of the greater effect of molecular weight variations on the latter (para. 95). Such variations result in varying background absorption, and since the state of cure of the elastomer and the conditions of sample preparation have considerable influence, valid intensity measurement beyond 10 mu is not too reliable in general.

123. The function relating absorption at these wavelengths to concentration generally includes the sample thickness, since concentration and thickness are equivalent variables, the absorption being proportional to their product. While the thickness factor can usually be eliminated from the function either by keeping it constant or by measuring its value, this is almost impossible to do accurately for films of rubber. A superior approach, therefore, is to eliminate the absorption dependency upon film thickness by employing ratios of absorption intensities instead of absolute intensities. This follows from the fact that the absorption intensity when measured as extinction is defined by: Extinction $\equiv \log_{10}\left(\frac{1}{\%\ \text{Transmission}}\right) = k \times \text{concentration} \times \text{thickness}$, which holds at all wavelengths. Accordingly, ratios of extinctions measured at two different wavelengths are independent of thickness, which cancels as a common factor. Hence, for a mixture of Natural/GR-S the ratio of extinctions at 6.70 and 7.25 mu will be a function only of composition. Unfortunately, (and unavoidably), this ratio cannot be determined accurately for all concentrations. Accurate transmission measurement is limited to the range 20 to 65%, and for blends of low concentration in either component the strengths of these bands differ so greatly that both do not fall in this range. (This fact alone adequately accounts for the poor quantitative accuracy reported by Barnes using this same ratio, an inaccuracy incorrectly attributed by him to unavoidable variation in film thickness!) Except for mixtures containing nearly equal amounts of Natural and GR-S, then, only one of the components can be measured directly with a given film, the other being determined, however, by difference. It is consistent with maximum sensitivity that the direct determination always be made of the weaker component, since this is affected by a change of composition proportionately much more than is the stronger one. The difficulty of eliminating the film thickness factor in separate Natural and GR-S determination may be resolved by forming extinction ratios using a third analytical wavelength, an "indifferent" band of medium strength common to both elastomers, which will serve then as an "internal standard". For this purpose, the moderately weak band at 7.60 mu is particularly suitable, since it occurs in both Natural and GR-S at nearly the same intensity. Not only will this band be nearly invariant with composition and thus serve as an equivalent thickness reference for all blends, but when the film thickness is adjusted for accurate measurement of this band the analytical wavelength corresponding to the minor component will always fall in the accurately measurable range. The extinction ratios ($E^{6.70}/E^{7.60}$) and ($E^{7.25}/E^{7.60}$), therefore, may be used as functions only of composition to determine GR-S and Natural, respectively. Consideration of the relative strengths of the three bands shows that the first ratio should be measurable from 0 to 60% GR-S and the second from 0 to 50% Natural. The combined use of both functions therefore enables determination of all Natural°GR-S compositions at optimum accuracy. Because of the invariance of the denominator, both functions should be linear over the useful concentration range.

124. The two working curves (Plate 4-8) are constructed empirically using data obtained for a series of standard samples of known composition. Spectral

measurements are made at the three analytical wavelengths, and the extinction ratios are calculated and plotted versus the known concentrations of the samples. Subsequent samples of known composition but unknown concentrations may be quantitatively analyzed by making the same measurements and applying the data to the working curves.

B. Presentation of Analytical Procedure.

125. The following procedure is considered reliable, accurate, and well adapted for routine analysis of finished rubber compositions composed of natural rubber and GR-S. Despite specific instructions below, it is understood that considerable latitude is allowable in nearly all of the sample preparation steps (para. 101). The fact that the validity and reproducibility of the results depend solely upon sample purity and the final adequacy of the extraction, solution, and filtration steps, and not upon definite procedures, is a particular advantage of this method for routine use. For purposes of shortening the exposition, paragraph reference to Part II has been employed below for description of experimental techniques which otherwise would require identical re-statement here.

(1) Preparation of Sample for Spectroscopic Study.

126. A 4-gram sample, which has been milled and cut by a Wiley Laboratory Mill (Plate 20) to pass through a #20 mesh screen (para. 71), is extracted for a minimum of 24 hours by two 80 ml. portions of a 68/32 blend of chloroform/acetone (para. 73), using the assembly of Plate 1. When dry, the extracted sample is placed in 250 ml. of o-dichlorobenzene (previously distilled), and the solvent is maintained at reflux for at least 24 hours, using the all-glass assembly of Plate 21. After an hour of settling, the solution is slowly poured into a clean flask, and any appreciable residue is treated with fresh solvent (para. 76), after which the solutions are combined. Blenderization may be employed (para. 37), provided the jar does not leak and does not have rubber gaskets. Carbon black is removed by filtration with "Celite" by the procedure of para. 80. Inorganic fillers (if present) are removed by centrifugation (para. 78). Following vacuum distillation of all but a few percent of the solvent (para. 82), the viscous concentrate of polymer is stored in a small bottle until used for film preparation. Films are spread by the method of para. 40 (see also Plate 4). If the sample is fairly viscous, the film can immediately be checked for thickness by measurement of the transmission at 7.60 mu (which should be between 40% and 60%), since o-dichlorobenzene is transparent at this frequency (Plate 47). After adjustment to an appropriate thickness, the film is allowed to dry in a level position for 4 hours under normal conditions or for 40 min. in a vacuum oven at 60°C. Of the several operations involved in the sample preparation, only that of film preparation requires great care. This operation is very important, and films of decidedly uneven surface and thickness should not be used.

(2) Spectroscopic Measurements and Calculations.

127. Percentage transmission of the film is measured at 7.60, 7.25 and 6.70 mu. Although this is best done by measuring alternately the deflection for the sample and for a "blank" plate at each fixed wavelength setting, the 7.25 and 6.70 mu bands should first be scanned carefully in order to locate their maxima, since both bands are very sharp. Films and measurements should be made at least in duplicate. Transmission values outside the range 20 to 65% are of questionable accuracy, and such results should be checked using more appropri-

ate films. For blends having 0 to 50% Natural the extinction ratio ($E^{7.25}/E^{7.60}$) must be obtained. For blends having 0 to 70% GR-S the extinction ratio ($E^{6.70}/E^{7.60}$) must be obtained. Extinction is related to percentage transmission by the relationship, $E = \log_{10}(1/T)$; for example, 50% transmission gives an extinction = $\log_{10}(100/50) = \log_{10}(2) = 0.301$. Each ratio is plotted as a function of concentration for a sufficient number of known blends to construct a working curve, and subsequent samples are analyzed by the converse procedure of applying the measured extinction ratios to the appropriate working curve (para. 124). Since this curve undoubtedly depends to some extent upon the instrument used and the conditions of operation, e.g., the spectral slit width, the working curves given in this report may not give valid results when generally applied, and the proper straight line working curves should be determined by measuring several known blends. The accuracy and general reliability of the over-all analytical method will be considered in the following paragraphs.

128. In application of this method to typical reinforced rubber the time required for analysis is largely that required by the sample preparation, since the spectroscopic measurements take only a few minutes. While the sample preparation cannot be done in less than four days, simultaneous preparation of a number of samples is readily feasible, and on a routine basis the time requirement can be reduced to less than 6 man-hours per sample (para. 102).

C. Experimental Results.

(1) Work with Standard Samples.

129. The analytical method was tested by applying it to a set of eleven standard samples of accurately known composition. These samples are described in Table XIV and were made by curing appropriate mixtures of two master batches, Natural (F-10) and GR-S (F-620), the compositions of which are given in Table VI. All samples contained 33% Statex (carbon black) as filler, and were cured for 30 minutes at 300°F. The standard samples were prepared in triplicate and several films of each preparation were studied. Not all these films were of the appropriate thickness to yield useful measurements, and only those transmission values which fell in the range 15 to 75% were used. These spectral measurements, the sample compositions, and the analytical results are presented completely in Table XIV. In order to present the analytical results in terms of percentage concentrations, the measured extinction ratios were plotted versus the known concentrations for each sample, and a working curve was drawn through the average value of each set of points (para. 127). As anticipated, the two curves obtained (Plate 48) proved to be linear over the concentration range to which they apply. These same extinction ratios were than applied to the appropriate average curve to obtain the corresponding "analyses" presented in Table XIV.

130. The reproducibility of the analytical results with respect to the several variables involved - sample preparation, film spreading, film thickness, and concentration - can best be seen by examination of Table XIV. For each blend the several "analyses" seldom differ from the average value on the working curve by as much as 2.5% and the average deviation for the fifty results comprising the table is ±1%. The reproducibility of the analytical values for the three preparations of each blend is seen to be equal to that obtained for duplicate films of any of the preparations. This proves the adequacy of the preparation method on the one hand, and shows the importance of the quality of the films measured on the

other. While some films appeared perfectly smooth, others which were used were slightly uneven, and this probably accounted for what little variation was obtained. For evaluation of the effects of film thickness, a number of films of widely different thicknesses were purposely studied, although it was found easy to spread films of the desired thickness by the procedure of para. 125. While some films (e.g., see Blend 4, no. 3 in Table XIV) differed as much as 3-fold in the 7.60 mu extinction, the consistently close reproducibility of the analytical results, entirely irrespective of such differences of film thickness, proves the independence of the spectral functions used with respect to this factor. Finally, the results show the same reproducibility for all concentrations on the linear portion of the working curve.

131. The reproducibility of the results, and hence the experimental accuracy of the method, is expressed by an average error of ±1%, calculated from the 58 results listed in Table XIV. In view of the fact that the results presented here include all data obtained during development of the method, and that no exceptional degree of regulation was used in any of the steps of the analysis, it is considered that this same accuracy, or better, may be obtained in the experimental application of the method.

(2) Work with Other Mixtures.

132. Analysis of the standard samples described above necessarily constituted favorable conditions for the application of the method in order that the limitations pertaining solely to the experimental aspect of the method could be established. The over-all usefulness of the method, however, depends also upon the consistency of analytical results when stocks of different origins are encountered. Although different stocks exhibit the same general spectral characteristics, slight quantitative differences in molecular structure may exist and produce corresponding quantitative differences in the spectral absorption intensities which would affect the results of quantitative spectral analysis. This degree of correspondence in general was checked by applying the method to known samples compounded from a different stock. Since GR-S stocks may be expected to show but little variation, (para. 122), attention was directed to a variation of Natural. To determine the maximum effect which would be encountered in practice, a Natural Tube Reclaim stock was used, since here the greatest deviations from the structural composition of Natural crepe are probably encountered. In fact, this constituted the most severe check on the method which could be imagined. Because of the widespread industrial use of Reclaim, however, these conditions are an important consideration in determining the applicability of the analytical method.

133. Six Reclaim-containing blends, whose compositions are given in Table XV, were obtained for Natural/GR-S analysis. These blends were made by curing appropriate mixtures of Tube Reclaim (F-10-1), Natural (F-10), and GR-S (F-620) stocks (see Table VI). Repeated analyses on each of these samples were made using the working curves (Plate 48) established previously with the standard samples (para. 129) and the analytical results are presented completely in Table XV.

134. Although no apparent difficulties were encountered in sample preparation, both the reproducibility and the correctness of the results are much inferior to that obtained for the standard samples (para. 130). The errors are roughly proportional to the Reclaim content, and far greater interference is found in the Natural determination (Natural + Reclaim) than in the GR-S determination. For the sample containing equal parts of Natural, Reclaim, and GR-S no

significant error in the GR-S analysis can be attributed to interference from Reclaim, but the Natural analysis is about 16% low. Similarly, for samples containing 50% GR-S the presence of 25% Reclaim lowers the Natural analysis about 12%, and 50% Reclaim lowers it about 18%, whereas the GR-S determinations are not seriously affected.

135. Since the interference of Reclaim with GR-S determination is small and unimportant except for the rather poor reproducibility (about ±3%) obtained for all Reclaim-containing samples, the best accuracy is obtained when GR-S determination is employed over the maximum possible range (from 0 to 70%). In this range the effect of Reclaim is serious only at very low GR-S concentrations. For zero GR-S concentration 50% Reclaim produces an error of about 5% and 100% Reclaim gives about twice this error. Although this case is unimportant since an examination of the spectrum would reveal the absence of the GR-S bands, it indicates that determination of low GR-S concentrations would be subject to as much as 10% error, depending upon the amount of Reclaim present. For GR-S concentrations of 10-70%, however, an accuracy of ±5% and better can be expected, and for samples of such composition the total Natural content is best obtained by difference. For GR-S concentrations above 70% the Natural analysis must be used. Here the upper limit of 30% for the Reclaim content will limit the maximum error to about 10%. Since Reclaim is generally used in conjunction with Natural, however, the maximum errors are probably never encountered in practice. If it is assumed, for example, that Reclaim is always accompanied by at least equal Natural content, then the over-all accuracy of the analytical method may be put at about ±5% for Reclaim-containing mixtures.

136. The seriousness of Reclaim interference with GR-S/ Natural analysis is minimized to some extent by the fact that the presence of Reclaim can be recognized for a wide range of compositions, so that for these compositions the reliability of the analytical results may be ascertained. In the absence of Reclaim, determinations for both GR-S and Natural can be made only for samples containing approximately equal proportions of the two components (see Plate 48), and in these cases (see Table XIV) the sum of the measured concentrations is 100% within the limits of experimental error. When Reclaim is present in sufficient quantity to cause serious interference, however, determination of both components becomes possible over a much wider range of compositions (see Table XV), and in every case the sum of the measured concentrations deviates appreciably from 100%. Hence, it is possible to recognize the presence of an interfering component such as Reclaim whenever it is present in concentrations great enough to cause serious error in the results. For this reason, measurements both at 6.70 and at 7.25 mu should always be obtained whenever possible.

137. The analytical error resulting from the presence of Reclaim in Natural/ GR-S mixtures is due either to abnormally strong Reclaim absorption at 7.60 mu (the reference wavelength) or to abnormally weak absorption at 7.25 mu (the Natural analysis wavelength) as compared to Natural stocks. The fact that the errors are more pronounced for Natural determination than for GR-S determination indicates that the latter condition exists. The 7.25 mu band has been correlated with the presence of methyl ($-CH_3$) groups (Appendix C), and the decrease in the relative intensity of this band for Reclaim must be attributed to a decrease in methyl content. Although the significance of this interpretation of these experimental results may be of importance to a consideration of the molecular structure of Reclaim as compared to that of raw Natural, it offers no suggestion for improvement of the analytical method considered here.

138. The applicability of the method, then, will vary to some extent with the type of rubber encountered in the mixture to be analyzed. For those containing a high-grade Natural stock the analytical results can be made accurate to within ±1%, while for those containing a low-grade stock, such as Tube Reclaim, the results will be accurate only to within approximately ±5%. But in most cases, the presence of this greater uncertainty may be recognized. Since infrared methods do not permit analysis of Natural and Reclaim mixtures because of their common molecular structure, it is unfortunate that some quantitative differences in their spectral absorption exist and thereby limit the accuracy of results for Reclaim-containing Natural/GR-S mixtures. In view of the basis of the analytical method, however, the accuracy of the results under the severe conditions imposed by the presence of Reclaim is considered surprisingly good.

(3) Work at Other Wavelengths

139. Since the interference of Reclaim in the analytical method, although surprisingly small, left something to be desired in accuracy of results, the possibility of improved accuracy was considered. Although previous choice of spectral measurements was considered best of those available for analytical work, selection of other measurements was again considered. The interference of Reclaim in the Natural determination indicated the desirability of a better band for this determination. Unfortunately, the only other Natural band which appears useful is that of 11.95 mu, and it has already been confirmed by several spectra (Plates 7 to 9, and 22 to 25) that the intensity of this band is not consistent, especially for Natural and Reclaim samples. Attention was directed, therefore, to the use of the strong GR-S bands at 10.35 and 10.95 mu with the hope that a more sensitive GR-S determination might render the errors in the Natural determination relatively less important.

140. As mentioned in para. 122, the intensity of these GR-S bands depends upon the amounts of 1:4 and 1:2 addition, respectively, so that if the analytical results are to be independent of the mode of addition, some combination function of these bands must be used. For the purpose of determining the advantage of using these bands for Reclaim-containing mixtures, however, it was unnecessary to determine such a function, since the mode of addition was invariant for the single GR-S stock used in this work. Accordingly, the functions $(E^{10.35}/E^{10.70})$ and $(E^{10.35}/E^{11.40})$ for measuring the intensity of the 10.35 mu band and $(E^{10.95}/E^{11.40})$ for that of the 10.95 mu band were employed, the 11.40 and 10.70 mu bands serving in place of the 7.60 mu band as thickness references.

141. These functions were measured first for the three preparations of the standard blends (para. 129), and working curves for each function were constructed (Plate 49). The reproducibility was determined as before and all results are shown in Table XVI. These GR-S determinations were only slightly less reproducible than those using the original method (av. deviation = ±2.0% as compared to ±1.0 %), and the working curves were linear over the range 0 to 60% GR-S. These working curves were then used for analysis of the Reclaim-containing mixtures (para. 133), and the results are presented in Table XVII. The accuracy here is seen to be inferior to that obtained using the original method (para. 134). Since no improvement was obtained by using these more intense GR-S bands, there appears but little hope of improving upon the original method for infrared analysis of Natural/GR-S mixtures.

D. General Conclusions Regarding Quantitative Analysis.

142. It has been shown in the preceding sections that accurate determination of the elastomer composition of typical Natural/GR-S mixtures can be made by appropriate spectroscopic measurements. For high-grade stocks an average error of ±1% has been established for the over-all method and is virtually independent of the compounding and curing conditions of the specimen. Even the presence of Natural Reclaim in the mixtures does not lessen the accuracy by a serious amount, and in most cases cognizance of the actual accuracy may be had by the analyst. The method involves no exacting experimental techniques, either in sample preparation or in spectral measurement; and the work requirement does not appear unreasonable, especially if the method is considered on a routine basis. Since the principles involved in this example analysis are in no way limited to Natural/GR-S determination, an analogous approach could be made successfully toward methods of analysis for other mixtures of elastomers. In certain polymer combinations some differences in the basic requirements of the method will be encountered, and these differences are considered briefly in the following paragraphs.

143. For each analytical method there exists the problem of selecting the optimum bands and functional combination thereof to be used as a measure of concentration only. It is particularly important that such selections be based upon a structural interpretation of the various bands considered, since the intensity of some bands may vary with some particular form of structure, such as the mode of addition, rather than with the total quantity of a given type of polymer. This arises from the fact that not all polymers are unique, and by the same token the analytical results will not be unique if these considerations are not taken into account. In selection of reliable analytical wavelengths, then, the degree of reproducibility of the elastomer with respect to the structures involved is an important consideration, and each selection should be checked experimentally, using specimens from various sources.

144. The number of spectroscopic functions to be considered must equal the number of independent composition variables involved. This is true even for a simple blend of only two structural units, although theoretically one of the two components might always be determined by difference; for the maximum accuracy is obtained when each component in turn is determined directly in its lower range of concentration. Mixtures of single-unit polymers, such as Natural, Butyl, Neoprene, allow the use of the simplest analytical scheme. Since the recurring units in each of these polymers are all alike (although the mode of addition may vary as in head-to-head or head-to-tail addition), any band originating in the vibrations of the structural units will vary only with the total numbers of units and thus may be used as a measure of concentration. For a mixture, measurement of one band for each elastomer is all that is required for analysis. A third wavelength may or may not be employed as an internal standard for elimination of thickness effects.

145. The presence of a copolymer in a mixture involves at least one additional variable since, structurally speaking, a copolymer is a mixture of two types of structural units. To determine the composition of a polymer-copolymer mixture it is requisite, therefore, that three components be determined (by measurement of three bands). Thus, a Natural/Buna-N analysis requires determination of isoprene, acrylonitrile, and butadiene units, and a Natural/Buna-S analysis requires determination of isoprene, styrene, and butadiene units. (In the Natural/GR-S analysis presented in this report, GR-S was considered a particular type of

Buna-S, and the analysis became a special case in which only isoprene and styrene units were determined, it being assumed that a fixed relationship existed between the number of styrene and butadiene units.) In addition, for a copolymer such as Buna-N or Buna-S two types of addition (1:2 and 1:4) may exist, and this introduces a fourth variable. Therefore, bands which depend upon the mode of addition must either be avoided in the analytical method or an additional (fourth) band must be used and both modes of addition be determined.

146. For analysis of a mixture of two copolymers similar considerations lead to the requirement of four bands for determination of the four types of polymer units, and if modes of addition are determined, two additional bands are required, making six measurements in all. In many cases, presence of a common unit in each copolymer will permit simplification of the analytical procedure. Buna-N/Buna-S mixtures, for example, can be determined rather easily since both the acrylonitrile and styrene units may be accurately determined independently of the butadiene units.

DETERMINATION OF ACRYLONITRILE IN BUAN-N COPOLYMERS

A. Basis of Method.

147. A second type of quantitative application of infrared spectral analysis to rubber is determination of the quantity of one or more of the structural units comprising some particular type of elastomer. Examples of this are: determination of the styrene content of Buna-S copolymers, determination of the acrylonitrile content of Buna-N copolymers, determination of the relative amounts of 1:4- and 1:2- addition structures in the various butadiene synthetics, etc. In addition to the analytical usefulness of such results, e.g., in differentiating between low- and high- nitrile Buna-N's, quantitative structural determination is of special value in studying the course of copolymerization, thereby enabling correlation of the elastomer structure with the conditions of preparation on the one hand and with the resulting performance characteristics on the other. In the present section a method for determination of the nitrile content of Buna-N copolymers is considered and experimentally confirmed. Completely analogous methods would apply to styrene determination in Buna-S, or to determination of 1:4- and 1:2- addition polymer units. The nitrile analysis was considered of immediate practical importance since a variety of Buna-N's with acrylonitrile contents from 18 to 45% are in current industrial use.

148. While total nitrogen determination by Kjeldahl methods has commonly been employed, this determination is equivalent to nitrile analysis only on the assumption that the nitrogen thus determined is combined in no other way. On the other hand, entirely specific determination of the nitrile structure can readily be made by measurements of the infrared absorption band at 4.47 mu, since this band is uniquely associated with the nitrile structure (Appendix C). This band is strong and sharp, and is completely isolated with respect to all other absorptions found in elastomer spectra (in which sense it affords an immediate tag for all nitrile rubbers).

149. The experimental method of approach for acrylonitrile determination is completely analogous to the method employed in the previous section for Natural/GR-S analysis, and the considerations of para. 121 and 123 apply equally here. Of these two types of determinations the present one is in many respects the simpler, since a preassumed correlation between the structural unit measured and total elastomer quantity is not involved. Also, in most applications structural determination is applied only to samples containing a single elastomer type.

In many cases the sample will be a relatively pure reaction product, thereby permitting application of a simplified sample preparation scheme.

150. The preparation of either cured or uncured Buna-N samples for infrared analysis presents in general no limitations to the method, since complete solution of either can be achieved (para. 56 and 99). (While desirable, this is probably not a necessary requirement here, since the numerous spectra obtained in Part II consistently proved to be reproducible whether or not complete solution was accomplished.) With regard to the spectroscopic requirements, the 4.47 mu band mentioned above is ideal for sensitive nitrile determination by reason of its occurrence in a broad region of otherwise uniformly high transmission; and the sole spectroscopic problem involved is that of deriving a spectral function independent of sample thickness. This is readily done by measuring the nitrile absorption at 4.47 mu relative to the C-H absorption at 3.50 mu, using the corresponding ratio of the extinction values, $E^{4.47}/E^{3.50}$, (para. 123). This function furnishes a sensitive measure of nitrile concentration only; and since both bands permit accurate transmission measurement for acrylonitrile contents between 15 and 45%, the function is useful for all Buna-N's of industrial importance.

151. When values of this function have been plotted versus the acrylonitrile contents for a series of known samples, the resultant working curve enables determination of future samples by the converse procedure. The curve thus constructed will not go to zero at 0% acrylonitrile (i.e., for pure polybutadiene), since perfect transparency at 4.47 mu will never be obtained because of surface scattering and slight general absorption of the film of sample. Although this factor is scarcely noticeable for band strengths corresponding to more than 15% acrylonitrile, the errors due to surface scattering cannot be disregarded for low nitrile concentrations. This factor can be eliminated very effectively by choosing as "100% transmission" the transmission of the sample film itself at a nearby region of minimum absorption (e.g., 4.60 mu) rather than the transmission of a "blank" plate at the analytical wavelength (4.47 mu). In this way the scattering losses are eliminated from the percentage transmission values of the sample film at the analytical wavelengths. (Transmission percentages thus corrected will be indicated by parentheses in the following paragraphs.) Using corrected transmission values, the corresponding extinction ratios then give a slightly lower working curve which necessarily goes to zero at 0% nitrile, regardless of surface scattering losses.

B. Presentation of Analytical Procedure.

152. The following procedure is presented for acrylonitrile determination of Buna-N copolymers. The method applies to either gum or finished Buna-N specimens with nitrile contents from 0 to 50%. While accuracy has been the primary consideration in development of the method, the method is simple and reliable and is therefore well suited for routine application. Although no rigid or exacting procedures are requisite to valid results (para. 101), for sake of definiteness specific instructions are given below. Operations adequately described in Part I or Part II of this report are given by reference in order to avoid needless repetition of technical details.

(1) Samples Preparation:

153. For gum rubber a 2-gram sample is cut into narrow strips (para. 33) and extracted for 20 hours using two 70 ml. portions of ethyl alcohol (95%). The extracted sample is placed in 100 ml. of ethylene dichloride, and after

preliminary swelling for 2 hours, solution is completed by blenderization (para. 37). The major portion of the solvent is then evaporated on a hot-water bath (para. 39) to obtain a mucilage suitable for film spreading (para. 40). For cured rubber a 4-gram sample, which has been milled (para. 71), is extracted for 20 hours using two 70 ml. portions of a 68/32 chloroform/acetone blend (para. 73). The extracted sample is then dissolved in 300 ml. of o-dichlorobenzene under reflux, the solvent being used successively in two 150 ml. portions (para. 76). The solution is filtered free of carbon black using Celite Filter Aid (para. 80), and the excess solvent is evaporated by vacuum distillation (para. 82) until a suitable mucilage is obtained for film spreading (para. 40). Of the several operations above, film preparation alone requires particular care, and films of decidedly uneven thickness and irregular surface should not be used.

(2) Spectroscopic Measurements:

154. Percentage transmission of the film is measured at 4.60, 4.47 and 3.50 mu. While this is best done by measuring the deflections alternately for the sample and for a "blank" plate at these fixed wavelength settings, the 4.47 and 3.50 mu bands should first be scanned carefully in order to locate the positions of maximum absorption, since both bands are very sharp. For all nitrile concentrations between 0 and 45% the film thickness should be chosen to give 20 to 25% transmission for the 3.50 mu band. The 4.47 mu absorption will then fall in the range 30 to 60% transmission for nitrile contents between 15 and 45%. For the comparatively unusual cases of less than 15% acrylonitrile it is preferable to use transmission values greater than 60% at 4.47 mu than to go much below 20% for the 3.50 mu band. The following steps are involved in calculation of the analytical functions: (1) The percentage transmission values at 3.50 mu and 4.47 mu are "corrected" for scattering losses (para. 151) by division by the fractional transmission at 4.60 mu. (Since pure polybutadiene absorbs equally at 4.47 mu and at 4.60 mu, this calculation will give in this case the correct result of 100% transmission for the 4.47 mu band); (2) the pair of corrected transmission values are converted to exteinction values by the relationship, $E = \log_{10}(1/T)$; (3) the ratio $E^{(4.47)}/E^{(3.50)}$ is formed. This ratio is plotted as a function of nitrile content for a sufficient number of known Buna-N's to construct a working curve, (Plate 50), and future samples are then determined by the converse procedure of applying the ratios measured to this working curve. Because of the narrowness of the bands in comparison to the spectral slit widths employed, the slope of the working curve is to some extent determined by the particular instrument and operating conditions used. Accordingly, the working curve in Plate 50 may not be valid for work in other laboratories, and a reliable curve should be determined as indicated above. The reliability and accuracy of the analytical results will be considered in the following paragraphs on the basis of experimental results obtained by application of the method to a representative variety of Buna-N copolymers.

155. In application of this method the time required for acrylonitrile determination is largely that required by the sample preparation. While this cannot be reduced below four days, a number of samples can be prepared simultaneously, and the time-requirement for routine application is approximately 6 man-hours per sample (para. 102).

C. Experimental Results and Discussion.

156. The experimental reproducibility of the proposed method was tested by applying the procedure to the following eight pure gum Buna-N's: Perbunan -18,

-25, -35, Chemigum-N-1, -2, -3, Hycar-OR-15, and -25. A number of films of each sample were measured, and the results are presented in Table XVIII under the designation Set 1. In order that the reproducibility might be evaluated in terms of percentage acrylonitrile, the nitrile contents of the eight samples were determined independently by Kjeldahl analysis (on the assumption that all nitrogen present was thus combined), and the best average curvewas drawn through the points obtained by plotting the measured extinction ratios versus the calculated Kjeldahl results for the eight samples (para. 154). This curve appeared nearly linear over the 20 to 42 % range of the eight samples and included all the points reasonably well except those for Hycar-OR-25. (This curve, because of its limited range, is not given in the report but is identical with curve (1) shown in Plate 50.) These same extinction ratios were than applied to this average working curve to obtain the "analyses" presented in Table XVIII. This work was in a sense preliminary since the optimum procedures of measurement had not been established. While a few of the transmission values were obtained by spot measurements, most were simply measured from recorded spectra of the sample and of a "blank" plate run at slow speed (para. 42). Also, no transmission measurements at 4.60 mu were obtained, nor was a correction applied for scattering (para 151). In addition, the films studied included many of greatly different thicknesses in order that any dependency of the analytical results on this factor might be shown. Nevertheless, the analytical results show a mean deviation equal to ±1%, and the maximum error is only rarely equal to twice this figure. The errors obtained are in no way consistent with film thickness variations and must be attributed largely to differences in the quality of the films.

157. The over-all method of analysis then was critically tested by preparing a set of the same Buna-N's which had been compounded and cured as finished rubber products (see Table VI, F-421) and applying the extinction ratios measured for these cured specimens to the working curve for the pure gum samples. These results are designated Sets 4a and 4b in Table XVIII. The agreement with the pure gum samples is seen to be fully as close as the reproducibility obtainable in either set for different films of the same sample. This is the most severe test of the method that could be applied, and shows the complete reliability of the over-all procedure on the one hand and the importance of obtaining high-quality films on the other.

158. For extension of the analytical working curve below 20% a special set of ten pure gum Buna-N copolymers covering the range 0 to 40% was obtained from Firestone Rubber Co. These samples were prepared in duplicate, and several films of each were measured. These measurements included the transmission at 4.60 mu, and extinction ratios were calculated both from corrected and uncorrected transmission values for comparison purposes. Using "total nitrogen" values supplied with the samples for calculating the "true" acrylonitrile contents, average working curves for each method of measuring the analytical function were constructed over the range 0 to 40% (Plate 50), enabling expression then of the measured extinction ratios as percentage acrylonitrile. For the uncorrected function the working curve in the 20 to 40% region was identical within the limits of the experimental error with the previous curve (para. 156), thus establishing the equivalence both of the spectroscopic results and of the chemical analyses for both series of samples. The analytical results for the Firestone samples are presented in Table XIX. The reproducibility of the results for the corrected and for the uncorrected functions is very nearly equal for samples containing above 15% acrylonitrile and corresponds to an average error of ±1.5%. Below 15% the corrected function maintains this accuracy, while the

uncorrected function is considerably less reliable. The errors involved can be attributed entirely to differences in the quality of the films, since the two preparations of each sample give results agreeing as closely as do duplicate analyses on the same sample, and since results with good-quality films of different thickness show the results to be independent of sample thickness. Since some preparations of the Firestone samples (7 to 10) were gelatinous, the films studied in this work differed greatly in quality; and, although only the best films were used, the errors in Table XIX probably represent an unusually severe check on the method. An accuracy of ±1% is therefore considered generally obtainable in practice. In the case of Sample #9 (see Table XIX), the films measured were very coarse; the results here show in a most significant meanner the merits of employing the scattering correction. While as much as 50% of the total "absorption" resulted from scattering losses (with the result that the uncorrected results were highly erroneous) the corrected results are well within twice the average error.

159. As a result of the superior reliability of the corrected function, it was desirable to obtain similar measurements on the original set of commercial Bun-N's (para. 156). Since insufficient quantities of the earlier preparation of the gum samples remained, a second preparation (identical with the first) was made of each sample. The cured samples previously prepared had dried out, but were redissolved in a minimum of o-dichlorobenzene and used as such. Measurements made on films of these samples were converted into acrylonitrile "analyses" using the working curbes established with the Firestone samples (Plate 50), (para. 158). The results for the gum samples are designated Set 3 in Table XVIII, and those for the cured samples are designated Set 4c. Except for Perbunan-35 of Set 3, which was badly gelled, the accuracy corresponds to an average error of ±1% for either the corrected or the uncorrected function. For Perbunan-35 (Set 3), the films of which were very coarse, scattering losses contributed nearly half the measured "absorption", and only the corrected function gave accurate results.

160. In conjunction with these improved measurements on the commercial samples, still an additional preparation of the gum samples was made without ethanol extraction. Measurements were made similar to those described above and are designated Set 2 in Table XVIII. While excellent reproducibility was obtained for duplicate measurements, in certain cases the analytical results deviated from the correct values by an error of nearly 3%. In view of the 1% average error established in the previous work, this 3% inaccuracy for certain samples of this set undoubtedly was due to the presence of appreciable unextracted impurity. This interpretation is consistent with the fact that the erroneous "analyses" were too low, inasmuch as impurity would generally contribute to the C-H absorption at 3.50 mu but only in very unusual cases (such as the presence of unreacted acrylonitrile) to the nitrile absorption at 4.47 mu. These results do not detract from the stated accuracy and reliability of the method, which is definitely established by the consistency of all the other work done, but do show that purification of the elastomer by extraction is a necessary part of the sample preparation if the highest accuracy is to be assured.

161. The results that have been presented in the previous paragraphs attest to the reliability of the proposed method for acrylonitrile determination in Buna-N copolymers. An accuracy of ±1% is considered obtainable in general application of the method either to gum or to finished Buna-N specimens. In obtaining this accuracy films of good quality are necessary but no further exacting requirements are demanded of the analyst. Although a good working rule is given (para. 154) for selection of sample thickness, this factor is without effect on the

results. A very simple correction for scattering losses superimposed on the actual absorption is entirely adequate and enables accurate results to be obtained in cases involving films which scatter as much as 40%. The actual accuracy of the particular analysis is also to some extent indicated by the correction required. In view of the very minimal experimental requirements of this method, the analytical procedure is well adapted for routine use and compares in this respect favorably with the usual chemical methods, such as Kjeldahl analysis. The greatest advantage that can be claimed for the spectroscopic determination is that it is completely specific, and in most applications this more than offsets any minor advantages of lesser work requirement and possibly higher precision (but not reliability!) that might be claimed for the standard chemical methods now in use.

D. General Conclusions and Further Applications.

162. It has been shown in the preceding section that accurate determination can be made of the acrylonitrile content of Buna-N copolymers by measurement of the infrared absorption at selected wavelengths. The method employed applies to specimens of any normal state of cure, and no exacting experimental techniques are requisite to accurate results. The average error obtainable in practice has been established as $\pm 1\%$. Since the principles involved in the analysis described are of general application, other structural determinations could be made successfully by analogous methods. Because of their importance and of the fact that their specific requirements follow logically from much of the work already presented, two further structural determinations will be considered briefly.

163. Determination of the styrene content of Buna-S copolymers presents a problem similar in all respects to that of the preceding section. On the basis of the work done in analysis of Natural/GR-S blends the extinction ratio $E^{6.70}/E^{7.60}$ appears to be a wholly satisfactory function of styrene concentration, independent of film thickness differences (para. 122 and 123). Since both these bands are accurately measurable for styrene contents from 0 to 70%, determination of a reliable working curve for this function (using appropriate samples of known styrene content) will enable accurate analysis of any Buna-S copolymers of industrial importance. Improved accuracy can probably be obtained by applying a correction for background absorption and scattering losses analogous to the correction employed in the nitrile determination (para. 151). For this purpose transmission measurements either at 7.20 mu or at 6.55 mu appear useful.

164. Determination of the 1:4 and 1:2 addition structures comprising a polymer or copolymer is an important problem with applications to synthesis and production control. For the common butadiene elastomers - Buna-S, Buna-N, and polybutadienes such as German Buna-85 - the 1:4 addition structure (which is of the type $R_1 CH = CHR_2$) gives rise to a strong band at ca. 10.35 mu, while the 1:2 addition structure (which is of the type $R_1R_2C = CH_2$) gives rise to a strong band at ca. 10.95 mu and also to a weaker band at ca. 10.02 mu (see Appendix C). While the extinction ratio $E^{10.35}/E^{10.95}$ would be a function only of the ratio of 1:4- to 1:2- addition, accurate measurement of this function is feasible only in a limited range (para. 123). For accurate determinations on a polymer having low amounts of either structure it would be necessary to employ a function involving only this structure and some "indifferent" band for use as a thickness index. For this purpose the 7.60 mu band appears useful. Good accuracy would further require elimination of the rather large variable background absorption in this region from the intensity measurements. This probably could be done by considering the transmission at 11.4 mu or at 9.7 mu as "100% transmission". If

this were done it seems justifiable to expect an accuracy of ±2% and probably twice this good. Work with appropriate samples of known structural content would be necessary to show whether the working curve determined for a particular type of butadiene copolymer would apply with equal validity to the butadiene structures of Buna-S, Buna-N, and sodium-polymerized polybutadiene rubbers.

GENERAL SUMMARY AND CONCLUSIONS

165. In Parts I and II of this report reliable procedures have been developed for isolating and examining spectroscopically the total polymer content of any rubber specimen. This work has involved obtaining spectra of gum and cured "rubber" of more than a dozen types, and it has been shown conclusively that:

(1) the various classes of elastomers possess characteristically different spectra; and

(2) these characteristic spectral features are always reproduced, independently of widely different conditions of cure and compounding or of sample preparation treatment.

Entirely adequate experimental and spectroscopic basis exists therefore, for characterization of unspecified rubber materials by spectral examination, the only limitation being ultimately the degree of spectral differences involved. In view of the uniqueness of the various elastomer spectra, no difficulty exists in recognizing the basic class of any single type of elastomer, and a more detailed comparison shows that any two elastomers when in binary mixture can be recognized in a concentration of 5% or greater. Such analysis simply involves systematic checking of the unknown spectrum against suitable reference spectra of pure elastomers.

166. The additional problems involved in quantitative analysis of elastomer mixtures have been studied for the particular case of Natural/GR-S blends. While accurate measurement or control of film thickness has long been recognized as a major problem in quantitative measurements on solids, the desired result has been achieved very simply by measuring the intensity of the absorbing structure relative to the intensity of an "indifferent" band. The analytical function thus obtained has proven entirely insensitive to great sample thickness differences and has enabled an analytical precision of $\pm 1\%$ to be established as a dependable estimate for the over-all method. Natural/GR-S mixtures containing Natural Reclaim have also been studied, and significant structural differences between high-grade and reclaimed Natural lead to an error of about -5% for high Reclaim contents. However, knowledge of this reduced accuracy can be had in nearly all cases of serious interference. The principles and methods involved in this problem are readily applicable to determination of other elastomer mixtures, and the general spectroscopic requirements for analysis of various types of polymer combinations have been considered briefly.

167. Quantitative determination of copolymer structure also has been demonstrated by nitrile determination of Buna-N copolymers of from 0 to 42% nitrile content. Here, too, a spectroscopic function insensitive to film thickness has been obtained by measuring the nitrile absorption relative to carbon-hydrogen absorption. A number of samples from various sources have been studied, and a uniform accuracy of $\pm 1\%$ has been obtained irrespective of the state of cure of the elastomer or of the sample preparation method. The methods employed are equally applicable to analogous problems, such as determination of the styrene content of Buna-S, or determination of the relative quantities of 1:4- and 1:2- addition units; and the spectroscopic requirements of these cases have been considered briefly.

168. It is concluded, therefore, that the methods of infrared spectroscopy are adaptable to investigation of the elastomer content of finished rubber products consisting of natural rubber or any of the common synthetics in typical states of vulcanization, compounding, and reinforcement. It is further concluded that the elastomer spectra constitute an extremely reliable means of identifying the various classes of "rubber" and that simple blends of elastomers can be analyzed quantitatively with an accuracy of the order of a few percent average error. Finally, the spectra of the elastomers afford a valuable means of investigating the molecular structures constituting the rubber polymer, and quantitative structural determination of this same order of accuracy can be made.

RECOMMENDATIONS

169. In view of the results of the present investigation, the methods of infrared analysis are generally recommended for determination of elastomer content of rubber products in all cases where the identity or structure of the elastomer is of particular importance, such as in the research and development stages of new or modified elastomers contemplated for Naval usage.

170. It is recommended that the infrared methods herein presented for quantitative analysis of Natural/GR-S blends and for acrylonitrile determination of Buna-N be considered for routine checking of specifications of material at the various Navy Yards and permanent Naval establishments concerned with large scale inspection of rubber products. It is further recommended that field tests of these methods and of similar methods of importance to Naval inspection be established for evaluation and comparison with existing methods.

171. It is also recommended that standard commercial instruments, such as the Perkin-Elmer Model 12-B Spectrometer or the Beckman Model IR-2 Spectrometer, be employed instead of special research-type equipment for routine infrared analysis of rubber products.

ACKNOWLEDGEMENT

The help of Dr. Peter King and Mr. Ralph Taylor, NRL High Polymer Section, and of other members of their section, especially Mr. Ferdinand Thurman who prepared the standard rubber samples and Mr. Donald Cohen who performed the nitrogen analyses, is gratefully acknowledged.

BIBLIOGRAPHY

(1) Barnes, Liddel, Williams - "Synthetic Rubber, A Spectroscopic Method for Analysis and Control", Ind. Eng. Chem., Anal. Ed. 15 (1943), 83-90.

(2) Barnes, Williams, Davis, Gieseke - "Physical Methods of Analysis of Synthetic and Natural Rubber", Ind. Eng. Chem., Anal. Ed. 16 (1944), 9-14.

(3) Barnes, Gore, Liddel, Williams - "Infrared Spectroscopy, Industrial Applications and Bibliography", (Reinhold (1944)).

(4) Sears - "Infrared Spectra of Rubber and High Polymers", Journal of Applied Physics, 12 (1944), 35-40.

(5) Thompson and Torkington - "Infrared Spectra of Compounds of High Molecular Weight", Trans. Faraday Soc., Vol. XLI, nos. 4 and 5 (1945), 246-260.

(6) Sheppard and Sutherland - "Some Infrared Studies on the Vulcanization of Rubber", Trans. Faraday Soc., Vol. XLI, nos. 4 and 5 (1945), 261-279.

(7) Sutherland, Thompson, and others - "The Application of Infrared Spectra to Chemical Problems", Trans. Faraday Soc., Vol. XLI, nos. 4 and 5 (1945), 171-295.

(8) Tentative Methods of Chemical Analysis of Rubber Products, A.S.T.M. Standards Supplement, Part III (1943), Section D, 297-43T.

(9) Williams and Taschek - "Effect of Stretch on the Infrared Absorption Spectrum of Rubber", J. Applied Physics, 8 (1937), 497.

(10) Hall, Hauser, and others - "Electron Microscope Studies of Natural and Synthetic Rubber Fibers", Ind. Eng. Chem. 36 (1944), 634-640.

(11) Wright - "Application of Infrared Spectroscopy to Industrial Research", Ind. Eng. Chem., Anal. Ed. 13 (1941), 1-8.

(12) Gore - "Infrared Spectroscopy as an Organic Analytical Tool", J. Chemical Education, 20 (1943), 223-9.

(13) Williams and Dale - "Further Studies on the Infrared Absorption of Rubber", J. of Applied Physics, 15 (1944), 585-591.

(14) Stair and Coblentz - J. Research Nat. Bur. of Standards, 15 (1935), 295.

(15) Williams, D. - "Infrared Absorption of Rubber and Related Hydrocarbons", J. Chem. Phy. 4 (1936), 460.

(16) Williams, D. - Physics 7 (1936), 399.

(17) Wells - J. Applied Physics 11 (1940), 137.

(18) Fox and Martin - Prac. Roy, Soc. A, Vol. 175 (1940), 208.

(19) Thompson and Torkington - "The Vibrational Spectrum of Acrylonitrile and of Perbunan", J. Chem. Soc. 11 (1944), 597.

(20) Mottlau - A.P.I. Report Serial No. 26, (1943).

(21) McAlister, Matheson and Sweeney - "A Large Recording Spectrograph for the Infra-Red to 15 mu", R.S.I. 12 (1941), 314.

APPENDIX A

GLASS CONDENSER FOR DIRECT USE WITH STANDARD ASTM "EXTRACTION" FLASK.

The glass condenser designed to replace the metal condenser of the standard ASTM reflux assembly is shown in Plate 21. The condenser is of the "cold-finger" type. Satisfactory seal for virtually complete condensation of vapor is achieved simply by loose contact of the largest condenser bulb with the flask neck. This has been tested with a solvent of high volatility, acetone, which was refluxed for 36 hours without appreciable loss. The avoidance of a more complicated seal was desirable in permitting the standard ASTM flasks to be used without addition of ground joints or other alteration. This is advantageous in rubber work, where charred residues in the flask frequently make discarding the flask more economical than cleaning. The glass condenser, therefore, was designed conformatory with simplest construction to achieve adequate condensation when used directly with ASTM flasks, enabling replacement of the latter at no unusual expense. The glass condensers used were made in the NRL Glass Technology Shop. They are inexpensive, less than two hours being required for construction.

Since in the present work pyridine and p-cymene reacted appreciably with the copper plate of the metal condensers, while unavoidable free hydrochloric acid in the tetrachloroethane completely perforated the tin coils, the all-glass condenser-flask assembly was far superior in inertness, while being no less effective or convenient in use. A particular further advantage was the ability to clean the glass condenser thoroughly in oxidizing-acid mixtures. In contrast, bits of rubber on the tin-coil condenser could not be removed adequately and largely went unnoticed before such cleaning of the glass condensers showed the presence of spattered rubber. Unquestionably the glass condenser permits far greater reliability and usefulness with respect to maintaining purity of the sample.

APPENDIX B

INVESTIGATION OF THE FILLER SEPARATION METHOD OF BARNES[2]

The method developed by Barnes (para. 64) for removal of carbon-blacks was tested critically in the following manner: Specimens of natural rubber and of Chemigum-N-1 were compounded and cured identically with Furnex (carbon black) as filler. A 4-gram sample of each was dissolved in 250 ml. of o-dichlorobenzene, and the resulting black "solutions" of rubber and colloidal carbon were diluted with n-hexane to a total volume of 400 ml. Within 30 minutes the Chemigum solution was clear several inches from the top, and was completely clear in six hours. Despite greater hexane dilution, the solution of natural rubber remained black and entirely without carbon black precipitation during several days of observation. The black residue in the Chemigum flask was highly rubbery and could not be redispersed by stirring. Re-solution in o-dichlorobenzene (by reflux) and subsequent filler removal by "Celite" filtration yielded a solution containing appreciable Chemigum. It might be added that the supernatant solution obtained by the first carbon black precipitation was nearly colorless - much lighter than equivalent solutions of Chemigum freed of carbon black by "Celite" treatment.

These results conclusively show the mechanism to be partial precipitation of the rubber by the hexane dilution, and subsequent precipitation of the filler by occlusion. Accordingly, such treatment is highly selective, and use of this technique would virtually eliminate accuracy in quantitative analysis.

APPENDIX C

STRUCTURAL INTERPRETATION OF ELASTOMER SPECTRA

Natural Rubber

It is generally agreed that natural rubber consists of long chain-like molecules composed of isoprene units to give the recurring skeleton:

$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

All of the strong bands in the spectrum are consistent with this structure.

Wavelength (mu)	Absorbing Structure
3.37	$-CH_3$ (Methyl groups)
3.42	$>CH_2$ (Methylene groups)
3.50	CH_3 , $>CH_2$
6.00	$>C=C<$ (Valence vibration)
6.90	$-CH_3$, $>CH_2$ (deformation vibration)
7.25	$-CH_3$ (deformation vibration)
11.95	$-\overset{CH_3}{\overset{|}{C}}=CH-$

The 3.37 band is not resolved in most of the spectra presented here (Plates 7 to 9, 22 to 25) because of too intense absorption obtained for the film thickness studied. Actually, several additional unresolved bands determine the exact contour of the 3.4 mu absorption region and thus confuse the assignment of the absorption to definite vibrations. However, the above correlations are consistent with the spectra of a large number of hydrocarbons which have been examined with this equipment and agree with the frequencies assigned to the stronger C-H bands by Fox and Martin. (18). The 3.67 mu band is undoubtedly a combination or harmonic of C-H frequencies, since it is characteristic of nearly all hydrocarbons. Similarly, the 2.32 mu band is common to all hydrocarbons and is probably a combination frequency for the 3.42 and 7.25 mu vibtations. Sheppard and Sutherland (6) suggest that the absorption around 3 mu is composed of a band at 3.1 which is to be distinguished from hydroxyl (oxidation) absorption at 3.0 mu. Increased resolution obtained here has located this band at 3.05 mu while the hydroxyl oxidation absorption which appears in the spectra of vulcanized and reclaim samples occurs at about 2.9 mu. The latter absorption undoubtedly originates in oxidation impuirities, since it corresponds to the hydroxyl valence vibration frequency; but the 3.05 mu band appears to be characteristic of the rubber polymer, although it is masked by strong hydroxyl absorption in some of the spectra. This 3.05 mu band has previously been assigned (6) either to a combination frequency or to the fundamental of the H vibration relative to a

tertiary carbon atom (-CH=). The latter assignment does not seem plausible since there is considerable evidence (18) that this fundamental occurs at approximately 3.30 mu.

Sheppard and Sutherland (6) report a new band at 4.98 mu which has not been confirmed here. Only for one sample was there any indication of this band, and it is concluded that it originates in an impurity. However, most hydrocarbons have weak bands in this spectral region, and under proper conditions (using a thick film) a band at 4.93 mu would be expected in the spectrum of natural rubber. All other bands found by Sheppard and Sutherland are also found in the spectra presented here.

The weak bands in the region of 5.8 mu are due to carbonyl oxygen (C = O) resulting from oxidation, and, as for the 2.9 mu hydroxyl absorption, these impurity bands are much stronger for reclaimed and cured samples. The olefinic abs orption at ca. 6.0 mu varies with structure, terminal olefin linkages (vinyl groups) absorbing at 6.10 mu, internal double bonds absorbing at slightly shorter wavelengths and in general at much less intensity, and double bonds at braching centers usually absorbing at slightly different wavelengths than the corresponding unbranched structure. The olefin absorption for the normal rubber skeleton appears to absorb at exactly 6.00 mu, and the weaker absorption at ca. 6.1 mu is probably contributed by olefinic groups modified by removal from methyl branching centers or by their proximity to the ends of the polymer chains, for example.

The absorption ca. 6.5 mu is not consistent in the various samples studied. This band was found by Barnes (1) but not by Sheppard and Sutherland (6) and is probably due to an impurity. The latter authors attribute a band at 6.52 which they found in some cases to the presence of stearates. It has also been shown here that most soaps of stearic acid absorb strongly at this wavelength, and the absorption of natural gum rubbers in this region probably results from the presence of unextracted vegetable soaps or esters. It is noted that after vulcanization, which would tend to decompose these impurity compounds, the absorption at 6.5 mu tends to become weaker.

The bands ca. 6.9 and 7.25 mu are characteristic of hydrocarbons and correlation of a large number of compounds has shown the 6.8 to 6.9 mu band to increase with the concentration of methylene groups while the 7.25 mu band increases with methyl groups. The first of these bands also appears in the absence of methylene groups (neopentane and 1,1-dineopental ethane, for example) and must be associated with vibrations of both methyl and methylene groups. The assignment of these bands to the CH deformation frequencies (3), (5), (6) is unquestionable.

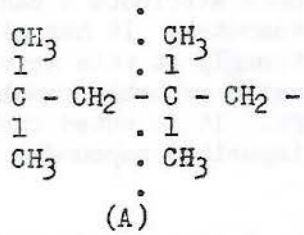
The bands beyond 7.5 mu are, in general, determined by the whole molecule or by molecular groupings larger than those involved in a single linkage, and as yet it has been impossible to correlate absorption with structure of natural rubber except for a few bands in this region. In addition, correlations which have been found for liquid hydrocarbons are not accurately applicable to the rubber spectra, since considerable variation in position and intensity of absorption occurs with change of state. However, the absence of a pair of bands at 10.1 and 11.0 mu indicates the absence of R-CH = CH_2 groups (where R = alkyl) in natural rubber, and similarly the absence of 10.35 mu absorption indicates

the absence of R-CH = CH - R groups. Apparently all double bonds occur at branching positions. Branching at the double bond generally shifts the C-H deformation frequency in this region to longer wavelengths. 2-methyl- 1-heptene absorbs at 11.25 mu, and since this structure corresponds to that of a terminal isoprene unit, the natural rubber absorption at 11.25 mu may result from $R-(CH_3)C = CH_2$ structure at the ends of the molecules. On this basis, the 11.25 mu band would be expected to vary with molecular weight. Althought variation in the intensity of absorption in this region has been observed, no correlations with molecular weight have been made nor has this correlation been established. The strong band at 11.95 mu has been assigned by Thompson and Torkington (5) to type $R_1R_2C = CHR_3$ structures, and this corresponds to the structure of natural rubber at the internal double bonds, provided that R_1 or R_2 is methyl. For compounds which have been observed at this Laboratory this correlation does not hold when R_1 and R_2 are identical.

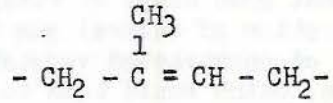
Finally, the band at ca. 13.5 mu may originate from the presence of methyl substitution on the hydrocarbon chain, since nearly all hydrocarbons with methyl substitution absorb in this region except when the substitution is near the end of the chain.

GR-I

Butyl rubber, or GR-I, designates a class of elastomer prepared by low-temperature copolymerization of isobutylene with a very small percentage of a diolefin, e.g., isoprene. On the basis of considerable chemical evidence the structure of the copolymer undoubtedly consists of long-chains of head-to-tail polyisobutylene units (A) separated occasionally by a 1:4- addition isoprene unit (B):

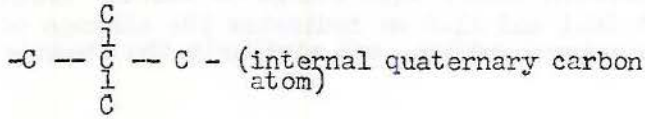


(A)



(B)

While the small olefin content of the copolymer (about 0.6 mol percent) contributes the necessary property of vulcanizability, the infrared absorption is insensitive to so small a quantity of double bond and accordingly indicates only the recurring polyisobutylene structure. The spectrum of GR-I thus corresponds to that of pure head-to-tail polyisobutylene (5), and all the prominent bands correlate entirely with structure (A).

Wavelength (mu)	Absorbing Structure
ca. 3.40	$-CH_3$, $>CH_2$
6.80	$-CH_3$, $>CH_2$ (deformation vibration)
7.20) 7.30)	$-CH_3$ (deformation vibration (two methyls on same carbon atom))
8.13	 (internal quaternary carbon atom)

The band at ca. 3.40 mu and the band at 6.80 mu are characteristic carbon-hydrogen vibrations found in all aliphatic hydrocarbons. The 3.40 mu band is resolved in only one of the spectra (Plate 27), showing the characteristic $-CH_3$ (3.38 mu) and $>CH_2$ (3.44 mu) absorptions. There is no band at 3.50 mu, and the reason for this is not known. The small band at 3.67 is characteristic of nearly all hydrocarbons and is generally considered to be a combination or harmonic of CH frequencies. The strong doublet at 7.20 and 7.30 mu is carbon-hydrogen deformation vibration, and is characteristic of two methyl groups attached to the same carbon atom.

Beyond 7.5 mu the absorption generally correspond to larger groupings. The intense band at 8.13 mu is undoubtedly due to a distoration vibration of the quaternary carbon structure $-C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-$ (5). Interpretation of the remaining bands at 8.56, 10.52 and 10.82 mu is less certain, but their origin certainly lies in distortion vibrations of this same structure, as proposed by Thompson and Torkington (5). A quaternary carbon atom does not seem fundamentally related to these last three bands, however, since many compounds containing an isopropyl or an isobutyl radical have corresponding bands at one or more of these wavelengths. Compounds examined which agree with this conclusion are: 1,1,6 -triisobutylhexane; 1,1,2 -triisobutylethane; 1,1 -diisobutyltridecane; isobutylbenzene; and isopropylbenzene. All but the last of these have bands at 8.55, 10.55 and 10.85 mu, (but not at 8.0 to 8.3 mu). Isopropylbenzene absorbs at 10.85 mu only.

Neoprene

This trade-name designates a variety of elastomers formed by polymerization of chloroprene to give the recurring structure $-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-$.

Superficially, neoprenes resemble natural rubber in that the methyl group of the latter is simply replaced by a chlorine atom. Accordingly, the infrared spectrum of neoprenes is consistent with that of natural if allowance is made for changes that might be expected from this substitution. The prominent absorptions are as follows:

Wavelength (mu)	Absorbing Structure
3.42	$>CH_2$
3.50	$>CH_2$
6.02	C = C (stretching vibration)
6.90 and 6.98	$>CH_2$ (deformation vibrations)
8.92	(Origin uncertain)
12.10	- Cl C = CH - (deformation vibration)

The CH absorptions at 3.42 and 3.50 mu are those common to aliphatic $>CH_2$. For neoprenes these bands are comparatively weak, a result consistent

with replacement of hydrogen with chlorine in any aliphatic hydrocarbon. The absence of a 3.38 mu band is consistent with the lack of methyl groups in neoprene as compared with natural rubber. An unresolved band at 3.30 mu is probably due to CH vibrations where only one H atom is attached to the carbon (18). The 2.90 mu band found in cured neoprenes is an impurity band due to hydroxyl groups resulting from oxidation. Much weaker bands in the carbonyl region between 5.5 and 6.0 mu undoubtedly have a similar origin. The intense 6.02 mu band must be correlated with C = C stretching, although Sears (4) suggests that a harmonic of the 12.10 mu band may contribute here, too. This band also has a poorly defined shoulder at ca. 6.12 mu. The 6.90 band is the usual aliphatic $>CH_2$ deformation vibration. The 6.98 band has a similar origin, butits location is a definite result of chlorine substitution (5).

Beyond 7 mu the bands correspond to larger groupings, and definite interpretation has been impossible for most of these because of insufficient information on related compounds of simple structure. These bands, which come at 7.42, 7.66, 8.16, 8.94, 9.20 and 10.00 mu, are entirely reproducible, and the strong 8.94 absorption is probably the most distinctive feature of the neoprene spectrum (for analytical purposes). The strong band at 12.10 is probably due to CH deformation vibrations associated with the $-\underset{\underset{C}{|}}{Cl} = CH -$ structure, by analogy with the 11.95 mu band of natural rubber. Sears (4) suggests that the weak shoulder at 12.85 mu may be a C-Cl vibration. There seems to be no evidence of bands between 13 and 20 mu, a region in which C-Cl vibrations would be expected.

Neoprene ILS is a polychloroprene modified by a small amount of acrylonitrile. Except for the nitrile absorption at 4.47 mu the spectrum of Neoprene ILS is identical with that of Neoprene-GN and of Neoprene-E.

GR-S

Buna-S is a generic designation for the copolymers of butadiene with styrene, of which GR-S is the particular copolymer formed by emulsion copolymerization of 3 parts butadiene with 1 part styrene. Condensation can occur by either 1:4- or 1:2- addition, giving respectively the structural units

$$-CH_2 - CH = CH - CH_2 - CH_2 - \underset{\underset{C_6H_5}{|}}{CH} -$$

(A)

and

$$- CH_2 - \underset{\underset{CH_2}{|}}{\underset{\underset{H}{|}}{CH}} - CH_2 - \underset{\underset{C_6H_5}{|}}{CH} -$$

(B)

The infrared spectrum of GR-S is consistent with a large mass of chemical evidence in showing the presence of both structures, the following bands being prominent:

Wavelength (mu)	Absorbing Structure
3.42	$>CH_2$
3.50	$>CH_2$
6.10	Aliphatic C = C (stretching)

Wavelength (mu)	Absorbing Structure
6.23	Aromatic C = C (stretching)
6.70	Phenyl ring, C_6H_5-
6.88)) 6.96)	$>CH_2$ (deformation vibration)
10.35	- CH = CH - (1:4 - addition)
10.97	- CH = CH_2 (1:2 - addition) (vinyl group)
13.16	Phenyl ring, C_6H_5
14.28	Phenyl ring, C_6H_5

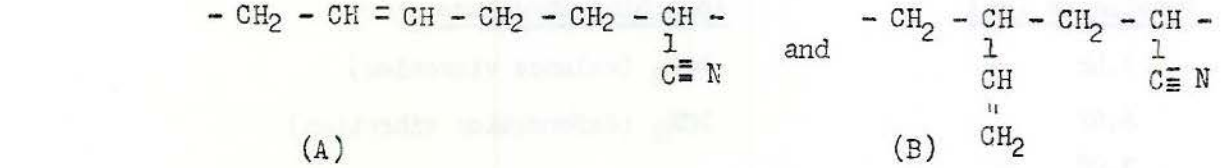
The CH absorption in the 3.4 mu region is not resolved, but the short-wavelength shoulder unquestionably is contributed by aromatic CH absorption at 3.30 mu and possibly also by olefinic CH at ca. 3.35 mu. Aliphatic $>CH_2$ absorption contributes strongly at 3.42 mu. $>CH_2$ deformation bands occur at ca. 6.90 mu. Bands at 2.9 mu and between 5.5 and 6.0 mu are due to oxidation impurities and are therefore weakest in uncured GR-S. A very weak band at 6.00 mu indicates internal olefinic C = C, and a stronger band at 6.10 is characteristic of terminal C = C, while aromatic C = C gives rise to the band at 6.23 mu. The much stronger band at 6.70 mu is characteristic of the aromatic ring.

The bands beyond 7 mu generally arise from larger structures, and those between 7 and 9 mu, while definitely reproducible for GR-S, have not been interpreted. The strong 10.35 mu band is shown by Thompson and Torkington (5) to be characteristic of the structure R_1 CH = CHR_2, and the 10.97 band (and also the weak band at 10.05 mu) are characteristic of a vinyl group, RCH = CH_2, these three bands arising from CH deformation vibrations. The relative strengths of these bands show that 1:4 addition predominates somewhat over 1:2 addition in GR-S.

The two strong bands beyond 13 mu are both due to the aromatic ring. Spectra of alkyl benzenes show that a band at ca. 13.20 mu occurs whenever the alkyl unit adjacent to the phenyl ring is not CH_2, a result consistent with GR-S. The 14.28 mu band is characteristic of the phenyl ring, and is nearly constant in position for all mono-alkyl benzenes.

Buna-N

Buna-N is a generic designation for a variety of copolymers - Hycar OR, Perbunan, Chemigum, Butaprene - formed by emulsion copolymerization of butadiene with 40 to 20% of acrylonitrile. Condensation can proceed by either 1:4- or 1:2-addition, giving respectively the structural units



(A) (B)

The infrared spectra of the above-mentioned elastomers are consistent and show the presence of both structures, the following bands being prominent:

Wavelength (mu)	Absorbing Structure
3.42	$>CH_2$
3.50	$>CH_2$
4.47	$-C\equiv N$ (nitrile group)
6.90	$>CH_2$ (deformation vibration)
10.32	$-CH = CH-$ (1:4- addition)
10.86	$-CH = CH_2$ (1:2- addition) (vinyl group)

The CH bands at 3.42, 3.50 and 6.90 mu listed above are found in all aliphatic hydrocarbons. The sharp band at 4.47 mu is characteristic of nitrile structure ($C\equiv N$), and thus, is a measure of the nitrile content of the copolymer. Bands at 2.9 mu and between 5.5 and 6.0 mu are due to oxidation impurities and accordingly are weakest for uncured Buna-N's. The pair of bands at 6.00 and 6.10 mu, respectively, are due to internal and terminal olefinic C = C valence strecthing vibrations.

The bands beyond 7 mu arise from larger groupings, and those between 7 and 9 mu, while reproducible, have not been interpreted. The strong band at 10.32 mu is characteristic of the structure $R_1\ CH = CHR_2$ (5), and the weaker band at 10.86 mu is characteristic of a vinyl group, $R\ CH = CH_2$, which group also gives rise to the shoulder (on the 10.32 mu band) at 10.00 mu. These bands are said (5) to have their origin in CH deformation vibrations. The great prominence of the 10.32 mu band in this region shows that 1:4- addition largely predominates in the Buna-N's examined. Beyond 11 mu the Buna-N spectra possess no significant bands.

Thiokol

The sulfur-containing elastic resins formed by condensation of sodium polysulfide with ethylenedichloride or its derivatives are commonly called Thiokol rubber. Thiokol-FA is one variety made by reaction of Na_2S_4 with

$$H_2C\begin{matrix}O - CH_2 - CH_2 - Cl \\ O - CH_2 - CH_2 - Cl\end{matrix}$$

(dichloroethylformal)

to give the recurring structure $(-CH_2 - CH_2 - O - CH_2 - O-CH_2 - CH_2-S-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}-)$.

As would be expected, the infrared spectrum of Thiokol-FA bears almost no resenblance to the spectra of the common hydrocarbon-type elastomers. Strong bands are found at:

Wavelength (mu)	Absorbing Structure
3.42	$>CH_2$ (valence vibration)
6.82	$>CH_2$ (deformation vibration)
7.08	

Wavelength (mu)	Absorbing Structure
7.26	
7.82	
8.36	
8.64	
8.98	
9.32	
9.68	
10.53	

Except for the S-H mercaptan frequency at 3.9 mu, which is not present here, very little is known about the characteristic absorption frequencies of sulfur compounds (6) and it is impossible as yet to assign definite bands to S = S, C-S-S-C, or related structures. The single C-H valency frequency at 3.42 is consistent with the proposed structure since only $>CH_2$ groups contribute here and since adjacent substituents have little effect upon this valency vibration. The $>CH_2$ deformation frequency occurs at 6.8 mu, but this vibration may be influenced by adjacent oxygen or sulfur linkages and may possibly account for the entire absorption in the region of 7.1 mu. Aliphatic ether oxygen groups absorb in the region of 9 to 10 mu and may account for the absorption envelope in the region of 8.5 to 10.5 mu in this elastomer. The origins of the discreet maxima in this envelope, however, are not known.

Thiokol-RD

This elastomer, contrary to the usual connection of "Thiokol" with the polysulfide elastic resins, is a non-sulfur containing material, said to be formed by inter-polymerization of butadiene, acrylonitrile, and di-isopropylidene ketone. As a result of lack of information on this unfamiliar elastomer (and the questionable formula of the above-named ketone), the molecular units involved in the interpolymer can hardly be predicted with any completeness. However, it is expected that the structures (A) and (B) characteristic of Buna-N's (which see) would be present plus other structures in some manner involving a ketonic group. The infrared spectrum gives evidence of just such structures, and probably furnishes the best basis for clarification of the structure of Thiokol-RD. The following prominent bands are found:

Wavelength (mu)	Absorbing Structure
3.42	$>CH_2$ (aliphatic)
3.50	$-CH_3$ and $>CH_2$
4.47	$-C\equiv N$ (nitrile)
5.86	$>C=O$ (carbonyl)
6.00	$>C=C<$ (aliphatic)
6.84 to 6.94	$-CH_3$ and $>CH_2$ deformation vibration
7.25	$-CH_3$ deformation vibration
7.38	
10.25	$-RH=CH-$ (1:4 addition)
10.86	$-CH=CH_2$ (1:2 addition) (vinyl group)

The CH absorptions at 3.42, 3.50 and 6.84 to 6.96 mu are characteristic of the structures assigned above and are found in all aliphatic hydrocarbons. The Buna-N part of the molecule is apparent in the nitrile absorption at 4.47 mu and in the CH deformation vibrations for the $R_1CH = CHR_2$ and $R\ CH = CH_2$ structures (5) which come respectively at 10.26 and at 10.86 mu (c.f. Buna N). The very intense 5.86 mu band is characteristic of ketonic carbonyl (C = O). Absorption at 6.00 mu and at 6.14 mu must be associated with C = C stretching vibrations. The 7.25 mu band is unquestionably a CH_3 deformation vibration, and the near-by 7.37 band probably has a similar origin. The bands at 8.53 and 8.94 have not been interpreted. There is also a band at 13.20 mu. This wavelength is frequently associated with aromatic structures, but this is impossible here, and the origin of the band is not known.

TABLE II

SOLVENTS FOR GUM ELASTOMERS

Elastomer	Satisfactory Solvents (a)	Poor Solvents (b)
Natural rubber	nitroparaffins, ethylene dichloride, aromatics	acetone
Butyl (GR-I)	aromatics, nitroparaffins, ethylene dichloride	acetone
Buna-S (GR-S)	nitroparaffins, ethylene dichloride, aromatics	acetone
Thiokol-FA	ethylene dichloride, nitroparaffins	--
Neoprene-GN	ethylene dichloride	aromatics, acetone
Neoprene-ILS	ethylene dichloride	acetone, aromatics
Buna-N types	methylethylketone, acetone, ethylene dichloride	aromatics
Thiokol-RD	ethylene dichloride	aromatics

(a) Complete solution of the elastomer as a clear ungelled liquid can be obtained in these solvents at normal temperatures by employing suitable solution techniques.

(b) Only very limited free solution of the elastomer is obtained in these solvents under comparable conditions to (a) despite considerable gelation of the rubber in many cases.

TABLE III

SOURCE AND QUALITY OF SOLVENTS

Solvent (or diluent)	Source	Grade	Quality (a)
Ethylene dichloride	Carbide & Carbon	Technical	Excellent
Methyl ethyl ketone	Eastman-Kodak	Practical	Excellent
Benzene	R.B. Elk Co., Inc.	A.C.S. (b)	Excellent
Nitroethane	Commercial Solvents	Technical	Satisfactory
Xylene (Xylol)*	R.B. Elk Co., Inc.	A.C.S. (b)	Excellent
p-Cymene	Eastman-Kodak	best (c)	Unsatisfactory; (contained peroxides and gums)

(a) Quality not determined by analysis. Rating applies to suitability of the solvent for the specific purposes employed. Essential requirements here are general inertness and absence of non-volatile impurities.

(b) Meets A.C.S. standards.

(c) Best grade sold in bulk quantities; better grade than "technical" or "practical".

(*) Mixture of the isomers.

TABLE IV

PART I: GUM RUBBER - SUMMARY OF INVESTIGATIONS

SAMPLE CLASS AND DESIGNATION					DETAILS OF PREPARATION			SPECTRAL STUDY			
ELASTOMER CLASS	REPRESENTATIVE TYPE	SAMPLE NO.	EXTRACTION (a)	SOLVENT	SOLUTION METHOD (b)	SOLUTION (c) COLOR AND CHARACTERISTICS	PEROXO NO. (d) WAVELENGTH BANDS (mu)		SPECTRUM (e)	SPECTRAL CHARACTERISTICS (f)
NATURAL RUBBER	NATURAL SMOKED SHEET	1	L	xylene + nitroethane (8:3)	S	gray, W	20	2-14	9	E
							22	2-14	-	E
							70	14-23	-	*
							149	2-14	-	E
	LEE PURE GUM CEMENT	1	-		-	colorless	432	2-14	8	E
							434	14-23	-	*
	TUBE RECLAIM(x)	1	M	p-cymene + xylene (4:1)	R	yellow,W+	66	2-14	-	
							67	2-14	9	E
							71	2-14	-	
		2	M	p-cymene + xylene	R	yellow,W+	71	2-14	-	
							82	2-14	-	A
		3	M	p-cymene + xylene	R	yellow,W+	120	2-14	-	
							121	7-14	-	A
ISOBUTYLENE--ISOPRENE COPOLYMER	GR-I	1	L	benzene	S	tan,W	50	2-14	10	E
CHLOROPRENE POLYMERS	NEOPRENE-GN	1	L	xylene + nitroethane	S	brown,G	D	-	-	-
		2	-	ethylenedichloride	S	brown,W	47	2-14	-	E
							157	14-23	-	*
		3	L	ethylenedichloride	B	brown,W	59	2-14	11	E
	NEOPRENE-ILS	1	L	xylene + nitroethane	S	brown,G	D	-	-	-
		2	L	ethylenedichloride	B	brown,P	52	2-14	-	E
		3	L	ethylenedichloride	B	brown,P	61	2-14		E
							157	14-23	-	*
		4	-	ethylenedichloride	B	brown,P	61	2-14	12	E
BUTADIENE--STYRENE COPOLYMER	GR-S	1	L	xylene + nitroethane	S	tan,W	29	2-14	13	E

SAMPLE CLASS AND DESIGNATION					DETAILS OF PREPARATION			SPECTRAL STUDY			
ELASTOMER CLASS	REPRESENTATIVE TYPE	SAMPLE NO.	EXTRACTION (a)	SOLVENT	SOLUTION METHOD (b)	SOLUTION (c) COLOR AND CHARACTERISTICS	PEROXO NO. (d) WAVELENGTH BANDS (mu)		SPECTRUM (e)	SPECTRAL CHARACTERISTICS (f)
BUTADIENE--ACRYLONITRILE COPOLYMERS	CHEMIGUM-N-1	1	L	xylene + nitroethane	S	brown,W	30	2-14	14	E
	HYCAR-OR-15	1	L	xylene + nitroethane	H	yellow,P	32	2-14	-	A
		2	L	methylethylketone	B	yellow,W	94	2-14	15	E
		3	-	methylethylketone	B	yellow,W	94	2-14	-	E
	HYCAR-OR-25	1	L	xylene + nitroethane	H	yellow,P	41	2-14	16	E
		2	L	methylethylketone	B	yellow,W	56	2-14	-	E
		3	-	methylethylketone	B	yellow,W	97	2-14	-	E
	PERBUNAN-35	1	L	nitroethane + xylene	S	yellow,P	D	-	-	-
		2	L	methylethylketone	B	yellow,W	53	2-14	17	E
		3	L	methylethylketone	B	yellow,W	114	6-14	-	
							119	2-14	17	E
	BUTAPRENE-NF	1	L	xylene + nitroethane	H	yellow,P	33	2-14	18	E
ETHYLENE POLYSULFIDE POLYMER	THIOKOL-FA	1	L	xylene + nitroethane	S	brown,W	24	2-14	-	
							26	2-14	-	
							27	2-14	19	E
							28	6-14	-	
							97	6-12	19	
COPOLYMER OF BUTADIENE, ACRYLONITRILE, & DI-ISOPROPYLIDENE KETONE	THIOKOL-ID	1	L	xylene + nitroethane	S	brown,N	D	-	-	-
		2	L	ethylenedichloride	B	brown,P	62	2-14	-	E

NOTES:

(x) This specimen contains a red iron oxide filler.

(a) L = Extraction by 95% ethyl alcohol; M = Extraction by 68/32 Chloroform/Acetone.

(b) S = Mechanical shaking at room temperature.
H = Shaking at room temperature followed by moderate heating (below 90°C).
R = Refluxing (above 100°C).
B = Blenderization (after preliminary swelling at room temperature.)

(c) W = Complete solution of sample; solution clear and ungelled.
P = Partial solution of sample as clear and ungelled solution (> 50% free solution); remainder of sample as gel.
G = Gelation of entire sample but little free clear and ungelled solution.
N = Little appreciable gelation or solution of sample.
+ Indicates removal of filler by centrifugation.

(d) D indicates sample discarded; no spectrum obtained.

(e) Plate number given for plotted spectra; otherwise: - .

(f) E = Entire spectrum satisfactory and considered valid.
A = Spectrum essentially satisfactory except for additional bands obviously of foreign origin and attributable to impurities.
* Indicates no appreciable absorption at all in this region.

TABLE VI - COMPOSITION AND CURE OF COMPOUNDED SPECIMENS*

SPECIMEN DESIGNATION	GUM ELASTOMER (SP. GR.) (A)	SULPHUR	ZINC OXIDE	STEARIC ACID	ACCELERATORS	ANTIOXIDANTS	PLASTICIZERS SOFTENERS TACKIFIERS	INHIBITORS WAXES EXTENDERS	CARBON BLACKS	BASIC OXIDES (B) CLAYS	TOTAL PARTS	CURE	PHYSICAL MEASUEMENTS SP GR	DUR	TEN.	ELONG.
P-2-1	Natural Smoked Sheet, 100. (0.92)	1.0	5.0	1.0	Methyl Zimate*, 0.1 Rotox*, 1.0	(Age Rite* (Hipar, 1.0	Reogen*, 2.0	-	-	-	111.1	15' @ 300°F.	-	30-40	3200#	725%
F-4	Natural Smoked Sheet, 100. (0.92)	1.0	5.0	0.5	Captax, 0.5	Neozone D, 1.0	-	Heliozone, 2.0	P-33, 0.5	-	112.5	30' @ 300°F.	0.97	35-40	2125#	775%
F-206	Neoprene-E 100.	1.0	10.0	0.5	-	Neozone D, 2.0	Circo X Oil, 10.0 F.F.Wood Rosin, 5.0	-	Thermax, 100.	L.C.Magnesium Oxide, 10.0	218.5	40' @ 300°F.	-	65	1800#	300%
F-207	Neoprene-ILS, 100.	-	10.0	0.5	-	Neozone D, 2.0 Permalux, 1.0	Dibutyl Phthalate, 20.	-	Thermax, 100.	L.C.Magnesium Oxide, 10.0	243.5	40' @ 300°F.	-	70	1875#	30%
F-210-2	Neoprene-GN, 100. (1.25)	-	10.0	0.5	#552, 0.2	(Neozone A, (2.0 (Parazone, (1.0 (Permalux, (2.0	Circo X Oil, 10.0	Acrawax, 2.0	P-33, 91.	L.C.Magnesium Oxide, 4.0	222.7	30' @ 300°F.	1.39	60-65	1225#	550%
F-1002	Butyl (GR-I) 100.	1.5	5.0	1.0	Monex, 1.0 Captax, 0.5	-	Dibutyl Sebacate, 10.0	-	P-33, 10.	-	131.0	45' @ 300°F.	-	45	1800#	825%
F-1010-1	Butyl (GR-I) 100.	1.5	5.0	1.0	Captax, 1.5 Tuex, 1.5	-	Circo X oil, 5.0	Paraffin, 1.0	-	Superex Clay,	220.5	45' @ 310°F.	1.34	45-50	1550#	785%
F-606	Buna-S(GR-S) (0.94) 100.	*	5.0	0.5	Selenac, 2.0	-	-	Heliozone, 1.0 Mineral Rubber, 2.5	Furnex, 1.0 Micronex, 12.0	-	150.0	37' @ 375°F.	-	45	1500#	750%
F-602	Buna-S(GR-S) (0.94) 100.	1.0	5.0	1.0	Methyl Zimate, 0.1 Rotox, 1.0	(Age Rite (Hipar, 1.0	Reogen, 2.0	-	-	-	113.1	20' @ 300°F.	-	-	-	-
F-804	Thiokol-FA (1.34) 100.	-	10.0	0.5	D.P.G., 0.1 Altax, 0.4	-	-	-	Furnex, 40.	-	150.9	40' @ 300°F.	1.52	60-65	665#	400%
F-801	Thiokol-ST 80.	-	0.5	0.5	G.M.F., 1.5	-	L.P.#2, 20.0	-	Furnex, 60.	-	152.5	30' @ 296°F.	-	65	1300#	325%
P-803	Thiokol-RD (1.03) 100.	1.5	5.0	1.0	Altax, 1.0	Neozone D, 2.0	Dibutyl Sebacate, 20.	-	Furnex, 40.	-	170.5	15' @ 300°F.	-	55	1375#	300%
F-1003	Chemigum-M-1 (1.03) 100.	2.0	5.0	1.0	Tuads, 0.5	-	Circo X Oil, 10.0	-	Furnex, 50.	-	168.5	30' @ 300°F.	-	65	1400#	260%
F-1302	Perbunan-35 100.	2.0	5.0	0.5	Altax, 1.0	-	Dibutyl Sebacate, 17.5 Tributoxy-ethyl-phosphate, 12.5	-	Thermax, 130.	-	273.5	15' @ 300°F.	-	60	1675#	610%
F-407	Hycar-OR-15 (1.00) 100.	1.25	5.0	0.5	Altax, 1.5	-	S.C., 15.0 (Tributoxyethyl-(-phosphate, 15.0	-	Thermax, 70.	-	208.25	30' @ 300°F.	1.22	45-50	1700#	700%
F-402	Hycar-OR-25 (0.98) 100.	1.25	5.0	0.5	Altax, 1.5	-	S.C., 15.0 Tributoxyethyl-phosphate, 15.0	-	Furnex, 70.	-	208.25	30' @ 300°F.	1.20	45-50	2000#	550%
F-415	Hycar-OR-25 100.	2.0	5.0	0.5	Altax, 1.5 Tetrone A, 0.75	-	-	Solnatic SR-66, 100.	Wyex, 35. Furnex, 35.	-	279.75	30' @ 300°F.	1.43	75-80	950#	125%
F-205	Butaprene-NF 100.	2.5	5.0	-	Altax, 1.0	-	Tetrabutoxy-ethyl-phosphate, 25.	-	P-33, 50.	-	181.5	50' @ 300°F.	-	48	600#	300%
F-10	Natural Smoked Sheet 100	2.0	5.0	1.0	Pardol, 5.0 Thionex, 0.5	Age Rite Resin, 1.0	-		Statex B, 50	-	164.5	15' @ 300°F.	1.13	60	1200#	500%
F-10-1	Tube Reclaim, 100	2.0	5.0	1.0	Altax, 1.0 Thionex, 0.5	Age Rite Resin D, 1.0	-	-	-	-	113.5	15' @ 300°F.	-	-	-	-
F-620	GR-S 100	2.0	5.0	1.0	Pardol, 5.0 Thionex, 0.5	Age Rite Resin D, 1.0	-	-	Statex B, 50	-	164.5	15' @ 300°F	-	-	-	-
F-421	Buna-N, 100	1.5	5.0	1.0	Ethyl Zimate, 0.1 Altax, 1.5	-	Triethyl Phosphate, 15.0	-	Furnex, 50	-	174.1	30' @ 300°F	-	-	-	-

P-2861

Notes:
(a) Underlined numbers give parts by weight.
(b) Basic oxides in this column are curing agents.

* For the identity and source of all compounding ingredients see Table VII.

TABLE VII

GLOSSARY OF COMPOUNDING INGREDIENTS

Name or Designation	Chemical Name, Description, etc.	Source
(1) GENERAL:		
Sulfur	Sulfur (sp.gr. = 2.07)	-
Zinc Oxide	Zinc Oxide (sp.gr. = 5.57)	-
Stearic Acid	Stearic Acid (sp.gr. = 0.85)	-
(2) ACCELERATORS:		
Altax	Benzothiazyldisulfide	R. T. Vanderbilt
Captax	Mereaptobenzothiazole	Nangatuck Chemical
D.P.G.	Diphenylguanidine	E. I. duPont
Methyl Zimate	Zinc Dimethyldithiocarbamate	R. T. Vanderbilt
#552	Piperidinium pentamethylene-dithiocarbamate	E. I. duPont
Monex	Thiuram monosulfide	Nangatuck Chemical
G.M.F.	Quinone dioxane	-
Tuex	Tetramethylthiuram-disulfide	Nangatuck Chemical
Tuads	Same as Tuex	
Rotox	Mercaptobenzothiazole	R. T. Vanderbilt
Tetrone A	Di-N-pentamethylenethiuramtetrasulfide	E. I. duPont
Selenac	Selenium diethyldithiocarbamate	R. T. Vanderbilt
(3) ANTIOXIDANTS:		
Age Rite Hipar	phenyl-B-naphthylamine	R. T. Vanderbilt
Neozone D	phenyl-B-naphthylamine	E. I. duPont
Neozone A	phenyl- -naphthylamine	E. I. duPont
Parazone	p-phenylphenol	E. I. duPont
Permalux	?	E. I. duPont
(4) PLASTICIZERS, SOFTENERS, TACKIFIERS:		
Circo-X oil	Sun Process Petroleum Oil	Sun Oil Co.
Dibutyl Phthalate	(same)	
Dibutyl Sebacate	(same)	
Tributoxyethyl phosphate	(same)	
Tricresyl phosphate	(same)	
Tetra butoxyethyl phosphate	(same)	
Plasticizer S.C.	(composition not available)	
L.P. #2	Liquid polymer of Thiokol disulfide type	
Reogen	Mixture of oil-soluble sulfonic acid and paraffin oil	R. T. Vanderbilt
F.F. Wood Rosin	(same)	Hercules

TABLE VII (CONT'D)

Name or Designation	Chemical Name, Description, etc.	Source
(5) INHIBITORS, WAXES, EXTENDERS, etc.		
Heliozone	Mixture of waxy materials	R. T. Vanderbilt
Acrawax	Synthetic wax	Glyco Co.
Paraffin	(same)	
Mineral rubber	(Asphalt-like substance)	
Silastic SR-66	Silicone Rubber	Dow-Corning
(6) CARBON BLACKS:		
Micronex	Black	Columbian Carbon Co.
Furnex	Semi-Reinforcing Furnace Black	Columbian Carbon Co.
Thermax	Medium thermal black	R. T. Vanderbilt
P-33	Fine thermal black	R. T. Vanderbilt
Wyex	Black	Barrett Chem.
(7) CLAYS, MINERAL PIGMENTS, and OXIDES:		
Superex clay	Kaolin clay	J. M. Huber, Inc.
L.C.Magnesium Oxide	Light calcined magnesium oxide	-

TABLE VIII

SOLVENTS FOR CURED ELAS

Rubber (Cured)	Good Solvents[a]	Fair
Natural	p-cymene, tce,[1] dcb,[2] and mar	
Buna-S(GR-S)	p-cymene, tce, dcb	
Butyl (GR-I)	p-cymene, tce, dcb	
Neoprene-E or -GN	p-cymene, tce, dcb	
Thiokol-FA or -ST	p-cymene, tce, dcb	
Neoprene-ILS	o-dichlorobenzene	p-cy
Buna-N types	o-dichlorobenzene	pyri
Thiokol-RD	o-dichlorobenzene	p-cy

(1) tce = tetrachloroethane

(2) dcb = ortho-dichlorobenzene

(a) complete solution possible

(b) partial solution possible

(c) entirely ineffective

TABLE IX

SOURCE AND QUALITY OF SOLVENTS

Solvent	Source	Grade	Quality (A)
o-dichlorobenzene	Dow Chemical	Technical	Excellent
o-dichlorobenzene	City Chemical	Technical	Excellent
o-dichlorobenzene	Eastman-Kodak	Technical	Excellent
tetrachloroethane	Eastman-Kodak	Technical	Satisfactory
pyridine	Baker	C. P.	Satisfactory
xylene (xylol)*	R.B. Elk Co.,Inc.	A.C.S.(b)	Excellent
nitropropane	Commercial Solvents	Technical	Satisfactory
p-cymene	Eastman-Kodak	best(c)	Unsatisfactory
cyclohexanone			very unsatisfactory
di-isobutylketone			very unsatisfactory
methylisobutylketone			very unsatisfactory

(A) Quality not determined by analysis. Quality rating applies to suitability for spectroscopic use. The necessary requirements here are general inertness and absence of non-volatile impurities.

(b) Meets A .C.S. standards.

(c) Best grade sold in bulk quantities; better grade than "Technical" or "Practical".

* Mixture of the isomers

TABLE X

PART II: COMPOUNDED AND CURED RUBBER - SUMMARY OF INVESTIGATIONS

SAMPLE CLASS AND DESIGNATION						DETAILS OF PREPARATION				SPECTRAL STUDY		SAMPLE CLASS AND DESIGNATION						DETAILS OF PREPARATION				SPECTRAL STUDY	
ELASTOMER CLASS	REPRESENTATIVE TYPE	SAMPLE NO.	COMPOUNDING DESIGNATION (a)	FILLER (b)	EXTRACTION (c)	SOLVENT (d)	FILLER SEPARATION (e)	SOLUTION (f) COLOR AND CHARACTERISTICS	RECORD NO. (g)	WAVELENGTH RANGE (mu)	SPECTRUM (h)	SPECTRAL CHARACTERISTICS (i)	ELASTOMER CLASS	REPRESENTATIVE TYPE	SAMPLE NO.	COMPOUNDING DESIGNATION (a)	FILLER (b)	EXTRACTION (c)	SOLVENT (d)	FILLER SEPARATION (e)	SOLUTION (f) COLOR AND CHARACTERISTICS	RECORD NO. (g)	WAVELENGTH RANGE (mu)	SPECTRUM (h)	SPECTRAL CHARACTERISTICS (i)
NATURAL RUBBER	NATURAL RUBBER	1	F-2-1	-	✓	tetrachloroethane	-	yellow,W	172	2-14	22	E		CHEMIGUM-N-1	1	F-1003	S.R.F.	✓	tetrachloroethane	F	amber,P	173	2-14	35	E
		2	F-2-1	-	✓	p-cymene	-	yellow,W	267	2-14	23	E			2	F-1003	S.R.F.	✓	p-cymene	F	amber,P	287	2-14	-	I
		3	F-4	F.T.	✓	o-dichlorobenzene	F	yellow,W	386	2-14	24	E			3	F-1003	S.R.F.	✓	pyridine	F	amber,P	-	4-5	-	A
									434	14-22	-	*			4	F-1003	S.R.F.	✓	o-dichlorobenzene	F	amber,P	368	2-14	36	E
	TUBE RECLAIM	1	(none)	R	✓	tetrachloroethane	C	amber,W	164	2-14	25	E			5	F-1003	S.R.F.	✓	o-dichlorobenzene	F	amber,P	426	2-14	37	E
		2	(none	R	✓	tetrachloroethane	C	amber,W	276	2-14	-	E		HYCAR-OR-15	1	F-407	M.T.	✓	tetrachloroethane	F	N	D	-	-	-
ISOBUTYLENE-ISOPRENE COPOLYMER	GR-I	1	F-1002	F.T.	✓	tetrachloroethane	F	amber,W	211	2-14	26	E			2	F-407	M.T.	✓	cyclohexanone	F	dark,U	194	2-14	-	I
		2	F-1002	F.T.	✓	p-cymene	F	amber,W	268	2-14	27	E			3	F-407	M.T.	✓	di-isobutylketone	F	dark,U	212	2-14	-	I
		3	F-1010-1	K	✓	o-dichlorobenzene	C	amber,W	385	2-14	28	E			4	F-407	M.T.	✓	pyridine	F	dark,P	339	2-14	-	E
									437	14-22	-	*			5	F-407	M.T.	✓	o-dichlorobenzene	F	amber,P	339	2-14	-	E
CHLOROPRENE POLYMERS	NEOPRENE-E	1	F-206	M.T.	✓	tetrachloroethane	F	amber,W	182	2-14	30	E			6	F-407	M.T.	✓	o-dichlorobenzene	F	amber,P	404	2-14	38	E
		2	F-206	M.T.	✓	p-cymene	F	amber,W	285	2-14	-	A	BUTADIENE-ACRYLONITRILE COPOLYMERS	HYCAR-AR-25	1	F-402	S.R.F.	✓	tetrachloroethane	F	N	D	-	-	-
		3	F-206	M.T.	✓	o-dichlorobenzene	F	amber,W	424	2-14	31	E			2	F-402	S.R.F.	✓	di-isobutylketone	F	dark,U	197	2-14	-	I
	NEOPRENE-GN	1	F-206	F.T.	✓	o-dichlorobenzene	F	amber,W	405	2-14	-	E			3	F-402	S.R.F.	✓	o-dichlorobenzene	F	amber,P	428	2-14	-	E
		2	F-210-2	F.T.	✓	o-dichlorobenzene	F	amber,W	416	2-14	29	E			4	F-416	S.R.F.	✓	o-dichlorobenzene	F	amber,P	457	2-14	39	E
	NEOPRENE-ILS	1	F-207	M.T.	✓	tetrachloroethane	F	N	D	-	-	-		PERBUNAN-35	1	F-1302	M.T.	✓	tetrachloroethane	F	N	D	-	-	-
		2	F-207	M.T.	✓	methylisobutyl ketone	F	dark,U	240	2-14	-	I			2	F-1302	M.T.	✓	p-cymene	F	dark,U	282	2-14	-	X
		3	F-207	M.T.	✓	p-cymene	F	brown,P	281	2-14	-	E			3	F-1302	M.T.	✓	o-dichlorobenzene	F	amber,P	375	2-14	-	E
		4	F-207	M.T.	✓	pyridine	F	brown,P	355	2-14	-	E										437	14-22	-	*
		5	F-207	M.T.	✓	o-dichlorobenzene	F	brown,P	355	2-14	-	E			4	F-1302	M.T.	✓	pyridine	F	dark,P	-	4-5	-	A
		6	F-207	M.T.	✓	o-dichlorobenzene	F	brown,P	396	2-14	-	E			5	F-1302	M.T.	✓	o-dichlorobenzene	F	amber,P	427	2-14	40	E
		7	F-207	M.T.	✓	o-dichlorobenzene	F	brown,P	425	2-14	32	E		BUTAPRENE-NF	1	F-205	F.T.	✓	tetrachloroethane	F	N	D	-	-	-
									435	14-22	-	*			2	F-205	F.T.	✓	o-dichlorobenzene	F	amber,P	394	2-14	41	E
BUTADIENE-STYRENE COPOLYMER	GR-S	1	F-602	-	✓	tetrachloroethane	-	brown,W	180	2-14	33	E	ETHYLENE POLYSULFIDE POLYMERS	THIOKOL-FA	1	F-801	S.R.F.	✓	tetrachloroethane	F	red,W	186	2-14	42	E
									438	14-23	-	*			2	F-801	S.R.F.	✓	p-cymene	F	red,W	291	2-14	-	A
		2	F-606	S.R.F.	✓	tetrachloroethane	F	brown,W	216	2-14	-	E			3	F-801	S.R.F.	✓	o-dichlorobenzene	F	red,W	403	2-14	43	E
		3	F-606	S.R.F.	✓	p-cymene	F	brown,W	288	2-14	-	A		THIOKOL-ST	1	F-801	S.R.F.	✓	o-dichlorobenzene	F	red,W	438	2-14	44	E
		4	F-606	S.R.F.	✓	o-dichloro-	F	brown,W	391	2-14	34	E										438	14-22	-	*
													COPOLYMER OF BUTADIENE, ACRYLONITRILE, AND DI-ISOPROPYLIDINE KETONE	THIOKOL-ND	1	F-803	S.R.F.	✓	tetrachloroethane	F	N	D	-	-	-
															2	F-803	S.R.F.	✓	di-isobutylketone	F	dark,U	231	2-14	-	I
															3	F-803	S.R.F.	✓	p-cymene	F	dark,P	269	2-14	-	A
															4	F-803	S.R.F.	✓	pyridine	F	dark,P	-	4-5	-	A
															5	F-803	S.R.F.	✓	o-dichlorobenzene	F	amber,P	369	2-14	45	E

NOTES:

(a) See Table VI for the composition and cure of vulcanizates.
(b) R = Red iron oxide; K = a Kaolin Clay; F.T., S.R.F., M.T., designate carbon blacks (described in Table VII).
(c) Extraction preceded by milling.
Extraction solvent = 68/32 chloroform/Acetone.
(d) Solution by refluxing.
(e) F = Filtration with Celite; C = Centrifugation.
(f) W = Complete solution of rubber specimen; solution clear.
P = Partial solution of specimen (> 40% solution); solution clear.
N = No appreciable solution of specimen (solvent colorless).
U = Extent of solution uncertain.
(g) D : indicates sample discarded; no spectrum obtained.
(h) Plate number given for plotted spectra; otherwise: - .
(i) E : Entire spectrum satisfactory; complete agreement with the spectrum of the pure gum elastomer.
A : Spectrum essentially satisfactory except for additional bands obviously of foreign origin and attributable to impurities.
I : Spectrum no good; the elastomer spectrum is absent or is almost wholly masked by the spectrum of impurities.
* : indicates no appreciable absorption at all in this region.

TABLE XI - CHARACTERISTIC BANDS OF THE ELASTOMERS**

ELASTOMER	WAVE LENGTHS OF BANDS (in Mu)*	CHARACTERISTICS
Natural	11.94 mu (B)	Interference from Neoprene
	7.25 mu (S)	Interference from Butyl, Thiokol-FA, Thiokol-RD
Neoprene	12.08 mu (B)	Interference from Natural
	8.92 mu (S)	Interference from Thiokol-FA
	6.02 mu (S)	Not unique but unusually intense for Neoprene
Butyl	8.13 mu (S)	Unique for Butyl
	(7.2 mu (S), 7.3 mu (S))	Interference from Natural, Thiokol-FA, Thiokol-RD
Buna-S	14.3 mu (B)	
	6.70 mu (S)	Unique for Buna-S
	6.2 mu (S)	
	6.1 mu (S)	
	(10.9 mu (S), 10.3 mu (S))	Interference from Buna-N, Thiokol-RD
Buna-N	4.465 mu (S)	Interference from Thiokol-RD, Neoprene-ILS
	10.9 mu (S)	Interference from Buna-S, Thiokol-RD
	10.3 mu (S)	
Thiokol-FA	7.80 mu (S)	
	9.30 mu (S)	Unique for Thiokol-FA
	9.70 mu (S)	
	7.06 mu (S)	Unique, but possible interference from all other elastomers (at 6.92 - 6.96)
	8.35 mu (S)	Unique for Thiokol-FA
	10.50 mu (S)	
	8.98 mu (S)	Interference from Neoprene
Thiokol-RD	5.86 mu (S)	Unique for Thiokol-RD
	4.465 mu (S)	Interference from Buna-N, Neoprene-ILS
	(10.9 mu (S), 10.3 mu (S))	Interference from Buna-N, Buna-S
	(7.2 mu (S), 7.3 mu (S))	Interference from Natural, Butyl, Thiokol-FA

* B = broad S = sharp ** only strong bands are listed

TABLE XII - ELASTOMER ABSORPTION AT VARIOUS WAVELENGTHS

WAVELENGTH (in mu)	ELASTOMERS WHICH ABSORB
4.465	Buna-N, Thiokol-RD, Neoprene-ILS (weak)
5.86*	Thiokol-RD
6.24	Buna-S
6.70*	Buna-S
7.25 (7.2,7.3)	Natural, Butyl, Thiokol-FA, Thiokol-RD
7.80*	Thiokol-FA
8.13	Butyl
8.35*	Thiokol-FA
8.92	Neoprene
8.98	Thiokol-FA
9.3	Thiokol-FA
9.7*	Thiokol-FA
10.3	Buna-S, Buna-N, Thiokol-RD
10.5	Thiokol-FA
10.9 (10.8)	Buna-S, Buna-N, Thiokol-RD
12.0 (0.1)	Natural, Neoprene
13.2	Buna-S
14.3	Buna-S

* absorption here is unambiguous

TABLE XIII - TYPICAL SCHEME OF ANALYSIS
(Blend of Natural + Buna-S)

ORDER	WAVELENGTH (in mu)	(a) RESULT	(b) CONCLUSIONS	(b) FURTHER CHECKS
1	8.13	-	No Butyl	Singlet at 7.250 rather than 7.20, 7.30 doublet
2	5.86	-	No Thiokol-RD	Singlet at 7.250
3	9.3	-		
	9.7	-	No Thiokol-FA	
	7.8	-		
4	6.70	+		
	6.24	+	Buna-S present	10.3(+), 10.85 (+)
	13.2	+		
5	4.475	-	No Buna-N	
6*	7.250	+	Natural Present	11.95(+)
7**	8.92	-	No Neoprene	Weak 6.00 band indicates no Neoprene

Notes:
(a) + indicates definite band; - indicates that no band is distinguishable.
(b) See table
* Specific because 1, 2, 3 are negative
** Specific because 3 is negative

TABLE XIV

ANALYSIS OF STANDARD NATURAL/GR-S BLENDS

SAMPLE (a)		MEASUREMENTS (b)			NATURAL ANALYSIS (c)		GR-S ANALYSIS (d)	
BLEND	NO.	7.60 mμ	7.25 mμ	6.70 mμ	7.25 / 7.60	%	6.70 / 7.60	%
F-620 (100% GR-S)	1	36.0/.445	52.0/.285	18.0/.745	0.64	00.0	1.68	*
	2	52.0/.283	66.5/.176	32.0/.498	0.63	00.0	1.76	*
#1 (90% GR-S) (10% Natural)	1	35.0/.456	32.5/.488	20.0/.700	1.07	10.5	1.54	*
	2	22.5/.647	21.5/.667	12.3/.910	1.03	9.5	1.41	*
	3 a	39.5/.404	37.0/.432	29.0/.502	1.07	10.5	1.34	*
	3 b	29.5/.306	47.0/.328	38.0/.417	1.07	10.5	1.36	*
	3 c	45.0/.349	42.0/.377	33.5/.474	1.08	10.7	1.36	*
	3 d	32.0/.492	29.0/.535	21.0/.672	1.08	10.7	1.37	*
#2 (80% GR-S) (20% Natural)	1	30.0/.523	17.5/.755	20.0/.700	1.44	20.0	1.34	*
	2	34.0/.470	20.0/.700	21.5/.667	1.49	21.5	1.42	*
	3 a	25.0/.556	17.0/.774	18.0/.712	1.39	19.0	1.33	*
	3 b	38.0/.424	25.0/.603	27.0/.573	1.41	19.5	1.35	*
	3 c	49.5/.305	37.5/.428	39.0/.409	1.40	19.0	1.35	*
	3 d	62.5/.206	50.0/.301	52.0/.284	1.46	20.5	1.38	*
#3 (70% GR-S) (30% Natural)	1	38.0/.420	16.3/.788	29.0/.538	1.87	31.0	1.28	72.0
	2	22.5/.647	-	15.7/.804	-	-	1.24	69.0
	3 a	40.5/.394	20.0/.701	31.5/.500	1.76	29.0	1.27	71.5
	3 b	50.0/.301	27.0/.567	41.0/.388	1.86	31.5	1.29	73.0
	3 c	35.0/.458	14.5/.842	-	1.84	30.5	-	-
	3 d	46.0/.339	23.0/.642	37.0/.428	1.89	31.7	1.24	69.0
#4 (60% GR-S) (40% Natural)	1	29.5/.530	-	25.0/.603	-	-	1.13	60.0
	2	38.5/.415	-	34.0/.470	-	-	1.13	60.0
	3 a	48.0/.320	20.0/.703	-	2.20	40.0	-	-
	3 b	36.5/.438	-	31.0/.512	-	-	1.17	63.0
	3 c	70.5/.152	46.0/.339	67.0/.174	2.23	40.5	1.14	61.0
	3 d	39.0/.408	-	35.0/.456	-	-	1.12	59.0
#5 (50% GR-S) (50% Natural)	1	32.0/.495	-	33.0/.482	-	-	0.975	47.5
	2	25.5/.595	-	26.0/.587	-	-	0.990	48.5
	3 a	31.5/.514	-	31.0/.506	-	-	0.980	48.0
	3 b	27.5/.558	-	26.5/.576	-	-	1.03	52.0
	3 c	57.5/.242	26.0/.584	57.0/.244	2.40	45.	1.01	50.0
	3 d	59.5/.224	27.0/.568	58.5/.232	2.53	45.	1.03	52.0
	3 e	41.0/.384	-	41.5/.382	-	-	1.00	50.5

SAMPLE (a)		MEASUREMENTS (b)		GR-S ANALYSIS (d)	
BLEND	NO.	7.60 mμ	6.70 mμ	6.70 / 7.60	%
#6 (40% GR-S) (60% Natural)	1	20.5/.690	24.5/.610	0.885	40.0
	2	41.5/.380	45.5/.340	0.885	40.0
	3 a	31.0/.506	35.0/.456	0.900	41.0
	3 b	38.5/.413	43.0/.368	0.890	40.5
	3 c	42.0/.376	46.0/.335	0.890	40.5
	3 d	32.5/.490	37.0/.428	0.875	39.5
#7 ** (30% GR-S) (70% Natural)	3 a	36.0/.444	45.5/.342	0.770	31.0
	3 b	32.0/.494	40.5/.393	0.795	32.5
	3 c	23.0/.642	32.0/.492	0.765	30.0
	3 d	29.5/.532	39.0/.410	0.770	31.0
	4 a	33.5/.472	42.0/.378	0.800	33.0
	4 b	59.0/.232	65.5/.184	0.790	32.0
#8 (20% GR-S) (80% Natural)	1	25.5/.595	43.0/.365	0.610	18.0
	2	27.0/.570	44.0/.355	0.620	18.5
	3 a	27.5/.558	43.5/.361	0.650	21.0
	3 b	32.0/.494	47.5/.324	0.655	21.5
	3 c	34.0/.465	51.5/.286	0.615	18.2
	3 d	30.0/.524	47.0/.330	0.630	19.5
#9 (10% GR-S) (90% Natural)	1	25.5/.595	50.5/.297	0.500	09.5
	2	38.0/.420	60.5/.218	0.520	10.5
	3 a	41.0/.387	64.5/.191	0.495	08.5
	3 b	37.5/.428	60.0/.220	0.515	10.0
	3 c	45.0/.346	67.5/.171	0.495	08.5
	3 d	28.0/.549	53.5/.273	0.500	09.5
	3 e	21.0/.620	49.5/.305	0.490	08.0
F-10 (100% Natural)	1	22.5/.647	55.0/.260	0.400	00.5
	2	36.0/.445	65.5/.185	0.415	02.0

NOTES:

(a) Numbers refer to the sample preparation; letters indicate the several films measured.

(b) Percentage Transmission (T) and Extinction (E) at each wavelength are given as T/E.

(c) Using indicated ratio of Extinction values and curve (2) of Plate 48.

(d) Using indicated ratio of Extinction values and curve (1) of Plate 48.

* Indicates that the extinction ratios (though measurable) are beyond the linear range of the working curve.

\- Indicates absorption too great for accurate measurement.

** Preparations 1 and 2 of Blend #7 were ruined prior to film preparation.

TABLE XV

ANALYSIS OF RECLAIM-CONTAINING MIXTURES

SAMPLE (a)		MEASUREMENTS (b)			NATURAL ANALYSIS (c)		GR-S ANALYSIS (d)	
BLEND	NO.	7.60 mu	7.25 mu	6.70 mu	7.25/7.60	%	6.70/7.60	%
F-10 (100% Natural)	1 a	36.0/.442	-	66.3/.179	-	-	0.405	01.0
	1 b	57.5/.241	13%	80%	-	-	-	-
	2 a	39.5/.404	-	68.0/.168	-	-	0.417	02.0
	2 b	57.5/.241	13%	80%	-	-	-	-
F-10-4 (50% Natural) (50% Reclaim)	1 a	32.2/.492	-	62.0/.209	-	-	0.425	02.5
	1 b	55.3/.258	18.2/.739	77.4/.112	2.86	*	0.435	03.5
	2 a	37.8/.422	-	64.3/.192	-	-	0.455	05.0
	2 b	51.7/.286	13%	74.0/.132	-	-	0.460	05.5
F-10-1 (100% Reclaim)	1 a	40.0/.398	-	67.0/.175	-	-	0.440	04.0
	1 b	58.2/.232	24.3/.614	78.0/.108	2.64	54.0	0.465	06.0
	2 a	33.9/.470	-	53.3/.273	-	-	0.580	15.0
	2 b	48.8/.311	22.2/.653	64.5/.191	2.10	36.0	0.615	18.0
	3	45.5/.342	14.0/.844	65.0/.187	2.46	47.0	0.550	13.0
	4	48.8/.311	15.0/.824	66.5/.177	2.64	54.0	0.570	14.5
F-10-2 (33.3% Natural) (33.3% Reclaim) (33.3% GR-S)	1 a	31.5/.499	-	41.5/.383		-	0.770	30.5
	1 b	54.0/.266	25.5/.594	63.5/.197	2.23	40.0	0.740	28.5
	2 a	34.0/.470	-	41.8/.379	-	-	0.805	33.5
	2 b	51.0/.292	18.3/.737	58.5/.234	2.52	49.0	0.800	33.0
	3	48.8/.311	15.5/.808	55.5/.256	2.60	52.0	0.825	35.5
F-10-5 (25% Natural) (25% Reclaim) (50% GR-S)	1 a	63.0/.200	37.2/.430	64.5/.190	2.15	38.5	0.950	45.5
	1 b	44.2/.354	17.8/.750	45.5/.342	2.12	38.0	0.965	46.5
F-10-3 (50% Reclaim) (50% GR-S)	1 a	34.0/.470	14.0/.860	37.0/.432	1.83	30.0	0.920	43.0
	1 b	53.0/.276	29.8/.525	55.8/.253	1.90	32.0	0.920	43.0
	2	49.4/.306	26.2/.582	50.5/.296	1.90	32.0	0.970	47.0
	3	47.8/.321	22.2/.653	46.1/.331	2.03	35.0	1.03	50.5
F-10-6 (15% Natural) (15% Reclaim) (70% GR-S)	1 a	59.2/.228	41.0/.386	52.2/.282	1.69	26.5	1.24	69.0
	1 b	45.5/.343	26.5/.575	37.2/.430	1.68	26.5	1.25	70.0
F-620 (100% GR-S)	1 a	37.2/.430	49.2/.308	23.2/.634	0.715	01.0	1.47	*
	1 b	50.5/.296	60.5/.219	37.0/.431	0.740	01.5	1.45	*
	2	50.0/.301	57.8/.238	34.0/.470	0.790	03.0	1.56	*

NOTES:

(a) Numbers refer to the sample preparations; letters indicate the several films measured.

(b) Percentage Transmission (T) and Extinction (E) at each wavelength are given as T/E.

(c) Using indicated ratio of Extinction values and curve (2) of Plate 48.

(d) Using indicated ratio of Extinction values and curve (2) of Plate 48.

* Indicates that the extinction ratios (though measurable) are beyond the linear range of the working curve.

\- Indicates absorption too great for accurate measurement.

TABLE XVII

ADDITIONAL GR-S DETERMINATIONS FOR RECLAIM-CONTAINING MIXTURES

SAMPLE (a)		MEASUREMENTS (b)				ANALYSIS FOR GR-S (c)					
BLEND	NO.	11.40 mu	10.95 mu	10.70 mu	10.35 mu	(10.35)/(10.70)	%	(10.35)/(11.40)	%	(10.95)/(11.40)	%
F-10	1 a	-	61.0/.213	54.3/.264	45.0/.347	1.32	00.0	-		-	-
(100% Natural)	1 b	53.3/.273	64.5/.191	58.3/.234	48.8/.312	1.33	00.0	1.14	00.0	0.70	00.0
	2	-	61.0/.213	53.5/.272	41.0/.386	1.42	00.0	-	-	-	-
F-10-4	1 a	50.0/.301	59.5/.226	55.0/.260	44.5/.352	1.35	00.0	1.17	00.0	0.75	05.0
(50% Natural)	1 b	57.1/.238	65.5/.184	61.5/.210	52.2/.282	1.34	00.0	1.18	00.0	0.78	07.0
(50% Reclaim)	3 a	50.0/.301	61.5/.210	56.0/.252	44.0/.357	1.42	00.0	1.19	00.0	0.70	00.0
	3 b	63.5/.198	72.7/.138	69.0/.162	59.5/.226	1.35	00.0	1.14	00.0	0.70	00.0
F-10-1	1	-	53.8/.268	51.5/.287	39.5/.404	1.40	00.0	-	-	-	-
(100% Reclaim)	2	-	51.0/.292	49.5/.307	42.2/.374	1.22	00.0	-	-	-	-
	3	47.2/.326	52.2/.282	50.0/.301	40.0/.398	1.32	00.0	1.22	00.0	0.87	09.0
	4	-	-	60.0/.222	49.0/.310	1.40	00.0	-	-	-	-
F-10-2	1	63.5/.198	51.5/.287	63.5/.198	24.5/.612	3.09	19.0	3.09	20.0	1.45	23.5
(33.3% Natural)	2	68.8/.162	53.3/.273	69.5/.159	22.2/.654	4.10	29.0	4.03	28.5	1.68	29.0
(33.3% Reclaim)	3 a	71.6/.145	55.5/.256	72.0/.142	24.0/.62	4.38	32.0	4.30	30.5	1.77	31.0
(33.3% GR-S)	3 b	71.2/.148	55.5/.256	72.0/.142	24.0/.62	4.38	32.0	4.20	30.0	1.73	30.0
F-10-5	1 a	71.6/.145	50.0/.301	70.0/.154	18.3/.738	4.80	36.5	5.10	38.0	2.08	38.5
(25% Natural)	1 b	55.0/.260	30.0/.522	53.3/.273	-	-	-	-	-	2.00	36.5
(25% Reclaim)											
(50% GR-S)											
F-10-3	1	66.7/.176	46.5/.331	65.0/.188	17.7/.750	3.99	28.0	4.25	30.0	1.88	33.5
(50% Reclaim)	2 a	72.7/.138	53.5/.273	70.0/.155	24.5/.612	3.95	27.5	4.44	32.0	1.98	36.0
(50% GR-S)	2 b	72.2/.142	53.3/.273	70.0/.155	23.5/.630	4.05	29.0	4.44	32.0	1.92	34.5
	3	68.2/.166	43.3/.364	66.7/.176	13.3/.876	4.98	38.5	5.28	39.5	2.20	41.0

NOTES:

(a) Numbers refer to the sample preparation; letters indicate the several films studied.

(b) Percentage Transmission (T) and Extinction (E) at each wavelength are given as T/E.

(c) Using indicated ratio of Extinctions and appropriate working curve from Plate 49.

\- Indicates absorption too great for accurate measurement.

TABLE XVII

ADDITIONAL GR-S DETERMINATIONS FOR RECLAIM-CONTAINING MIXTURES

SAMPLE (a)		MEASUREMENTS (b)				ANALYSIS FOR GR-S (c)					
BLEND	NO.	11.40 mu	10.95 mu	10.70 mu	10.35 mu	(10.35)/(10.70)	%	(10.35)/(11.40)	%	(10.95)/(11.40)	%
F-10	1 a	-	61.0/.213	54.3/.264	45.0/.347	1.32	00.0	-		-	-
(100% Natural)	1 b	53.3/.273	64.5/.191	58.3/.234	48.8/.312	1.33	00.0	1.14	00.0	0.70	00.0
	2	-	61.0/.213	53.5/.272	41.0/.386	1.42	00.0	-	-	-	-
F-10-4	1 a	50.0/.301	59.5/.226	55.0/.260	44.5/.352	1.35	00.0	1.17	00.0	0.75	05.0
(50% Natural	1 b	57.7/.238	65.5/.184	61.5/.210	52.2/.282	1.34	00.0	1.18	00.0	0.78	07.0
(50% Reclaim)	3 a	50.0/.301	61.5/.210	56.0/.252	44.0/.357	1.42	00.0	1.19	00.0	0.70	00.0
	3 b	63.5/.198	72.7/.138	69.0/.162	59.5/.226	1.35	00.0	1.14	00.0	0.70	00.0
F-10-1	1	-	53.8/.268	51.5/.287	39.5/.404	1.40	00.0	-	-	-	-
(100% Reclaim)	2	-	51.0/.292	49.5/.307	42.2/.374	1.22	00.0	-	-	-	-
	3	47.2/.326	52.2/.282	50.0/.301	40.0/.398	1.32	00.0	1.22	00.0	0.87	09.0
	4	-	-	60.0/.222	49.0/.310	1.40	00.0	-	-	-	-
F-10-2	1	63.5/.198	51.5/.287	63.5/.198	24.5/.612	3.09	19.0	3.09	20.0	1.45	23.5
(33.3% Natural	2	68.8/.162	53.3/.273	69.5/.159	22.2/.654	4.10	29.0	4.03	28.5	1.68	29.0
(33.3% Reclaim	3 a	71.6/.145	55.5/.256	72.0/.142	24.0/.62	4.38	32.0	4.30	30.5	1.77	31.0
(33.3% GR-S)	3 b	71.2/.148	55.5/.256	72.0/.142	24.0/.62	4.38	32.0	4.20	30.0	1.73	30.0
F-10-5	1 a	71.6/.145	50.0/.301	70.0/.154	18.3/.738	4.80	36.5	5.10	38.0	2.08	38.5
(25% Natural	1 b	55.0/.260	30.0/.522	53.3/.273	-	-	-	-	-	2.00	36.5
(25% Reclaim											
(50% GR-S)											
F-10-3	1	66.7/.176	46.5/.331	65.0/.188	17.7/.750	3.99	28.0	4.25	30.0	1.88	33.5
(50% Reclaim)	2 a	72.7/.138	53.5/.273	70.0/.155	24.5/.612	3.95	27.5	4.44	32.0	1.98	36.0
(50% GR-S)	2 b	72.2/.142	53.3/.273	70.0/.155	23.5/.630	4.05	29.0	4.44	32.0	1.92	34.5
	3	68.2/.166	43.3/.364	66.7/.176	13.3/.876	4.98	38.5	5.28	39.5	2.20	41.0

NOTES:

(a) Numbers refer to the sample preparation; letters indicate the several films studied.

(b) Percentage Transmission (T) and Extinction (E) at each wavelength are given as T/E.

(c) Using indicated ratio of Extinctions and appropriate working curve from Plate 49.

\- Indicates absorption too great for accurate measurement.

TABLE XVIII - ACRYLONITRILE ANALYSIS OF COMMERCIAL BUNA-N COPOLYMERS

SAMPLE			MEASUREMENTS (c)					NITRILE DETERMINATION (d)			
(a) COPOLYMER	SET (b) and RUN		4.60 mu	4.47 mu	(4.47)	3.50 mu	(3.50)	4.47/3.50	%	(4.47)/(3.50)	%
PERBUNAN-10	1	a	98.0%	83.5/.078	85.0/.070	16.7/.777	17.0/.770	.100	07.2	.091	08.2
		b	96.0%	86.7/.062	90.0/.046	34.0/.468	35.2/.453	.132	09.4	.101	08.8
	2	a	99.0%	85.5/.068	86.5/.063	26.7/.574	27.0/.568	.108	08.0	.101	08.8
		b	100.0%	84.5/.072	84.5/.072	20.0/.699	20.0/.699	.103	07.4	.103	09.0
PERBUNAN-16	1	a	98.5%	72.8/.138	74.0/.130	20.6/.686	20.9/.680	.201	14.0	.191	14.8
		b	99.5%	86.7/.062	87.2/.060	47.8/.320	48.0/.318	.194	13.6	.189	14.6
	2	a	97.0%	70.0/.155	72.5/.140	20.0/.699	20.7/.684	.222	15.2	.205	15.6
PERBUNAN-26 (20.5%)	1	a	-	59.2/.227	-	17.3/.761	-	.298	19.6	-	-
		b	-	68.0/.167	-	20.8/.681	-	.309	20.0	-	-
		c	-	63.8/.196	-	22.0/.658	-	.298	19.6	-	-
	2	a	99.0%	77.6/.106	78.5/.105	36.0/.444	36.7/.438	.241	16.5	.242	17.6
		b	97.5%	85.7/.176	89.0/.160	21.1/.675	21.8/.662	.261	17.4	.244	17.6
	3	a	97.5%	61.0/.214	63.0/.200	17.8/.750	18.3/.738	.285	18.6	.271	19.0
		b	95.5%	80.5/.218	83.3/.198	16.9/.724	19.6/.704	.301	19.5	.282	19.5
	4	a	-	62.0/.208	-	22.0/.602	-	.324	20.6	-	-
		b	-	63.8/.195	-	24.7/.607	-	.321	20.4	-	-
		c	87.5%	58.3/.234	67.0/.174	18.3/.738	21.0/.678	.317	20.2	.257	18.4
PERBUNAN-26 (25.7%)	1	a	-	54.7/.262	-	25.5/.593	-	.442	26.2	-	-
		b	-	65.8/.339	-	17.2/.764	-	.444	26.4	-	-
		c	-	62.7/.203	-	33.0/.483	-	.420	25.2	-	-
		d	-	61.0/.214	-	33.0/.485	-	.442	26.2	-	-
	2	a	97.5%	63.5/.197	65.0/.187	32.8/.484	33.7/.472	.407	24.6	.396	24.8
		b	95.5%	45.5/.342	47.5/.323	15.5/.810	16.3/.788	.422	25.4	.410	25.4
	3	a	98.0%	51.7/.286	52.8/.278	22.8/.642	23.2/.632	.445	26.4	.440	26.6
		b	98.0%	52.8/.277	54.0/.268	26.1/.583	26.7/.574	.475	27.8	.467	27.7
	4	a	-	47.8/.320	-	17.4/.755	-	.425	25.4	-	-
		b	-	51.7/.287	-	22.7/.644	-	.447	26.4	-	-
		c	88.0%	47.8/.320	54.5/.264	17.8/.750	20.2/.696	.427	25.6	.378	
PERBUNAN-35 (33.5%)	1	a	-	37.5/.426	-	21.6/.664	-	.643	34.6	-	-
		b	-	50.8/.294	-	35.4/.452	-	.651	34.8	-	-
		c	-	40.1/.397	-	23.8/.624	-	.638	34.4	-	-
	2	a	80.5%	39.0/.408	48.3/.316	24.4/.612	30.3/.518	.667	35.4	.610	33.2
		b	84.5%	54.0/.267	64.0/.194	39.5/.403	46.6/.330	.662	35.2	.590	32.6
	3*	a	68.5%	31.6/.500	45.3/.334	20.6/.686	30.0/.523	.730	37.6	.640	34.2
		b	73.4%	35.0/.456	47.7/.322	23.3/.633	31.8/.498	.720	37.4	.647	34.5
	4	a	-	38.3/.416	-	22.8/.642	-	.650	34.8	-	-
		b	-	51.1/.292	-	35.0/.456	-	.640	34.4	-	-
		c	81.0%	44.5/.352	54.8/.260	27.0/.566	34.2/.466	.633	34.2	.557	31.2

SAMPLE			MEASUREMENTS (c)					NITRILE DETERMINATION (d)			
(a) COPOLYMER	SET (b) and RUN		4.60 mu	4.47 mu	(4.47)	3.50 mu	(3.50)	4.47/3.50	%	(4.47)/(3.50)	%
CHEMIGUM-N-1 (30.8%)	1	a	-	46.7/.328	-	24.5/.608	-	.540	30.6	-	-
		b	-	51.0/.292	-	28.4/.544	-	.537	30.4	-	-
		c	-	36.2/.440	-	19.7/.804	-	.548	30.8	-	-
	2	a	97.0%	44.0/.356	45.5/.342	16.7/.777	17.3/.762	.456	27.0	.448	27.0
		b	98.5%	56.7/.224	57.6/.210	27.8/.556	28.2/.550	.402	26.2	.436	26.4
	3	a	95.0%	43.3/.364	45.5/.342	20.0/.700	21.0/.678	.520	29.6	.505	29.2
		b	96.5%	51.1/.292	53.0/.276	26.6/.575	27.6/.560	.500	29.2	.493	28.8
	4	a	-	47.2/.326	-	25.8/.588	-	.555	31.0	-	-
		b	-	51.7/.287	-	31.6/.515	-	.556	31.2	-	-
		c	93.5%	51.0/.292	54.8/.260	29.0/.538	31.0/.510	.542	30.6	.510	29.6
CHEMIGUM-N-2 (20.7%)	1	a	-	65.6/.181	-	24.8/.604	-	.300	19.2		
		b	-	52.7/.276	-	11.6/.834	-	.332	21.0		
		c	-	56.8/.244	-	16.2/.788	-	.310	19.8	-	-
	2	a	98.5%	74.5/.128	75.7/.120	30.0/.523	30.5/.516	.245	16.2	.232	17.0
		b	97.5%	67.8/.168	69.7/.156	21.6/.665	22.3/.652	.253	16.6	.240	17.4
	3	a	98.0%	63.3/.196	64.6/.188	20.0/.700	20.4/.690	.283	18.2	.272	19.0
		b	93.5%	60.0/.222	63.3/.192	19.4/.712	20.8/.682	.312	20.1	.282	19.5
	4	a	-	54.0/.268	-	15.0/.820	-	.327	20.6	-	-
		b	-	64.5/.191	-	26.4/.578	-	.330	20.8	-	-
		c	90.0%	64.0/.194	71.0/.150	20.0/.620	26.5/.576	.313	20.0	.260	18.4
CHEMIGUM-N-3 (40.0%)	1	a	-	53.5/.270	-	44.0/.354	-	.764	39.0	-	-
		b	-	34.4/.452	-	25.0/.566	-	.790	39.8	-	-
	2	a	90.0%	21.6/.655	21.0/.820	15.0/.824	16.1/.777	.806	40.2	.798	39.8
		b	94.5%	37.5/.403	41.8/.380	31.7/.500	33.5/.475	.806	40.2	.800	40.0
	3	a	94.0%	32.8/.484	35.0/.456	26.1/.584	27.8/.556	.830	41.0	.820	40.6
		b	90.0%	27.8/.556	30.8/.511	22.2/.654	24.7/.608	.850	41.7	.840	41.2
	4	a	-	42.2/.375	-	33.1/.472	-	.795	39.8	-	-
		b	-	51.2/.291	-	41.0/.356	-	.820	40.8	-	-
		c	94.5%	34.5/.462	36.5/.438	27.8/.556	29.5/.530	.830	41.0	.828	41.0
HYCAR OR-15 (41.8%)	1	a	-	26.5/.574	-	18.0/.740	-	.776	39.2	-	-
		b	-	32.8/.484	-	24.5/.611	-	.793	39.8	-	-
		c	-	44.8/.348	-	38.0/.420	-	.830	41.0	-	-
	2	a	96.0%	31.0/.508	32.4/.490	21.6/.665	22.6/.646	.780	39.4	.758	38.6
		b	98.0%	54.5/.264	55.5/.256	46.7/.330	47.7/.322	.800	40.0	.795	39.8
	3	a	97.0%	32.2/.492	33.4/.476	25.6/.592	26.4/.578	.830	41.0	.825	40.8
		b	95.5%	32.8/.484	34.3/.464	27.4/.566	28.5/.545	.870	42.3	.853	41.7
	4	a	-	35.4/.451	-	27.2/.566	-	.796	40.0	-	-
		b	-	54.4/.264	-	47.0/.321	-	.822	40.8	-	-
		c	87.0%	39.0/.410	44.8/.348	30.5/.516	35.2/.454	.795	39.8	.785	39.4
HYCAR OR-25 (33.0%)	1	a	-	42.2/.373	-	20.2/.692	-	.540	30.4	-	-
		b	-	38.8/.411	-	18.0/.715	-	.552	31.0	-	-
		c	-	49.7/.303	-	28.2/.549	-	.553	31.0	-	-
	2	a	95.5%	59.0/.230	61.8/.210	37.2/.430	39.0/.408	.535	30.4	.515	29.6
		b	96.0%	39.0/.408	40.5/.392	17.8/.750	18.5/.732	.544	30.6	.535	30.4
	3	a	95.5%	42.2/.375	44.2/.355	22.2/.654	23.2/.634	.575	32.0	.560	31.2
		b	92.5%	40.5/.392	44.0/.356	21.7/.664	23.5/.629	.590	32.6	.566	31.5
	4	a	-	42.0/.377	-	20.3/.692	-	.545	30.6	-	-
		b	-	45.3/.344	-	24.2/.616	-	.559	31.4	-	-
		c	87.5%	46.7/.331	53.8/.269	25.6/.592	29.4/.532	.560	31.2	.506	29.2

NOTES:

(a) The nitrile content as determined by Kjeldahl analysis is given in parentheses.

(b) Numbers refer to sample preparations; letters designate the several films studied. Preparations 1,2,3 are of gum samples; preparation 2 is without extraction; preparation 4 is of cured and compounded samples.

(c) Percentage Transmission and Extinction at each analytical wavelength are given as T/E. Parentheses at head of column indicate values corrected to 100% transmission at 4.60 mu.

(d) Using the indicated extinction ratio and the appropriate working curve of Plate 50.

(e) Indicates a gellatinous sample and correspondingly unsatisfactory films.

TABLE XIX

ACRYLONITRILE ANALYSIS OF SPECIAL BUNA-N COPOLYMERS

SAMPLE		MEASUREMENTS (c)					NITRILE DETERMINATION (d)			
(a) COPOLYMER	SET (b) and RUN	4.60 mu	4.47 mu	(4.47)	3.50 mu	(3.50)	4.47 / 3.50	%	(4.47) / (3.50)	%
1 (0.9%)	1 a	90.0%	89.0/.050	99.0/.00	19.0/.720	21.0/.678	.070	04.8	.00	0.0
	1 b	93.5%	92.5/.034	99.5/.00	17.2/.764	18.5/.732	.040	02.4	.00	0.0
	2 a	96.5%	96.0/.020	99.5/.00	09.0/1.05	09.1/1.04	.020	00.0	.00	0.0
	2 b	98.0%	97.5/.010	99.5/.00	19.0/.720	19.3/.715	.010	00.0	.00	0.0
2 (4.2%)	1 a	98.5%	91.0/.040	92.7/.032	20.5/.688	21.0/.678	.058	04.0	.047	4.4
	1 b	99.0%	93.3/.030	94.5/.024	29.4/.532	29.8/.526	.056	03.6	.046	4.2
	2 a	99.0%	92.2/.035	93.2/.030	19.0/.270	19.2/.717	.049	03.2	.042	4.0
	2 b	99.0%	92.3/.035	93.3/.030	20.0/.699	20.2/.695	.050	03.2	.043	4.0
3 (8.7%)	1 a	97.5%	79.5/.100	81.7/.087	14.5/.838	14.8/.828	.119	08.8	.105	9.2
	1 b	97.5%	85.5/.068	88.0/.055	25.0/.602	25.7/.590	.113	08.2	.093	8.6
	2 a	99.0%	84.0/.075	85.0/.070	20.0/.699	20.2/.695	.107	07.8	.101	8.8
4 (14.0%)	1 a	98.0%	76.7/.115	78.5/.105	23.3/.632	23.8/.622	.182	12.8	.169	13.6
	1 b	98.5%	71.0/.148	72.5/.140	15.5/.810	15.8/.800	.183	12.8	.175	13.8
	2 a	98.5%	74.0/.130	75.2/.124	19.0/.720	19.2/.716	.180	12.6	.173	13.8
	2 b	99.0%	75.5/.122	76.5/.116	20.6/.686	20.8/.682	.178	12.6	.170	13.6
5 (17.0%)	1 a	95.5%	74.5/.128	78.0/.108	34.0/.470	35.5/.450	.272	18.0	.240	17.4
	2 a	97.5%	60.5/.218	62.2/.206	14.5/.840	14.8/.830	.260	17.6	.248	17.8
	2 b	98.0%	66.7/.176	68.0/.168	21.1/.676	21.6/.666	.260	17.6	.252	18.0
6 (21.7%)	1 a	97.5%	51.5/.288	53.0/.276	16.7/.777	17.0/.768	.370	23.0	.360	23.2
	1 b	97.5%	61.7/.210	63.5/.198	24.4/.612	25.2/.598	.343	21.6	.332	22.0
	2 a	96.0%	62.8/.202	64.2/.192	26.0/.584	26.7/.574	.346	21.8	.335	22.0
	2 b	92.5%	57.2/.242	58.5/.232	20.6/.686	21.0/.678	.352	22.2	.342	22.4
7 (27.0%)	1 a	96.5%	58.3/.234	60.5/.218	34.0/.468	35.0/.456	.500	28.8	.478	28.2
	2 a	96.0%	51.7/.286	53.8/.270	25.0/.602	26.0/.584	.475	27.8	.463	27.6
	2 b	92.5%	43.3/.363	47.0/.328	19.0/.722	20.4/.670	.503	29.0	.475	28.0
8 (32.3%)	1 a	90.0%	30.0/.523	33.5/.474	15.5/.810	17.3/.762	.645	34.6	.622	33.6
	2 a	93.5%	37.8/.422	40.5/.392	19.5/.710	20.8/.682	.595	32.8	.575	31.8
	2 b	91.0%	39.0/.410	42.7/.370	20.0/.699	22.0/.658	.585	32.4	.563	31.4
9(*) (35.2%)	1 a	68.0%	35.5/.450	51.5/.288	29.0/.538	42.0/.378	.836	41.2	.762	38.6
	1 b	54.5%	35.5/.450	65.3/.184	31.0/.508	57.0/.244	.885	42.8	.755	38.4
	2 a	67.0%	29.0/.538	43.3/.363	19.5/.710	28.2/.550	.756	38.6	.660	35.0
10 (38.2%)	1 a	85.5%	24.0/.620	28.0/.554	16.7/.778	19.5/.710	.797	40.0	.780	39.2
	1 b	98.0%	35.0/.456	39.5/.404	26.7/.574	30.0/.523	.795	40.0	.775	39.0
	1 c	88.0%	26.0/.585	29.8/.526	19.0/.722	21.5/.668	.810	40.4	.788	38.6
	1 d	83.0%	27.2/.566	33.0/.482	20.6/.686	24.8/.606	.825	40.8	.795	38.8

NOTES:

(a) The nitrile content as determined by Kjeldahl analysis is given in parentheses.

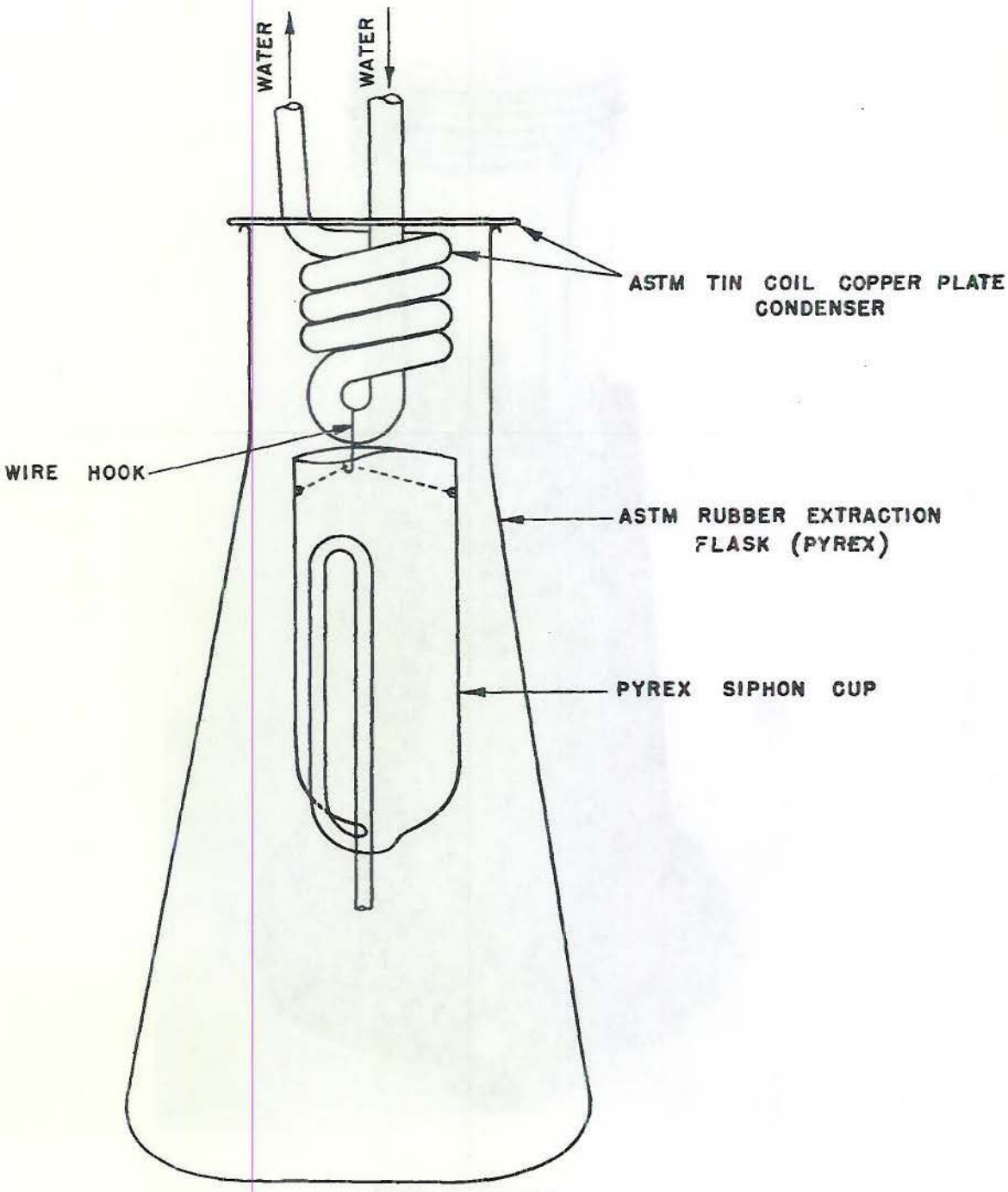
(b) Numbers refer to sample preparations; letters designate the several films studied. Both preparations are of gum samples.

(c) Percentage Transmission and Extinction at each analytical wavelength are given as T/E. Parentheses at head of column indicate values corrected to 100% transmission at 4.60 mu.

(d) Using the indicated extinction ratio and the appropriate working curve of Plate 50.

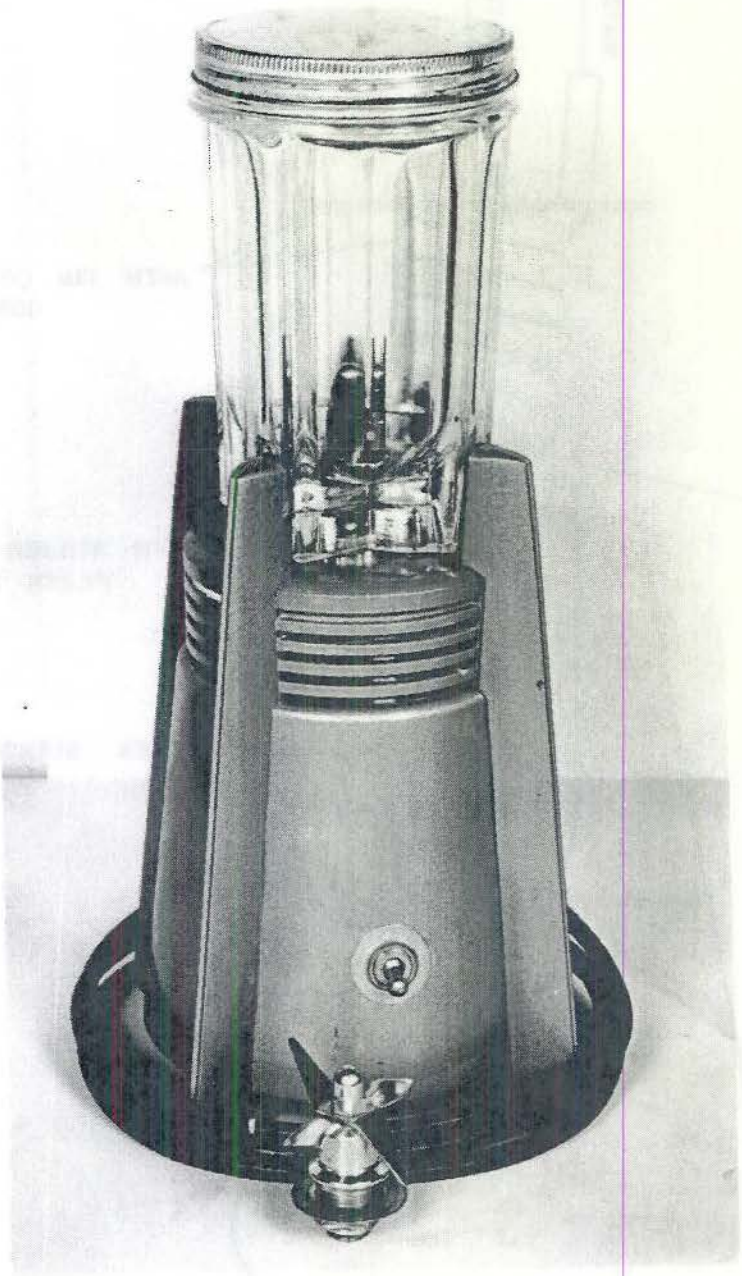
(*) Indicates a gellatinous sample and correspondingly unsatisfactory films.

ASTM ASSEMBLY FOR EXTRACTION



P-2861

PLATE 1



WARING BLENDOR

PLATE 2

FLASK AND ASSEMBLY FOR SOLVENT DISTILLATION

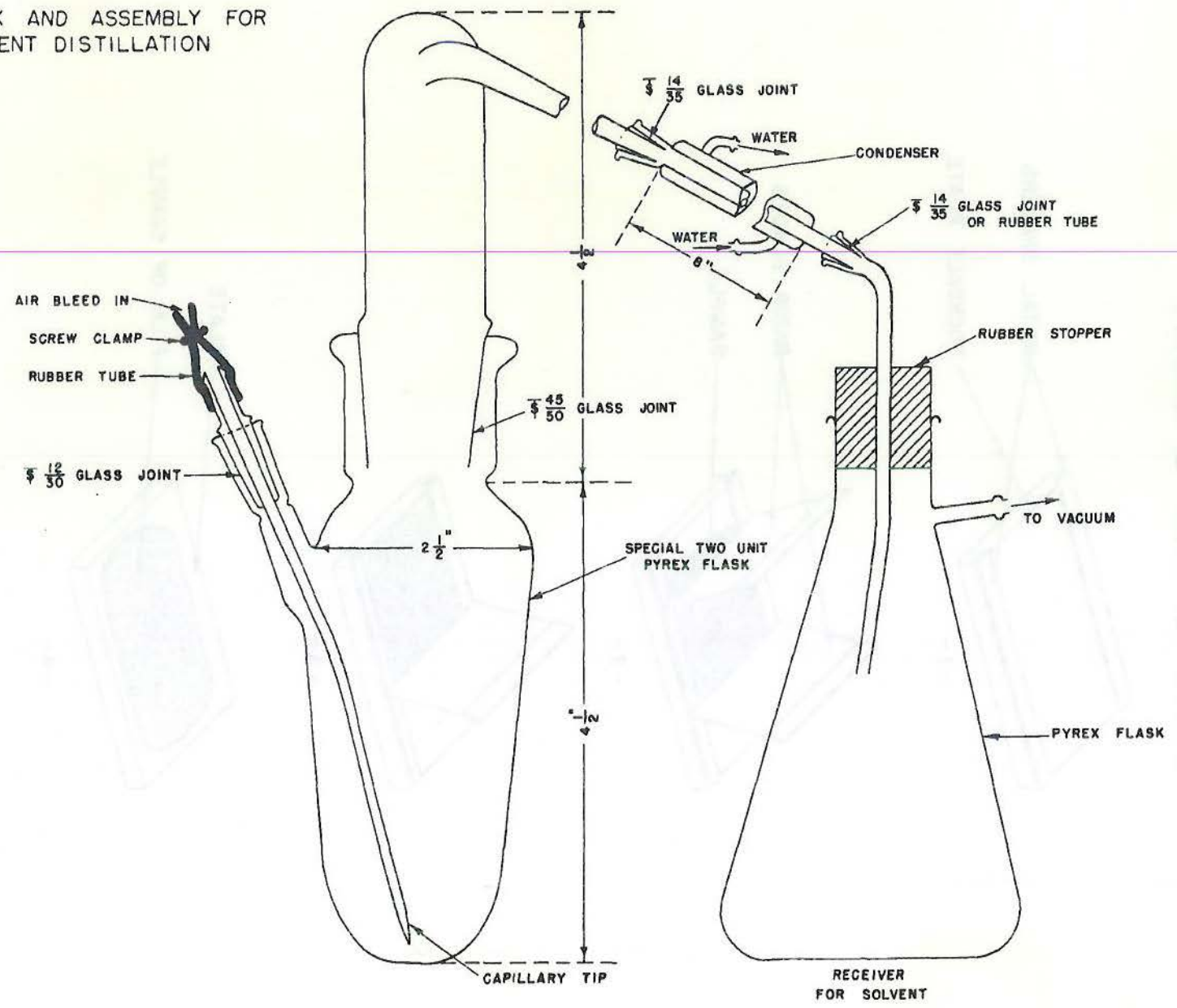
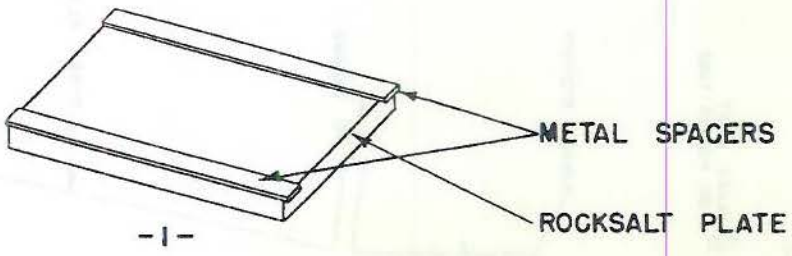
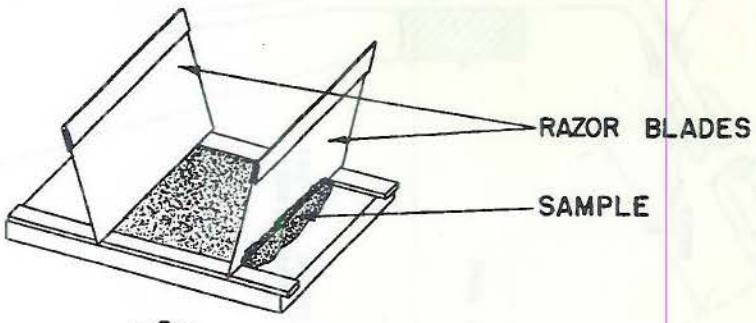


PLATE 3

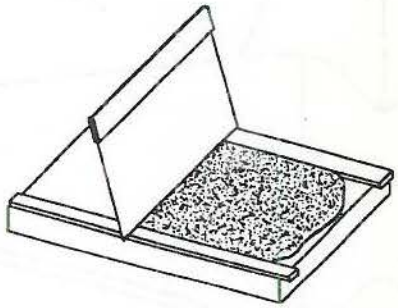
METHOD OF FILM SPREADING



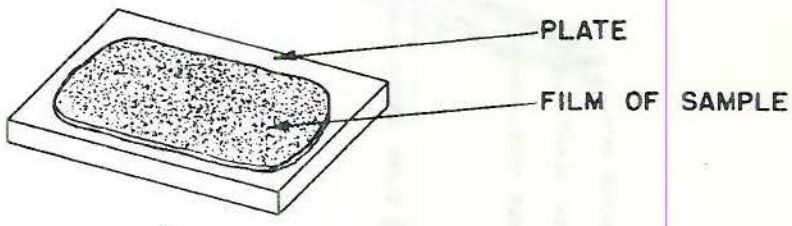
-1-



-2-

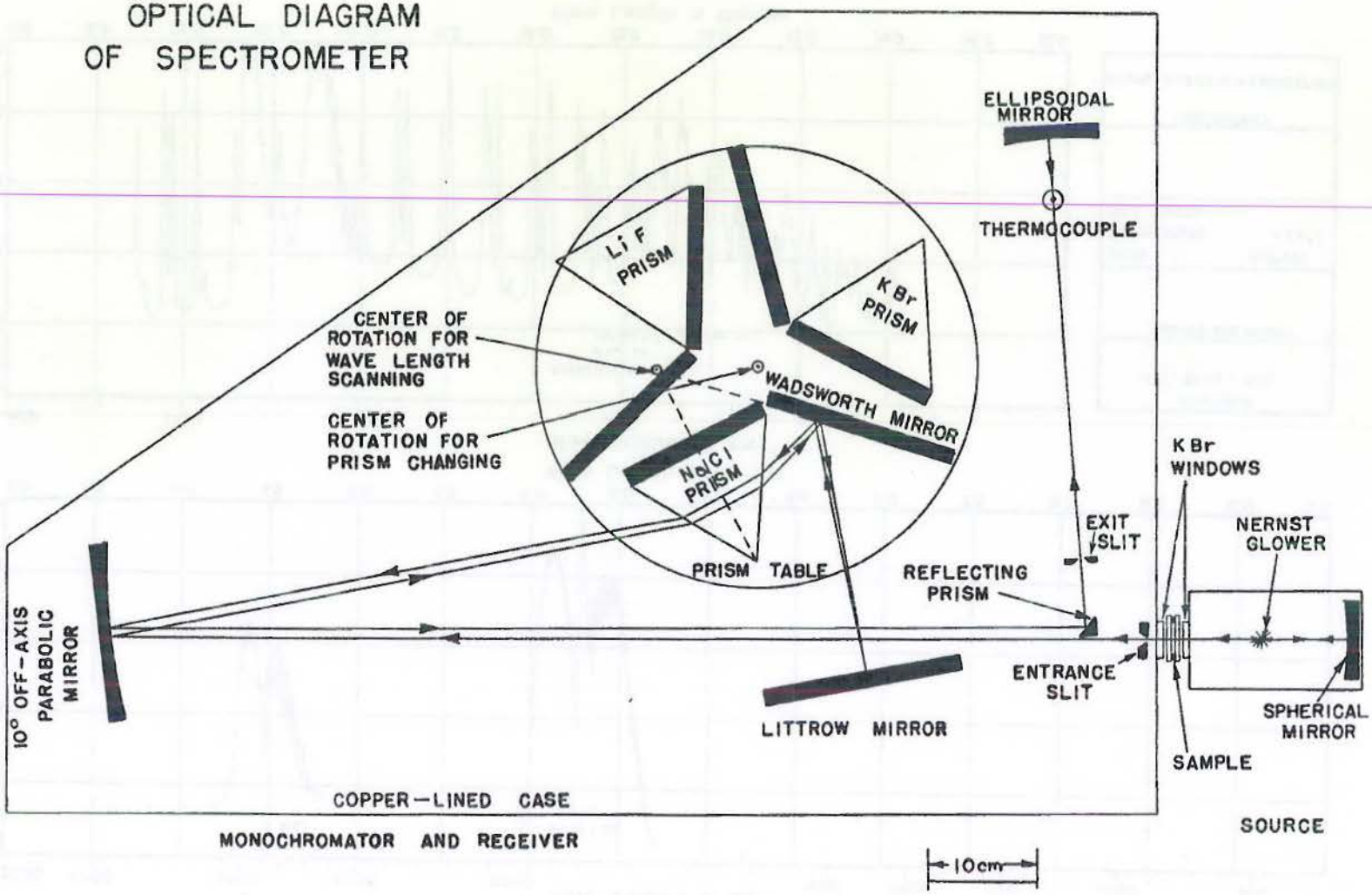


-3-



-4-

OPTICAL DIAGRAM OF SPECTROMETER



P-2861

PLATE 5

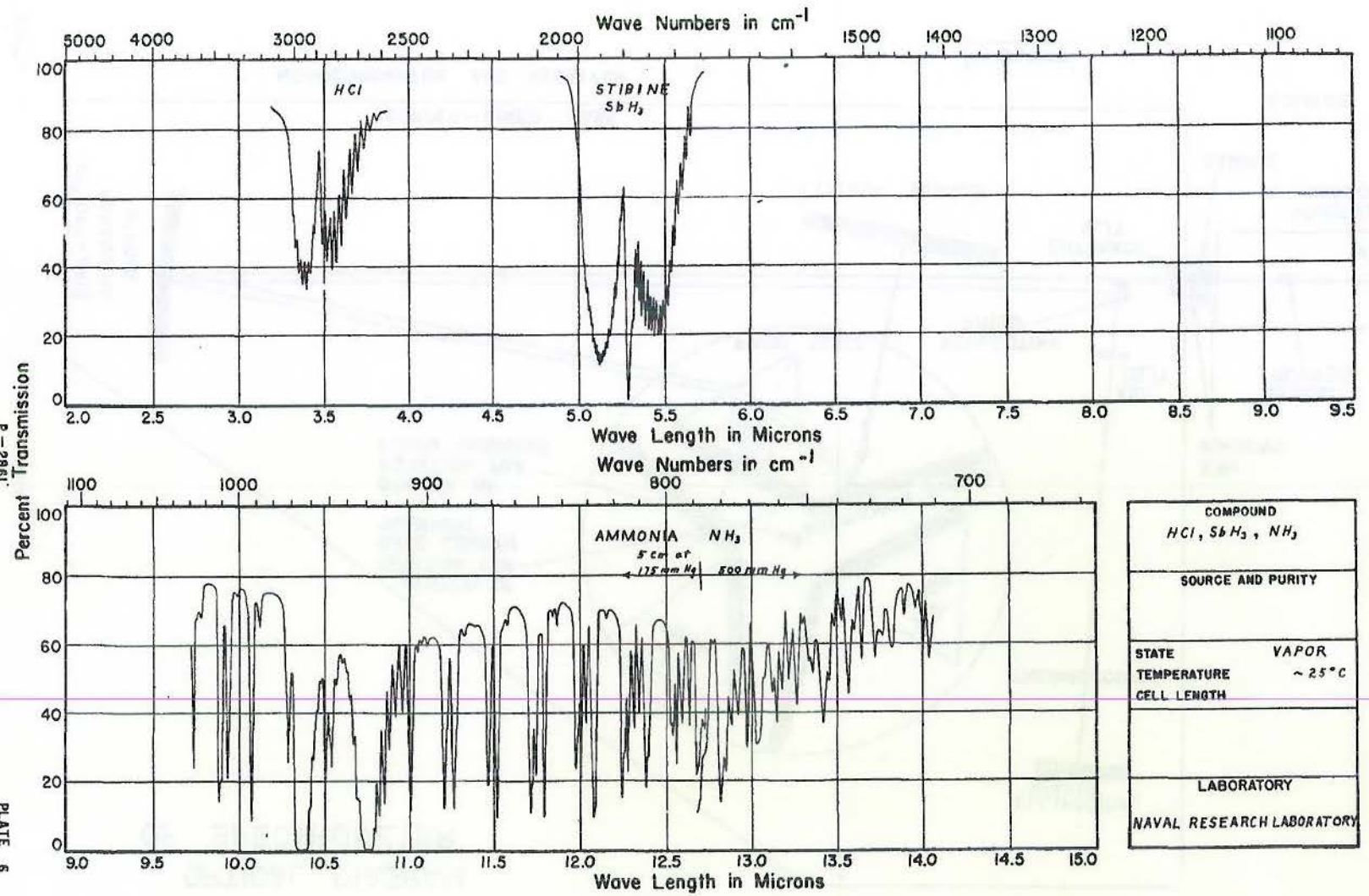


PLATE 6

p-2861

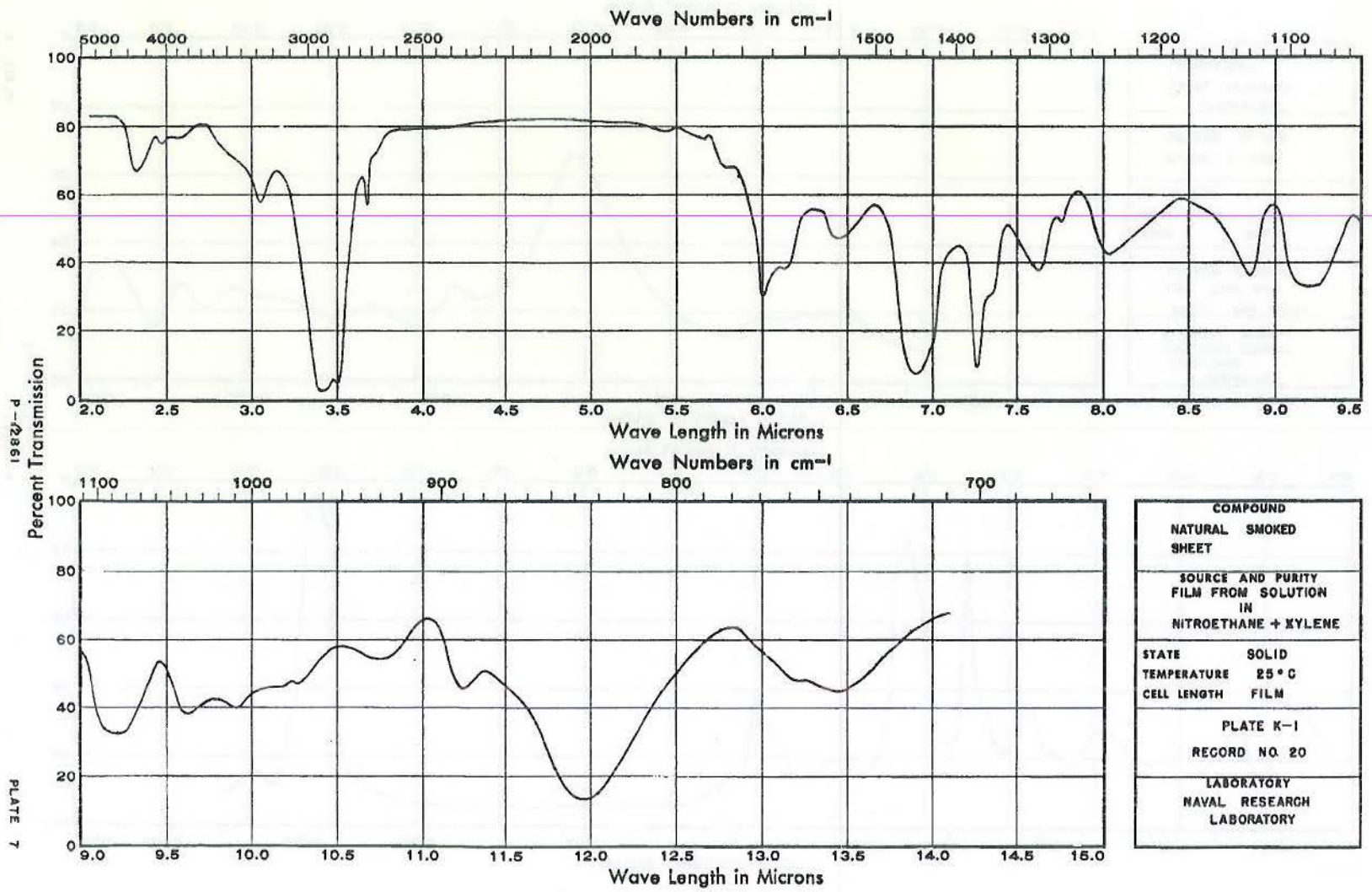
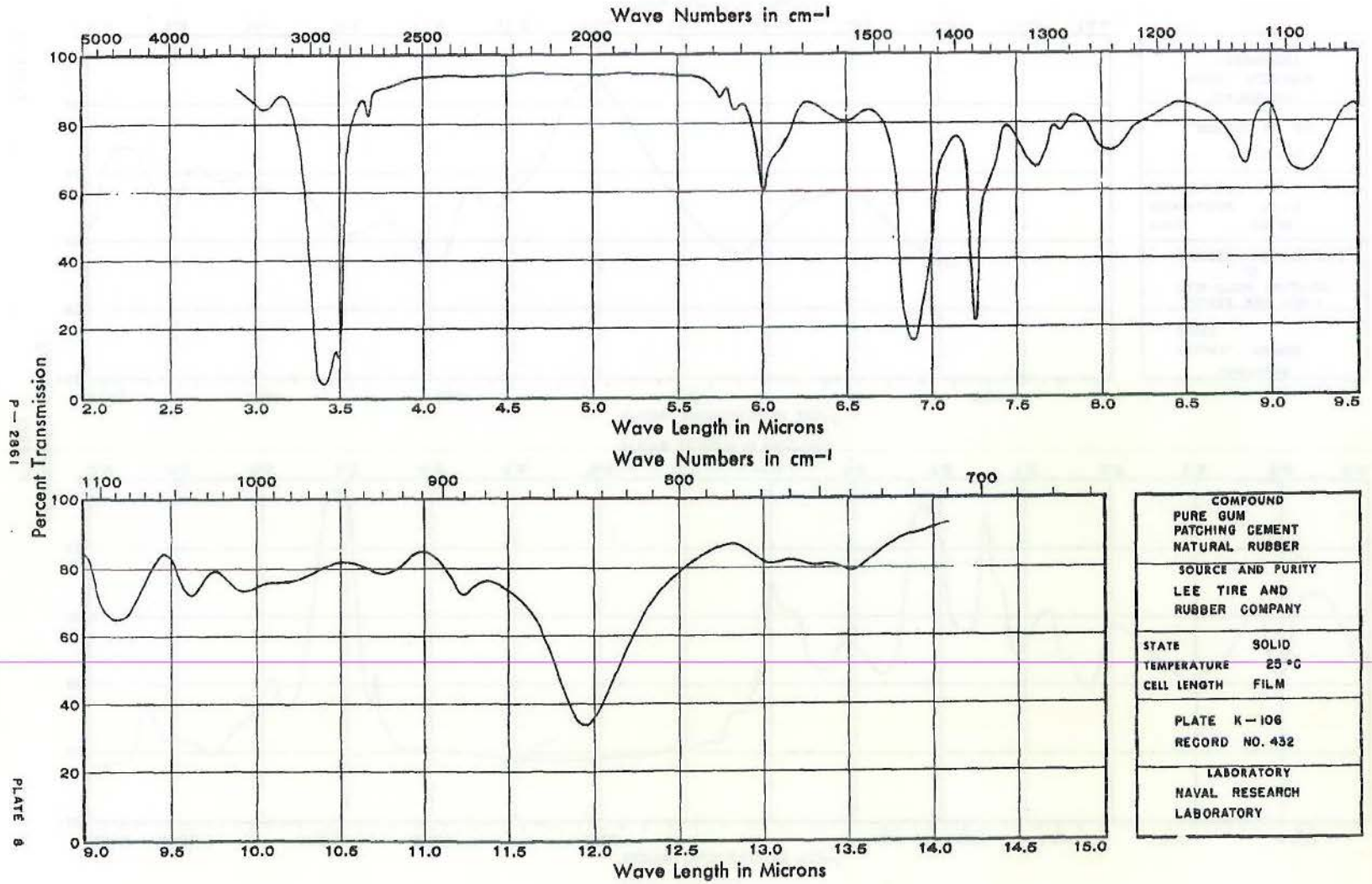
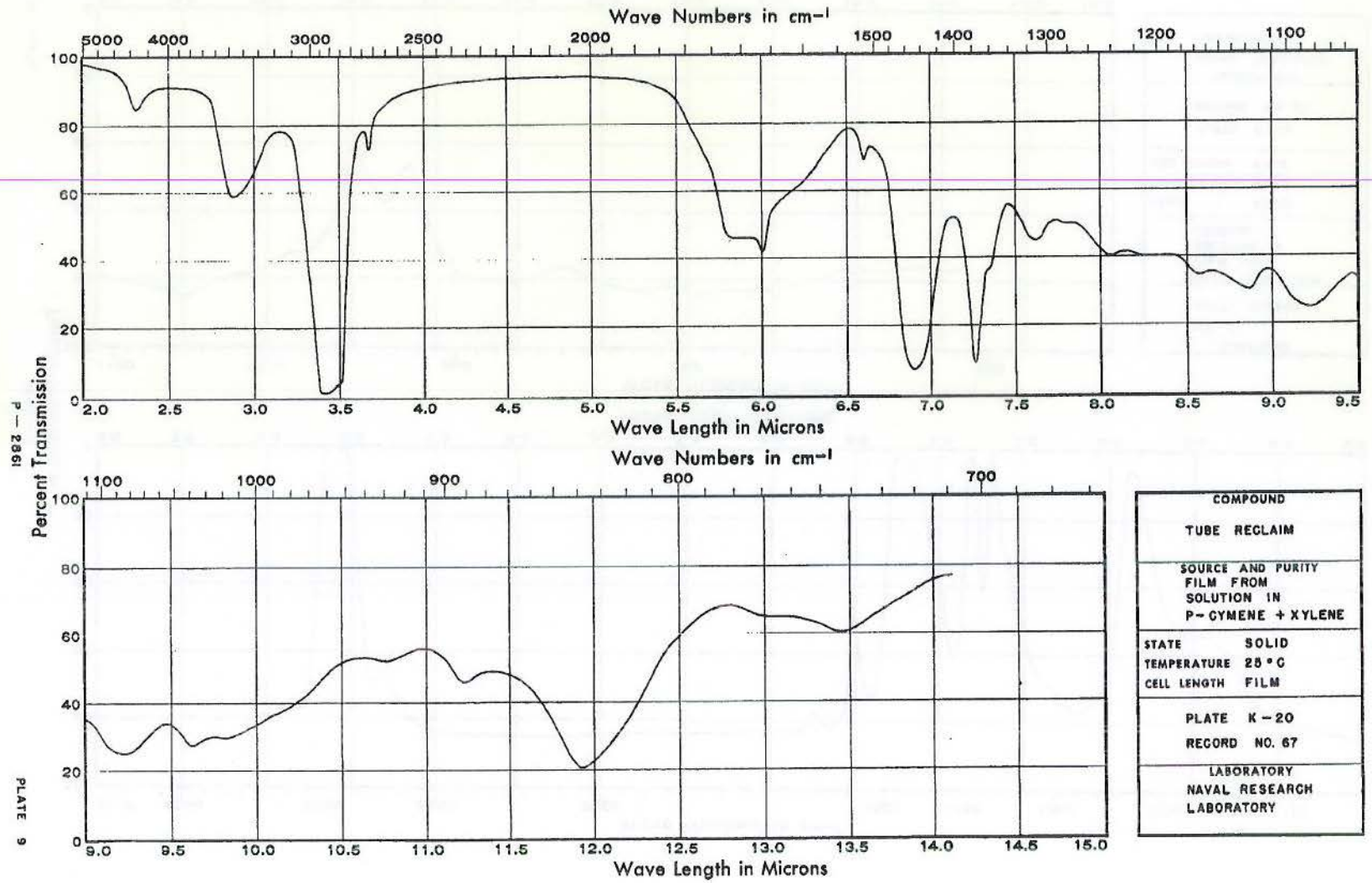
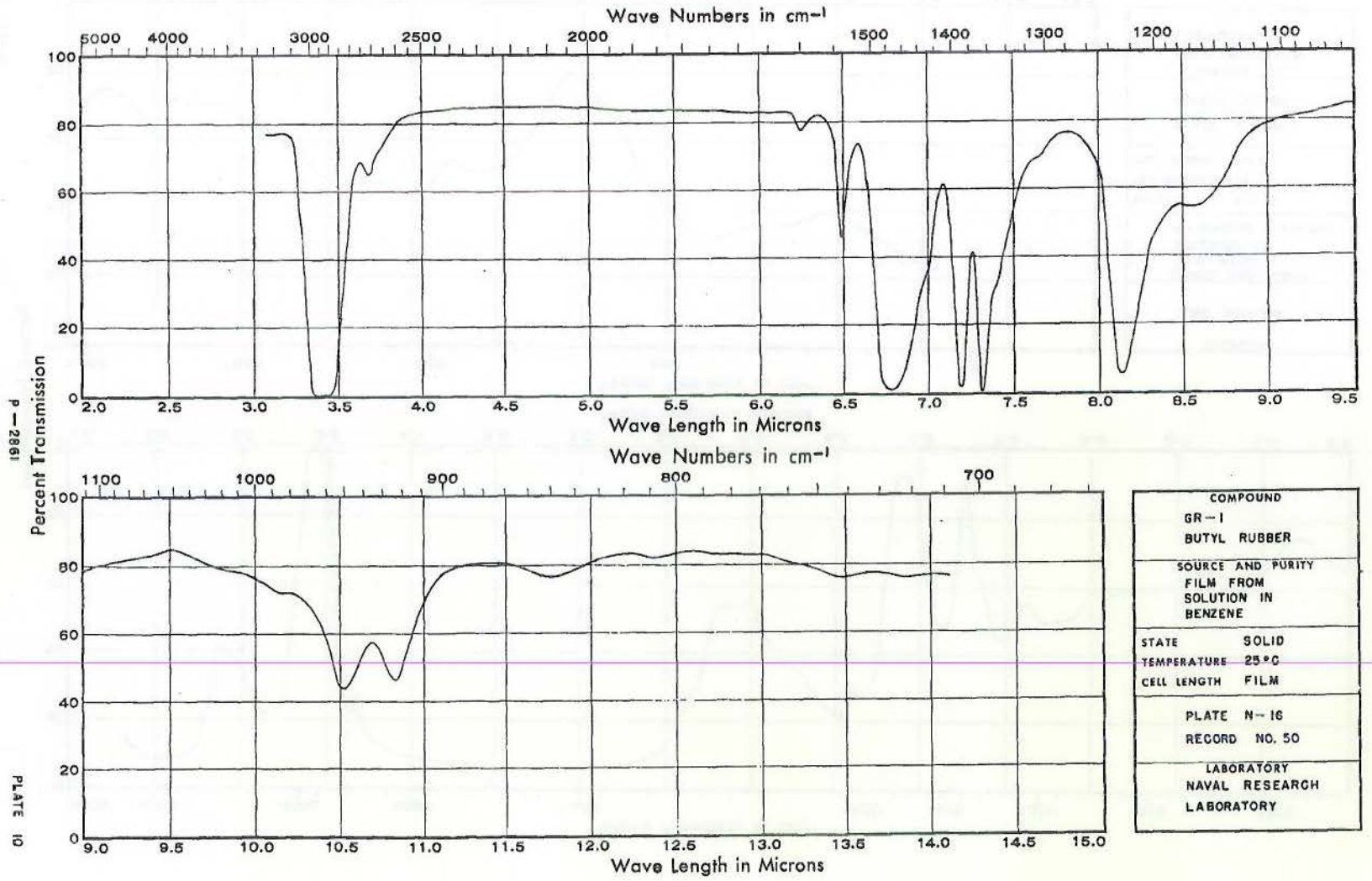


PLATE 7

1982-d

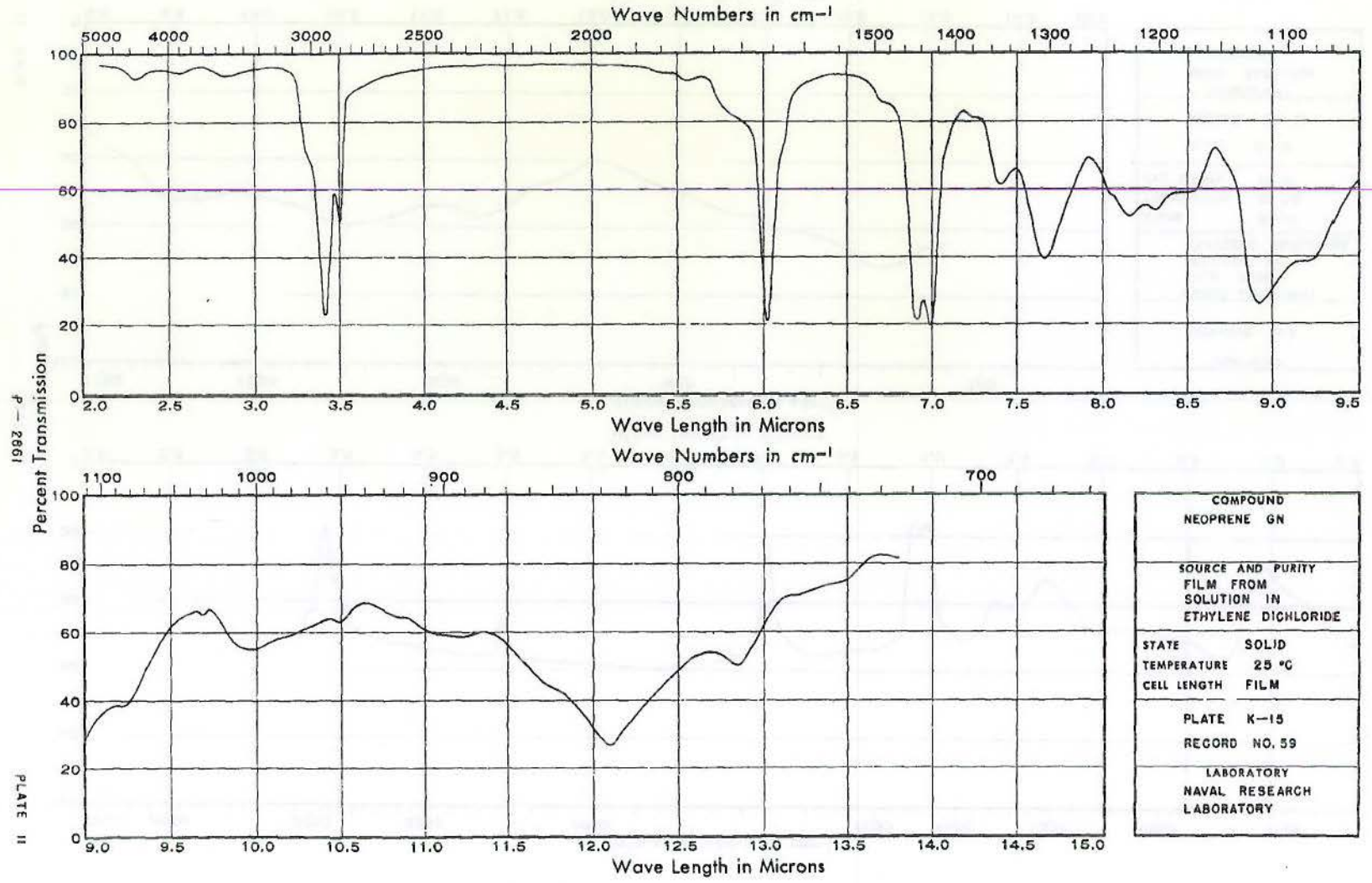

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
PURE GUM
PATCHING CEMENT
NATURAL RUBBER
SOURCE AND PURITY
LEE TIRE AND
RUBBER COMPANY
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
PLATE K-106
RECORD NO. 432
LABORATORY
NAVAL RESEARCH
LABORATORY
P-2861
PLATE 8


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
TUBE RECLAIM
SOURCE AND PURITY
FILM FROM
SOLUTION IN
P-CYMENE + XYLENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
PLATE K-20
RECORD NO. 67
LABORATORY
NAVAL RESEARCH
LABORATORY
P-2861
PLATE 9



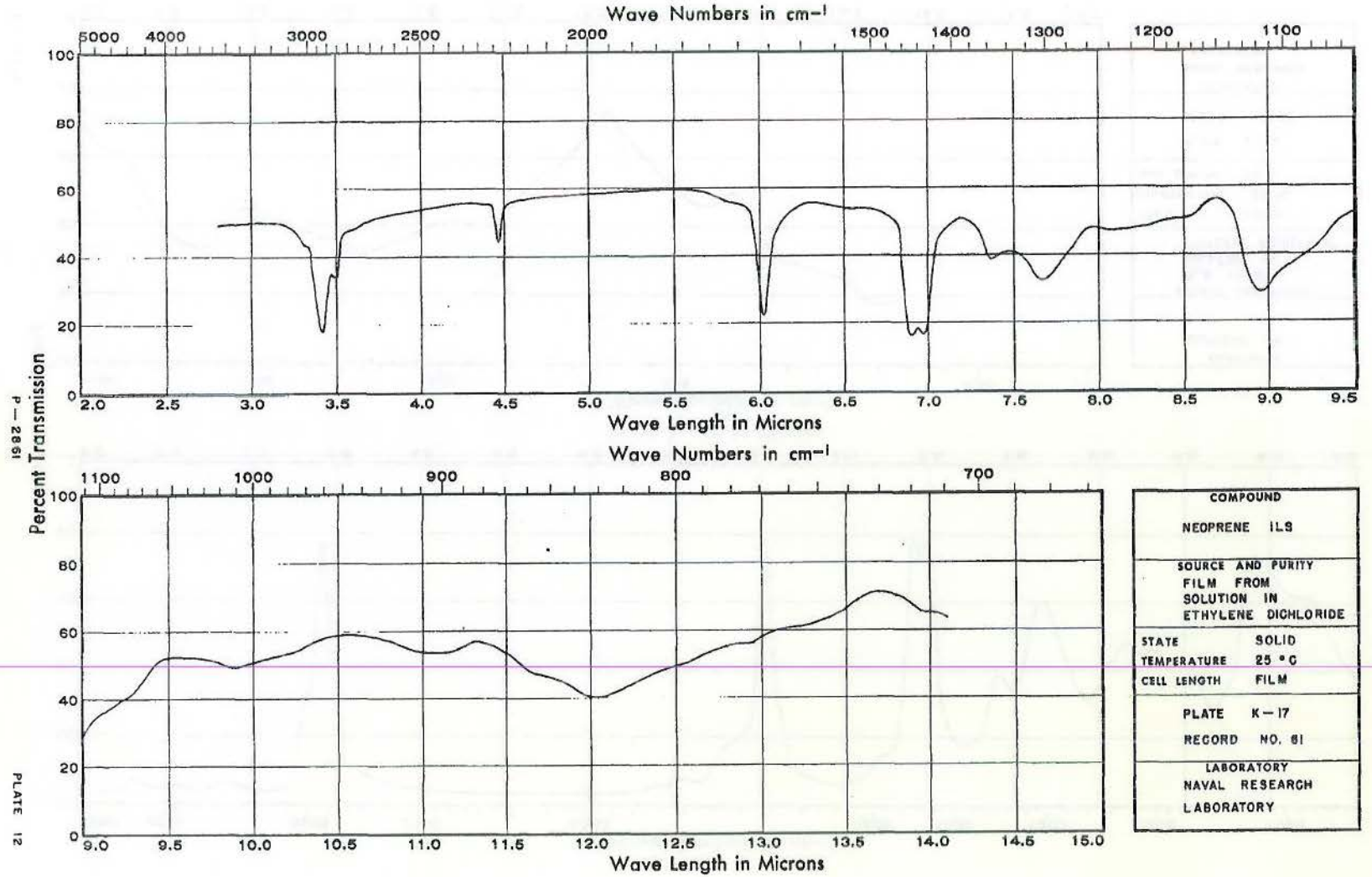
P — 2861

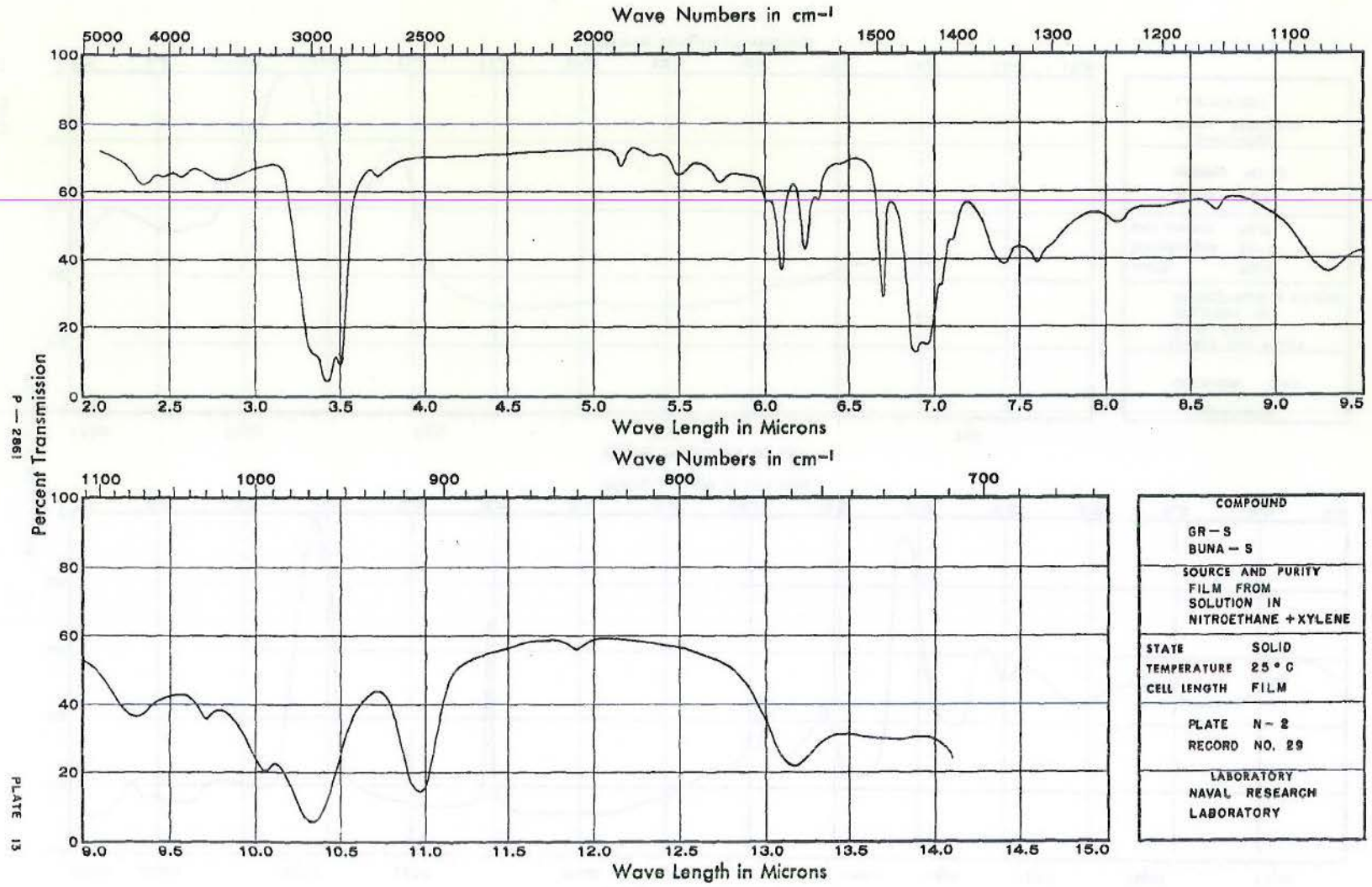
PLATE 10



P — 2861

PLATE 11


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
P — 2861
PLATE 12
COMPOUND
NEOPRENE ILS
SOURCE AND PURITY
FILM FROM SOLUTION IN ETHYLENE DICHLORIDE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
PLATE K — 17
RECORD NO. 61
LABORATORY
NAVAL RESEARCH LABORATORY



P – 2981

PLATE 13

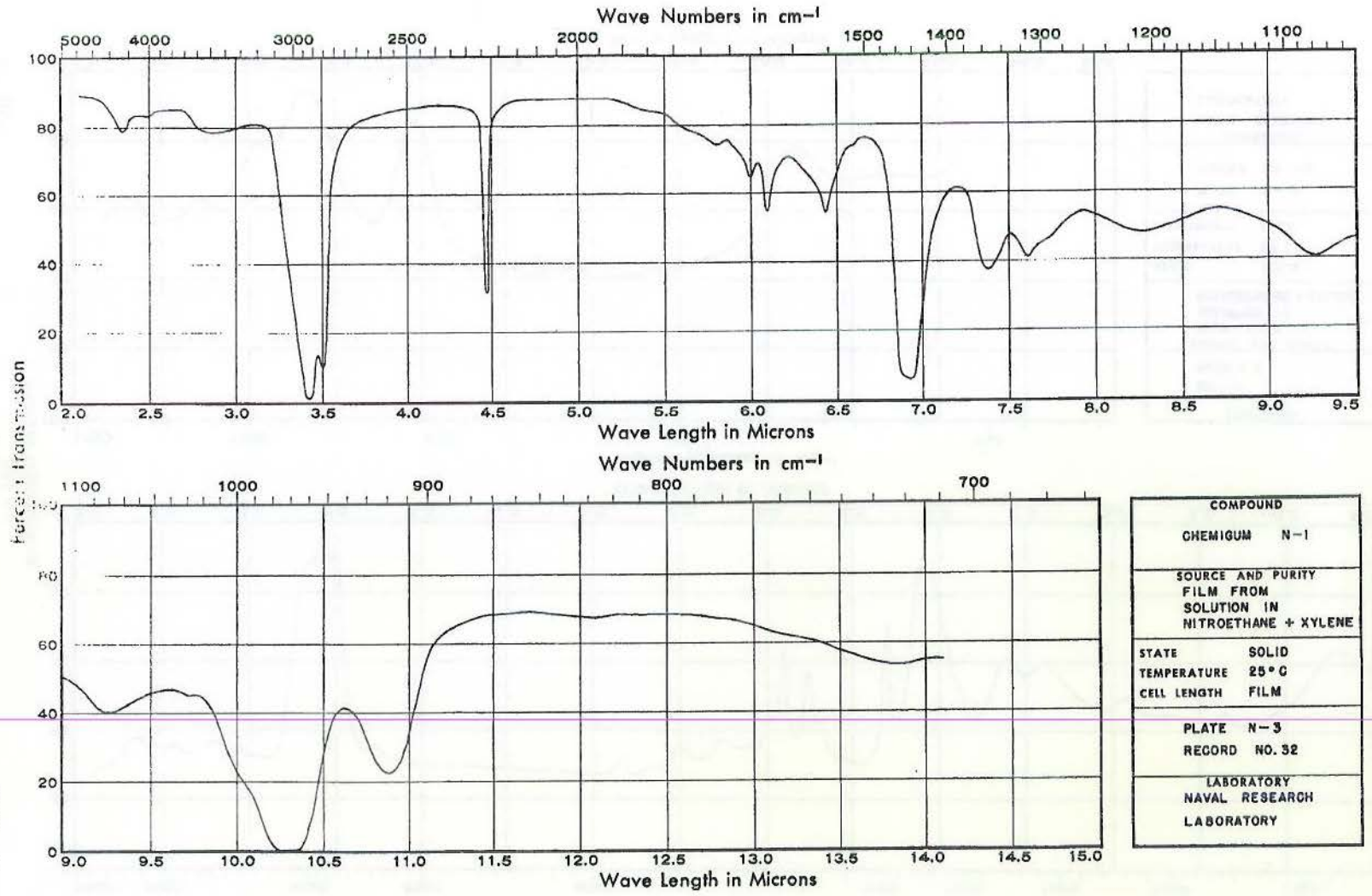
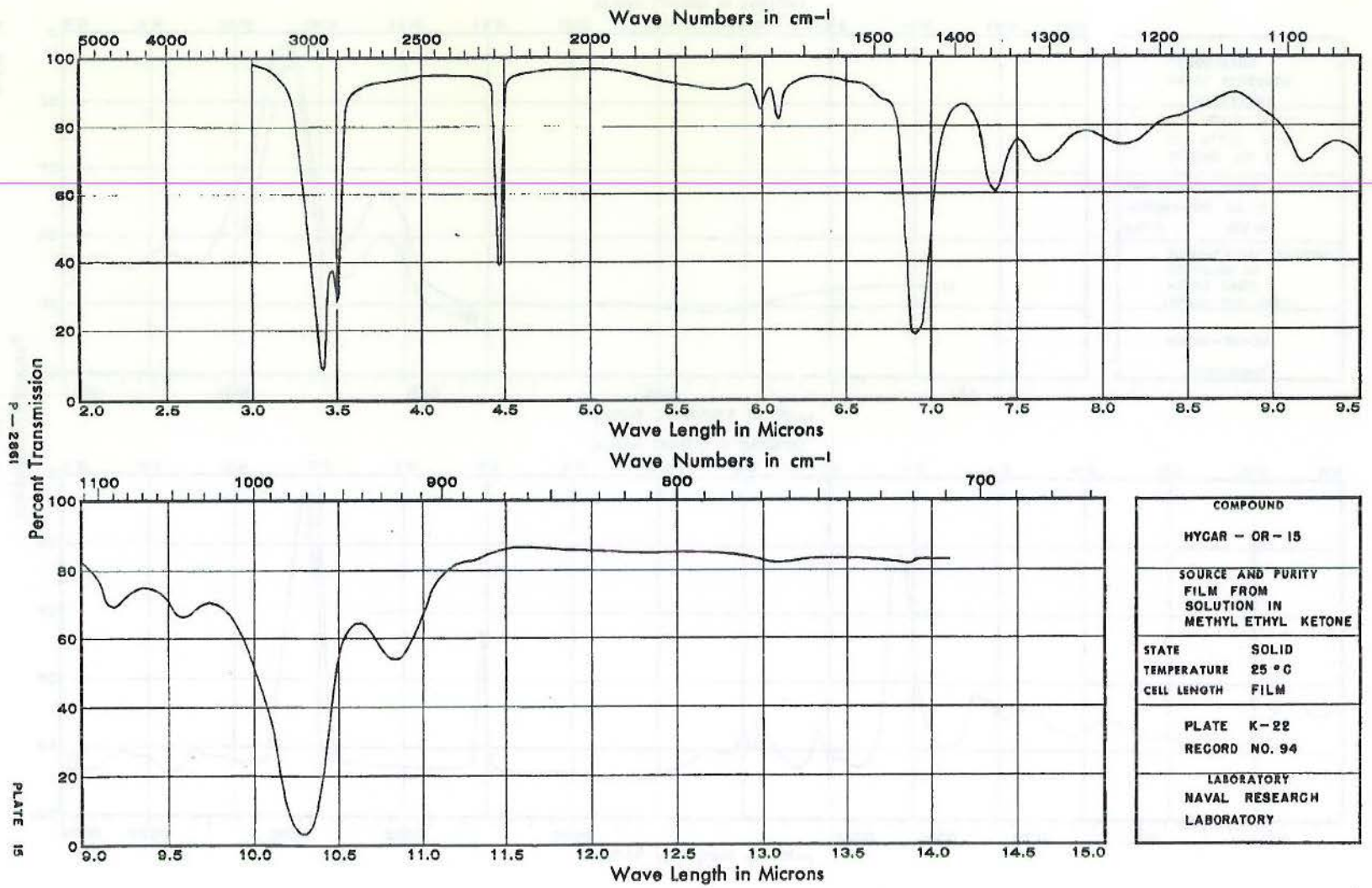
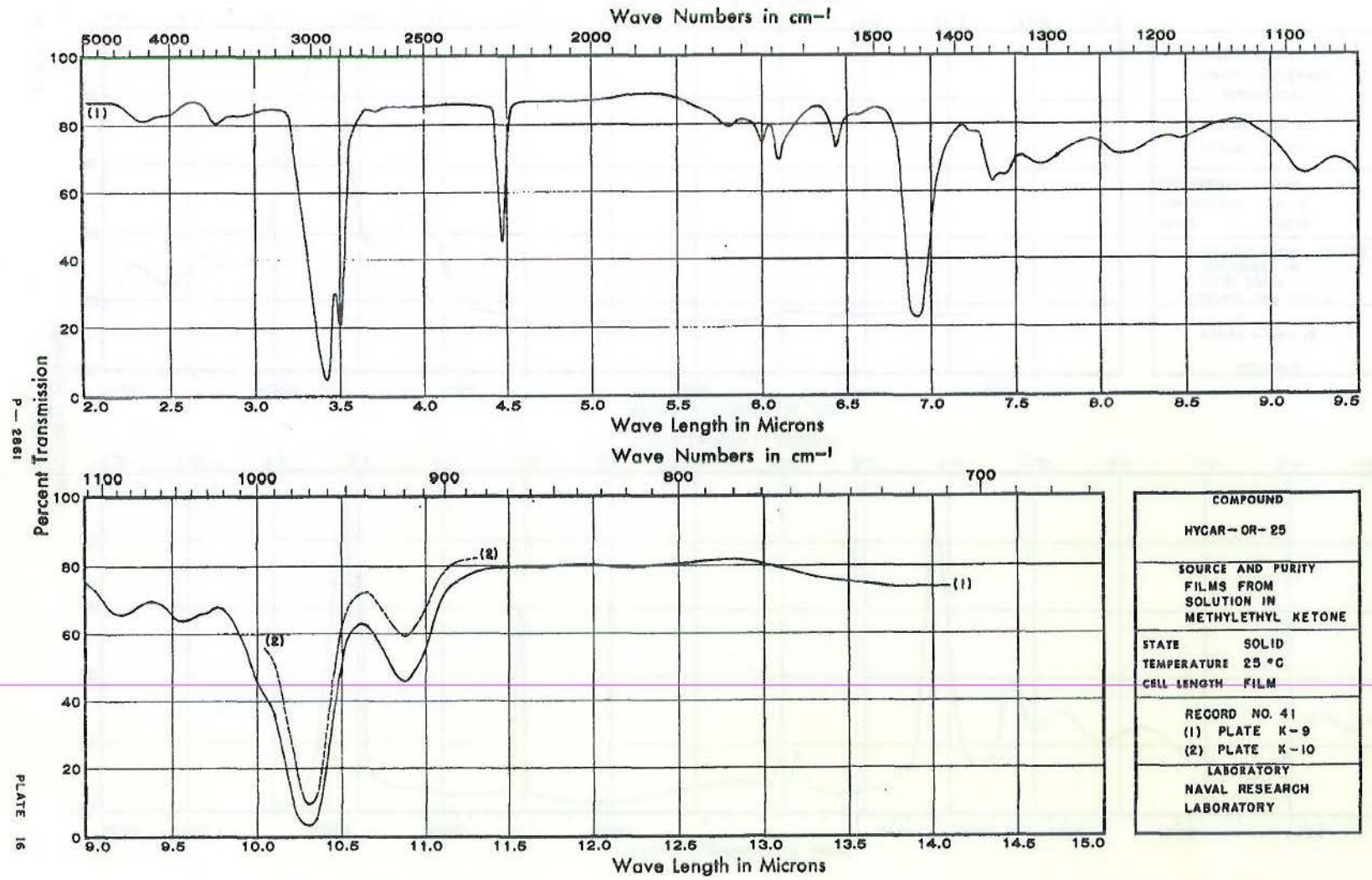

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
CHEMIGUM N-1
SOURCE AND PURITY
FILM FROM SOLUTION IN NITROETHANE + XYLENE
STATE SOLID
TEMPERATURE 25° C
CELL LENGTH FILM
PLATE N-3
RECORD NO. 32
LABORATORY
NAVAL RESEARCH LABORATORY

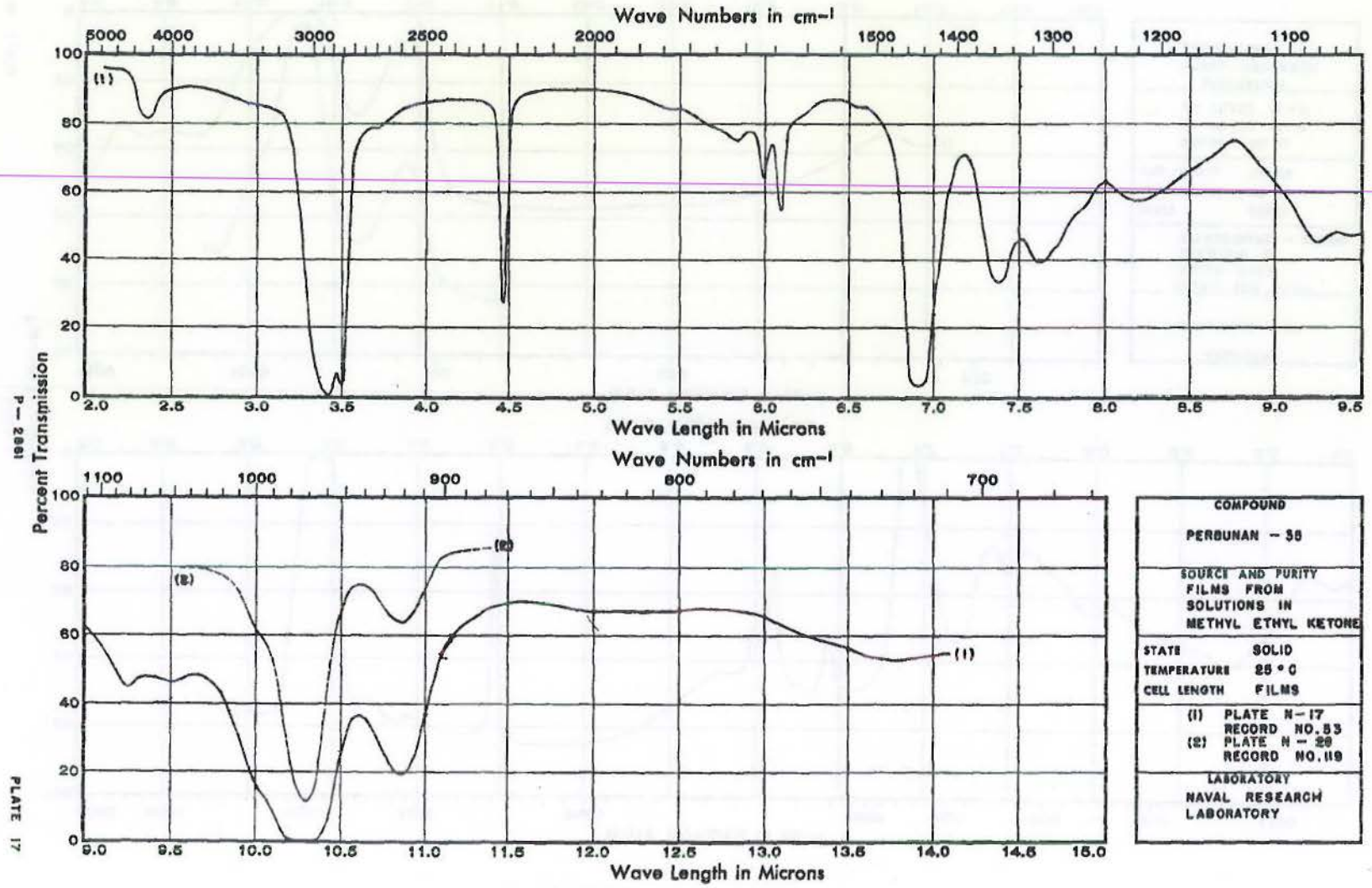
PLATE 14

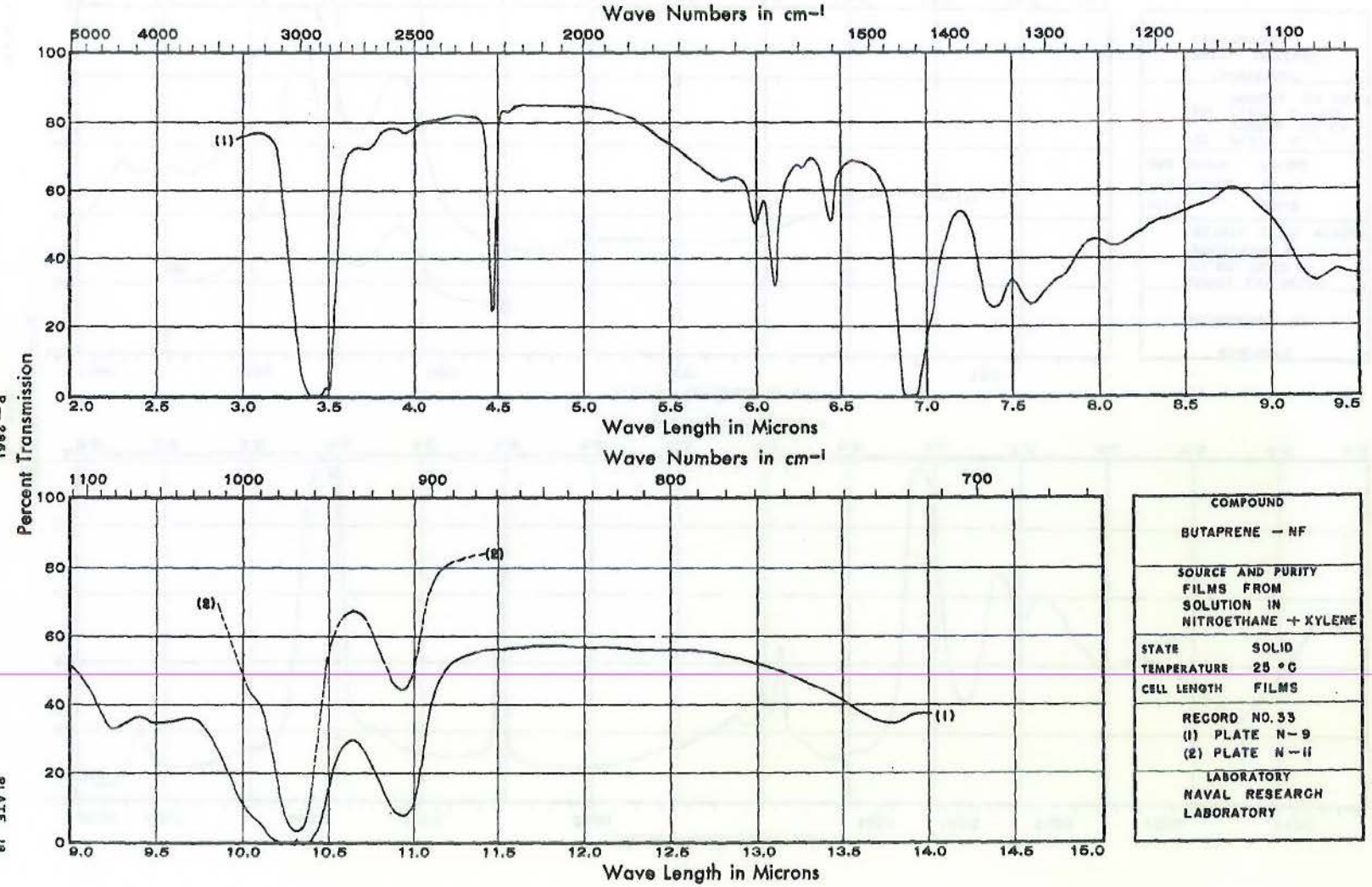

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
HYCAR – OR – 15
SOURCE AND PURITY
FILM FROM SOLUTION IN METHYL ETHYL KETONE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
PLATE K-22
RECORD NO. 94
LABORATORY
NAVAL RESEARCH LABORATORY
1992 – P
PLATE 15

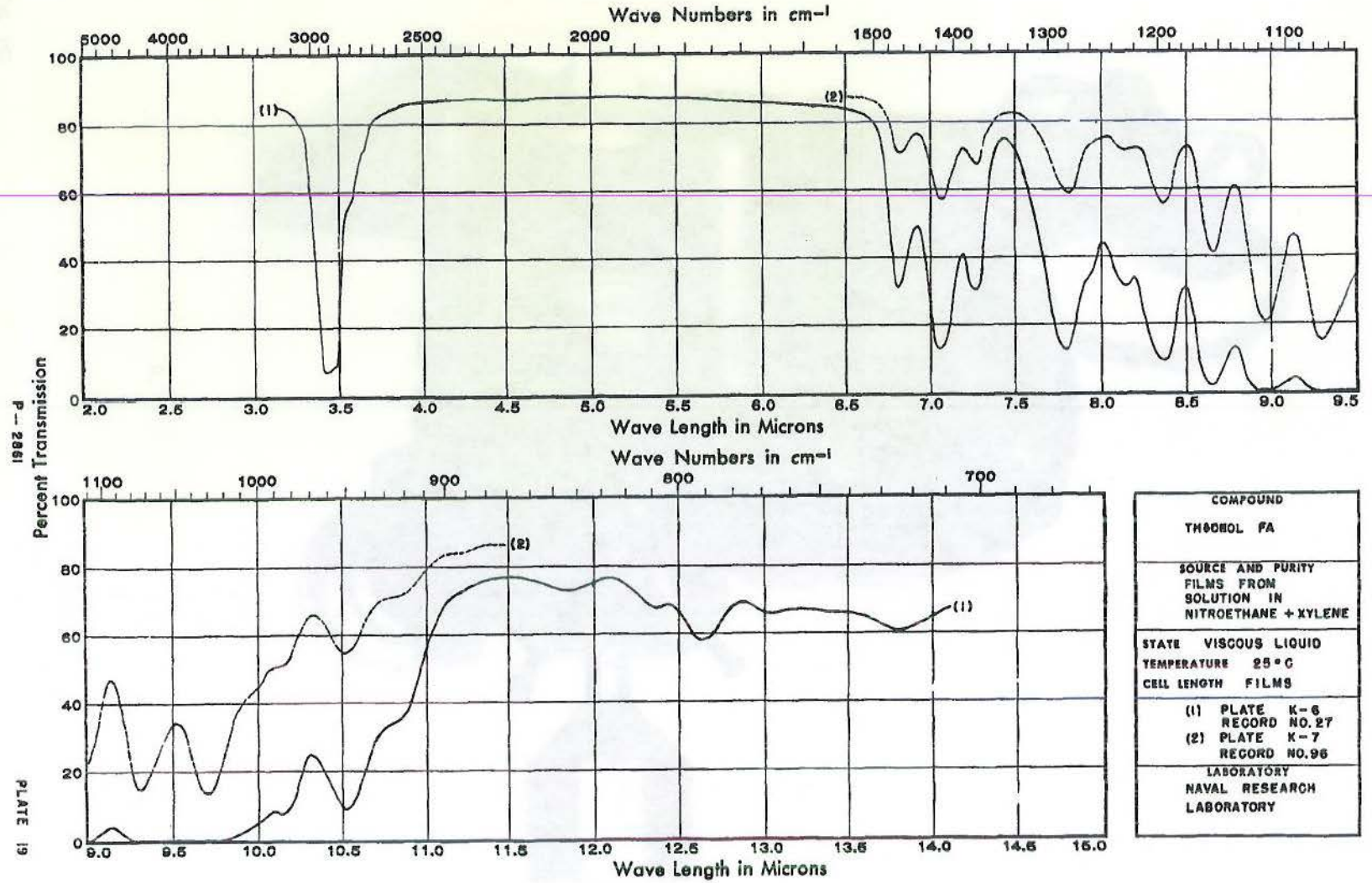


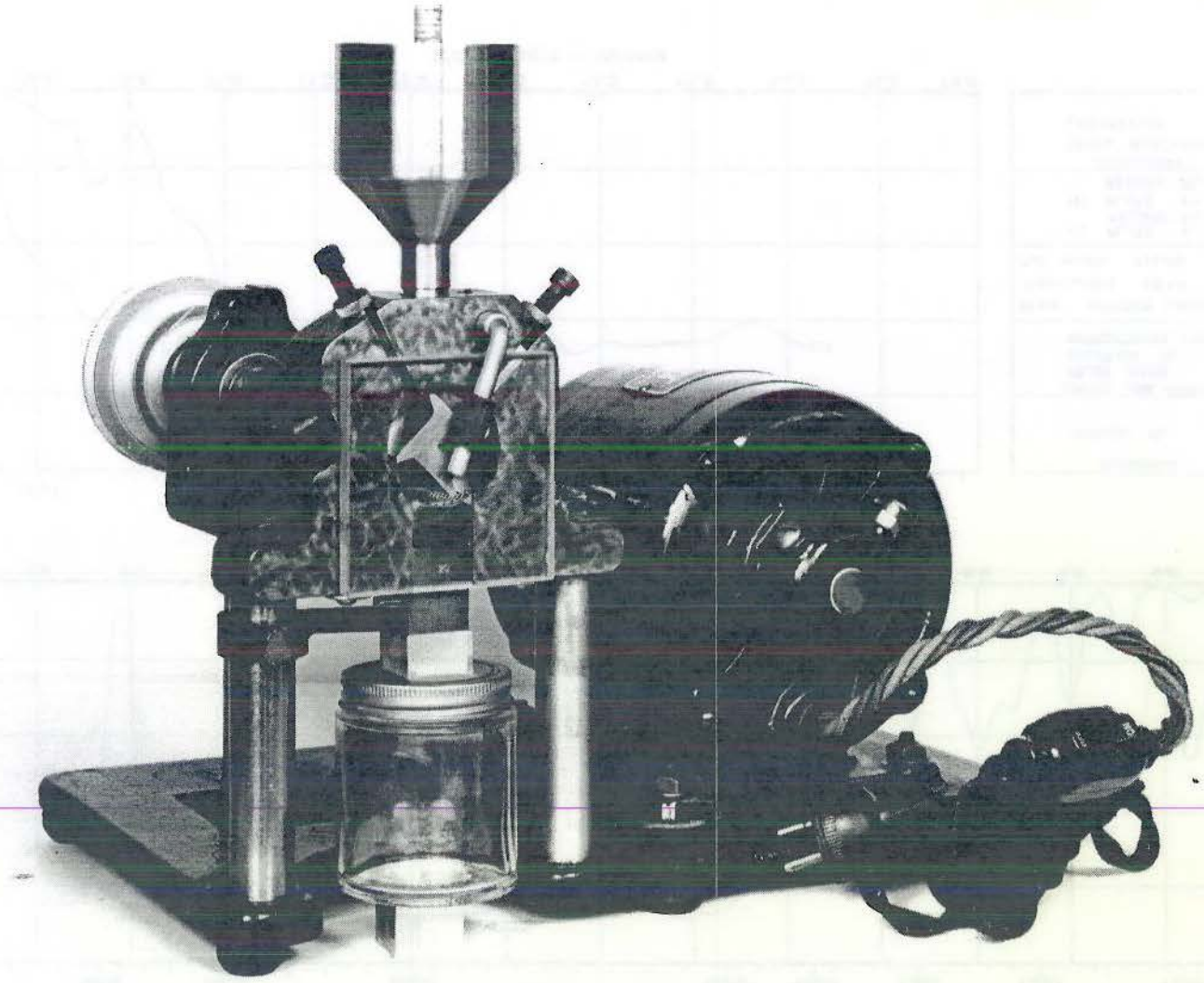
P — 2681

PLATE 16


Wave Numbers in cm-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
(1)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm-1
1100 1000 900 800 700
100 80 60 40 20 0
(2)
(2)
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
PERBUNAN – 38
SOURCE AND PURITY
FILMS FROM SOLUTIONS IN METHYL ETHYL KETONE
STATE SOLID
TEMPERATURE 25 ° C
CELL LENGTH FILMS
(1) PLATE N – 17 RECORD NO. 53
(2) PLATE N – 29 RECORD NO. 119
LABORATORY
NAVAL RESEARCH LABORATORY
P – 2681
PLATE 17


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
(1)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
(2)
(2)
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
BUTAPRENE — NF
SOURCE AND PURITY
FILMS FROM SOLUTION IN NITROETHANE + XYLENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILMS
RECORD NO. 33
(1) PLATE N-9
(2) PLATE N-11
LABORATORY
NAVAL RESEARCH LABORATORY
P-2861
PLATE 18

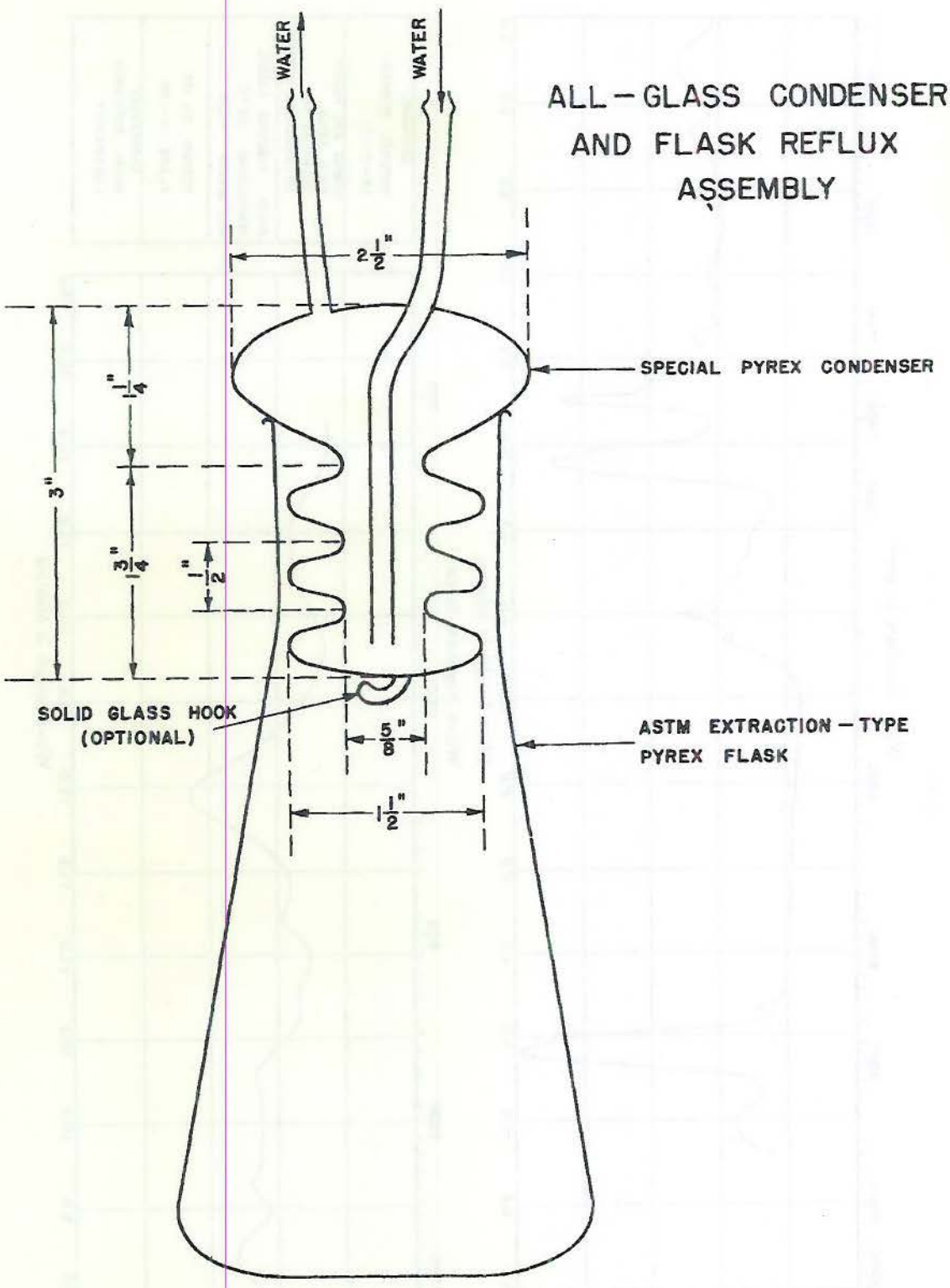

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
(1)
(2)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
(2)
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
THIOCHOL FA
SOURCE AND PURITY
FILMS FROM SOLUTION IN NITROETHANE + XYLENE
STATE VISCOUS LIQUID
TEMPERATURE 25° C
CELL LENGTH FILMS
(1) PLATE K-6 RECORD NO. 27
(2) PLATE K-7 RECORD NO. 96
LABORATORY
NAVAL RESEARCH LABORATORY
P-2861
PLATE 19



WILEY LABORATORY MILL

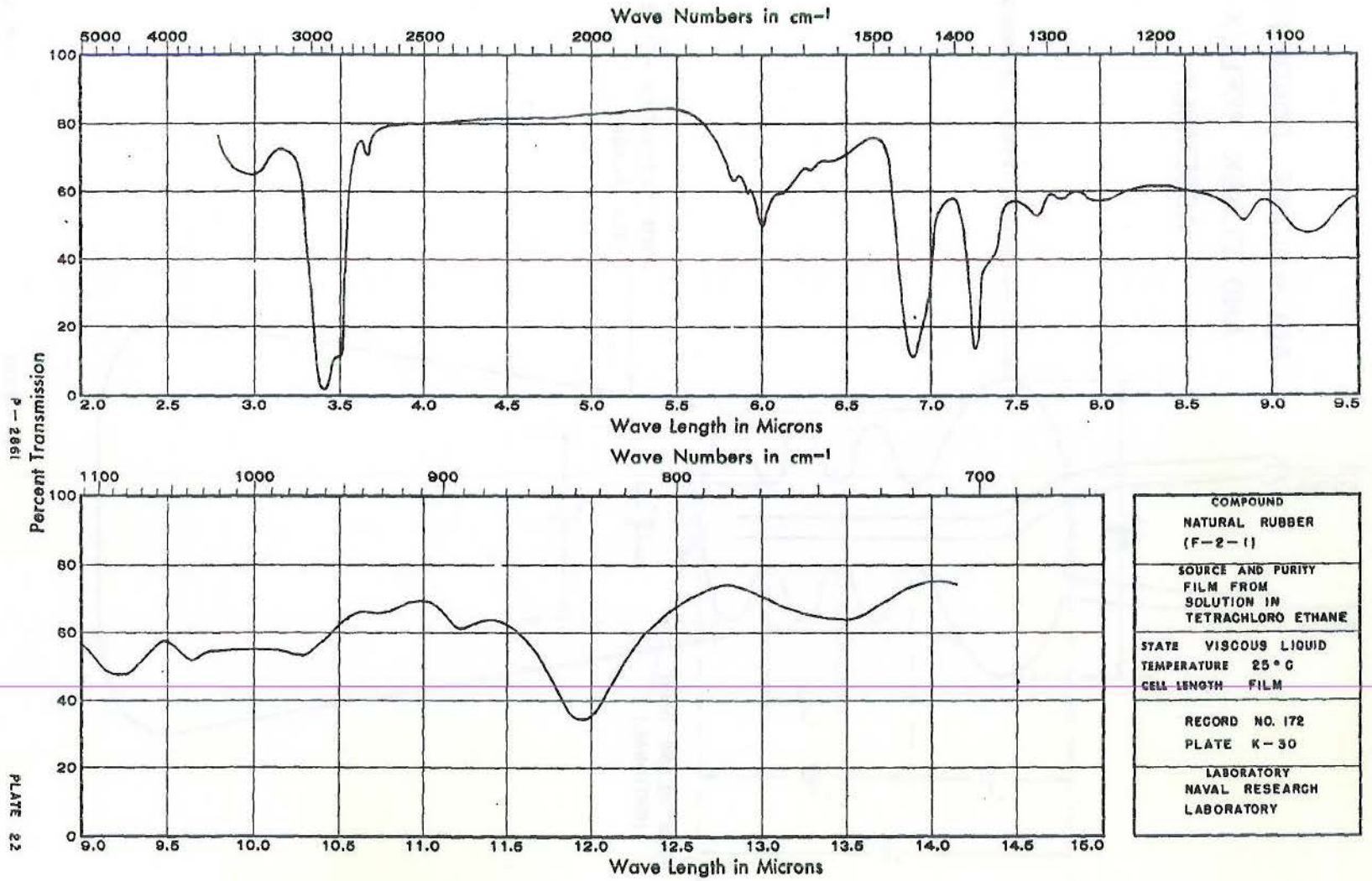
PLATE 20

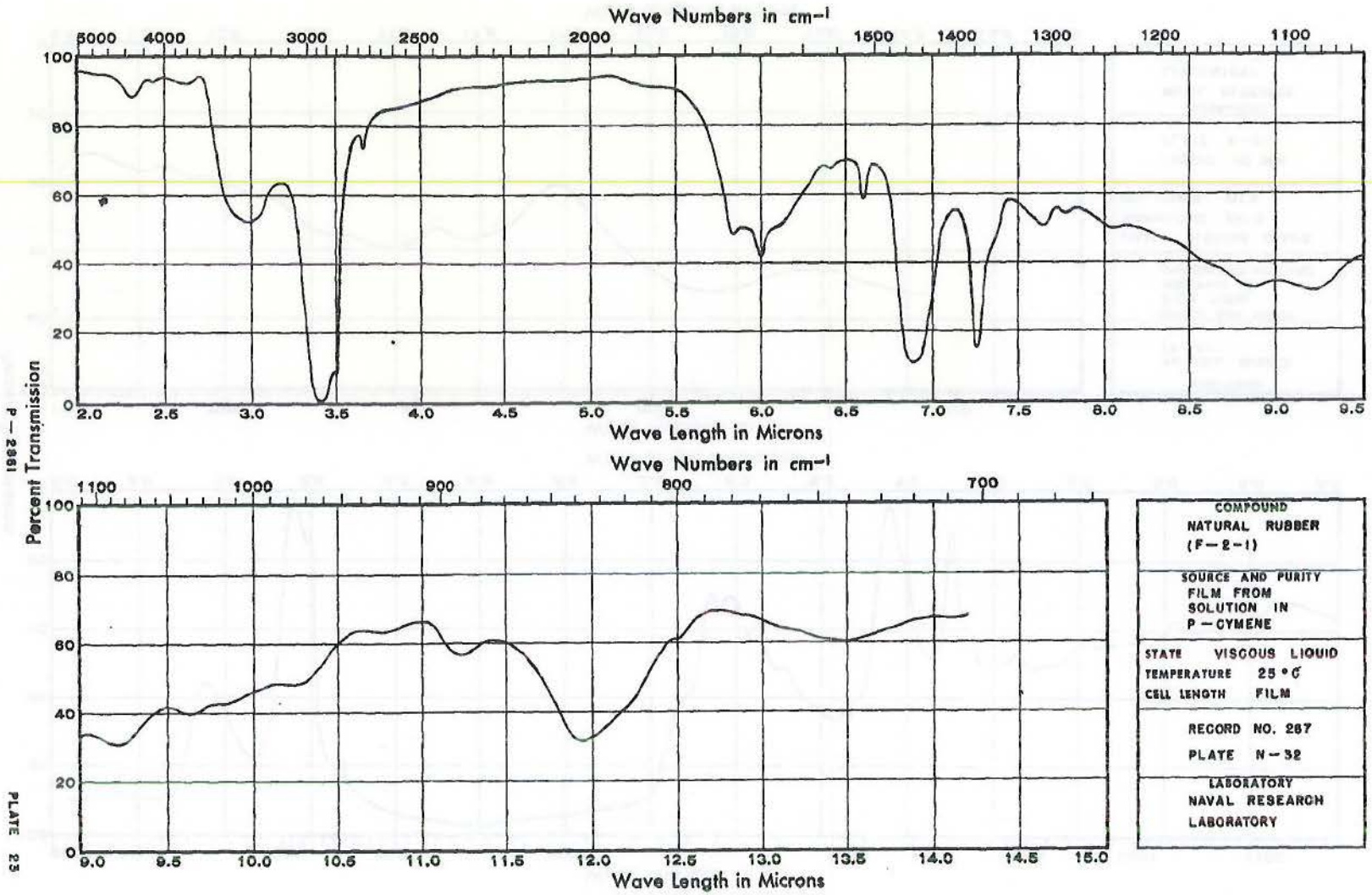
ALL-GLASS CONDENSER AND FLASK REFLUX ASSEMBLY

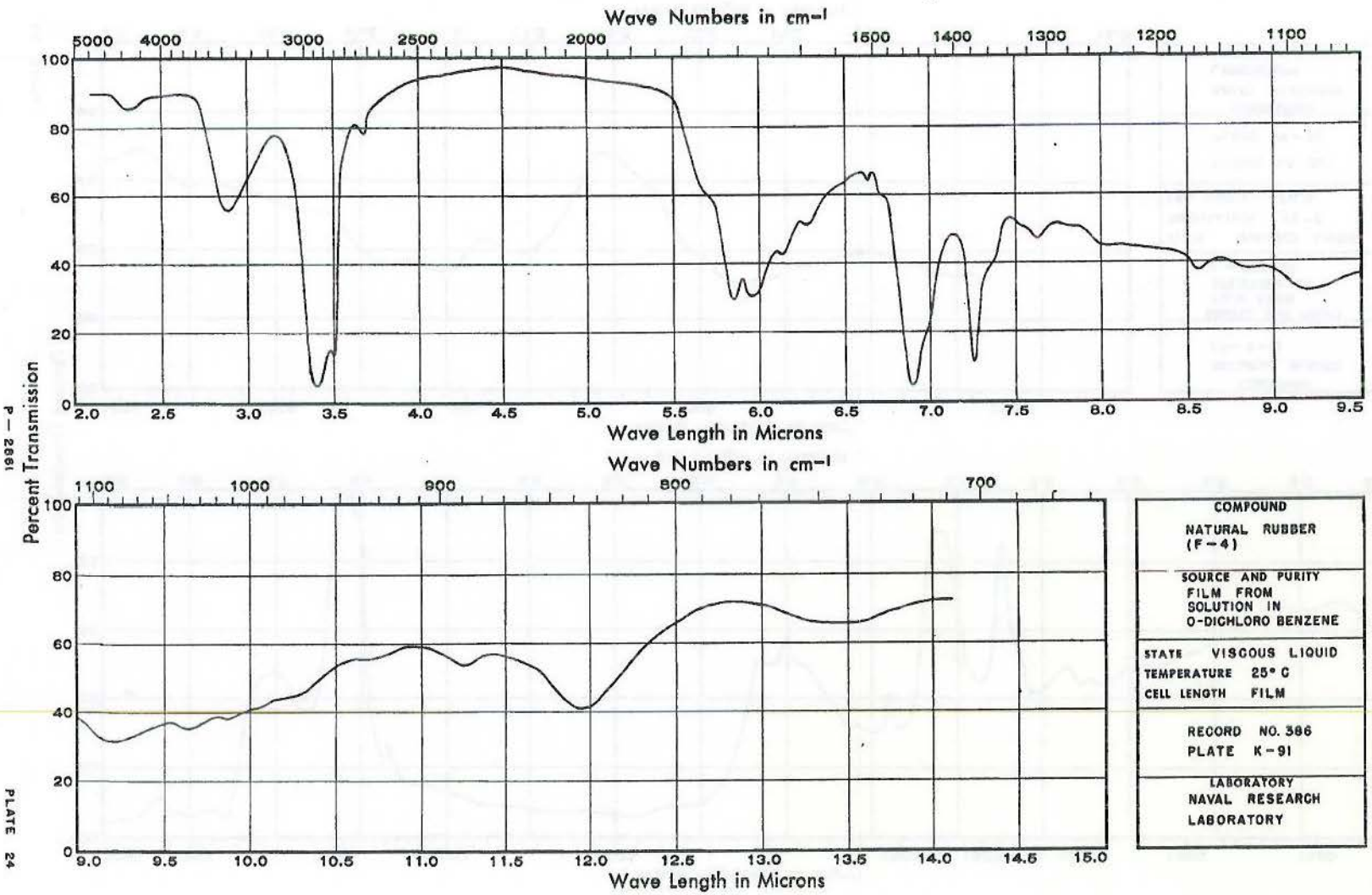


P—2861

PLATE 21

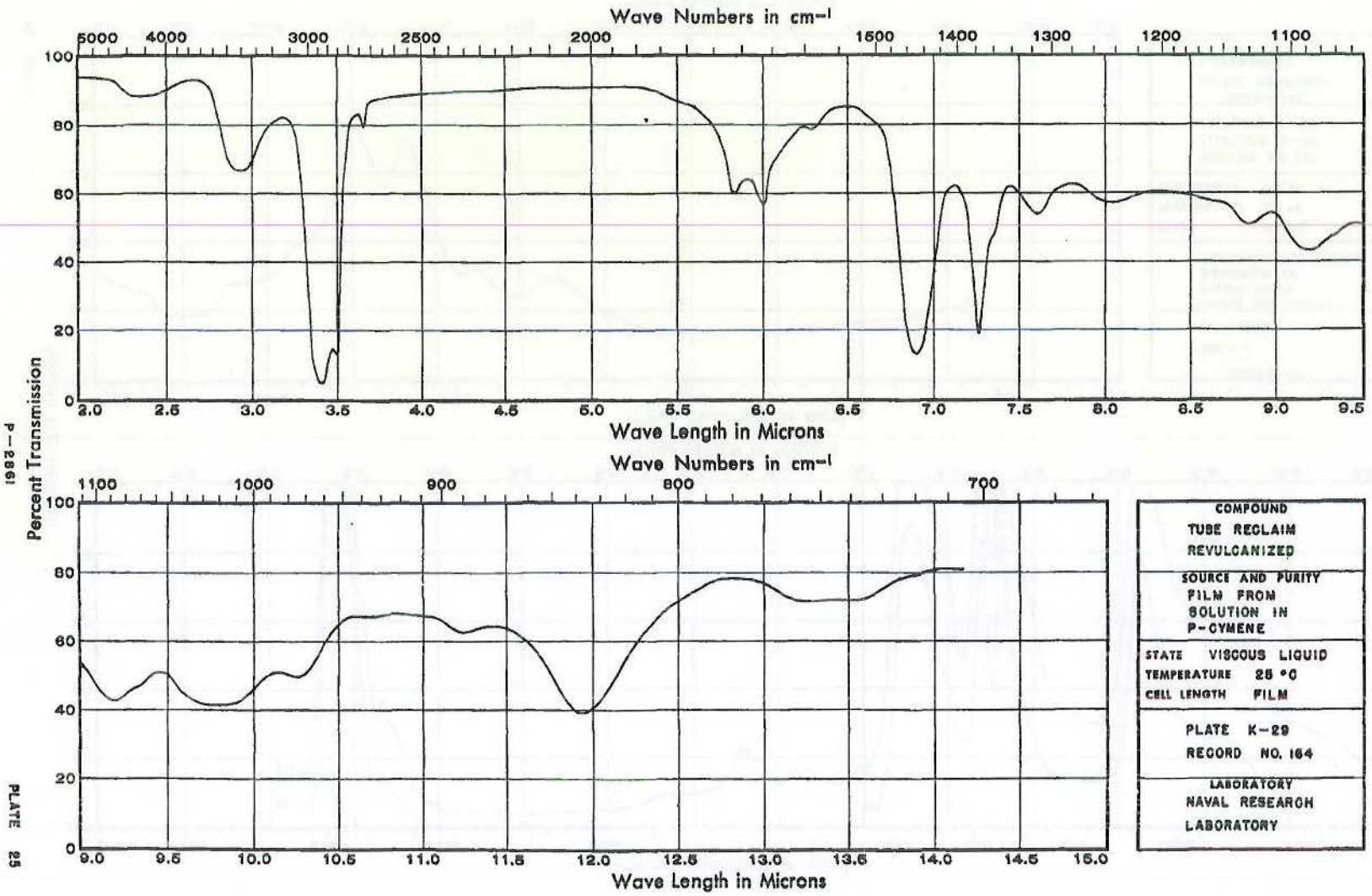

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
COMPOUND
NATURAL RUBBER
(F-2-1)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE VISCOUS LIQUID
TEMPERATURE 25° C
CELL LENGTH FILM
RECORD NO. 172
PLATE K-30
LABORATORY
NAVAL RESEARCH
LABORATORY
1992 - 261
PLATE 22

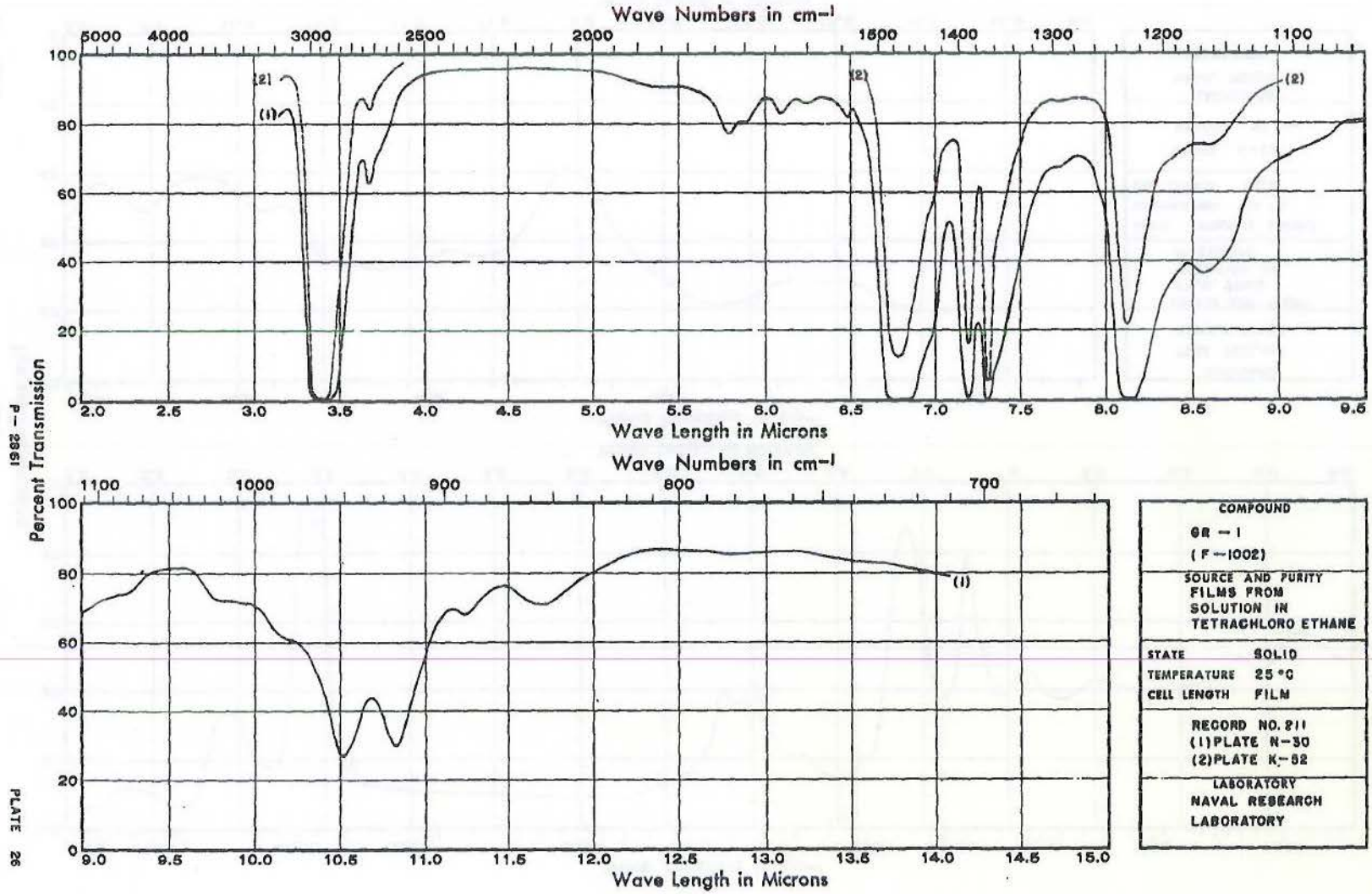

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
NATURAL RUBBER
(F-2-1)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
P-CYMENE
STATE VISCOUS LIQUID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 267
PLATE N-32
LABORATORY
NAVAL RESEARCH
LABORATORY
P-2881
PLATE 23

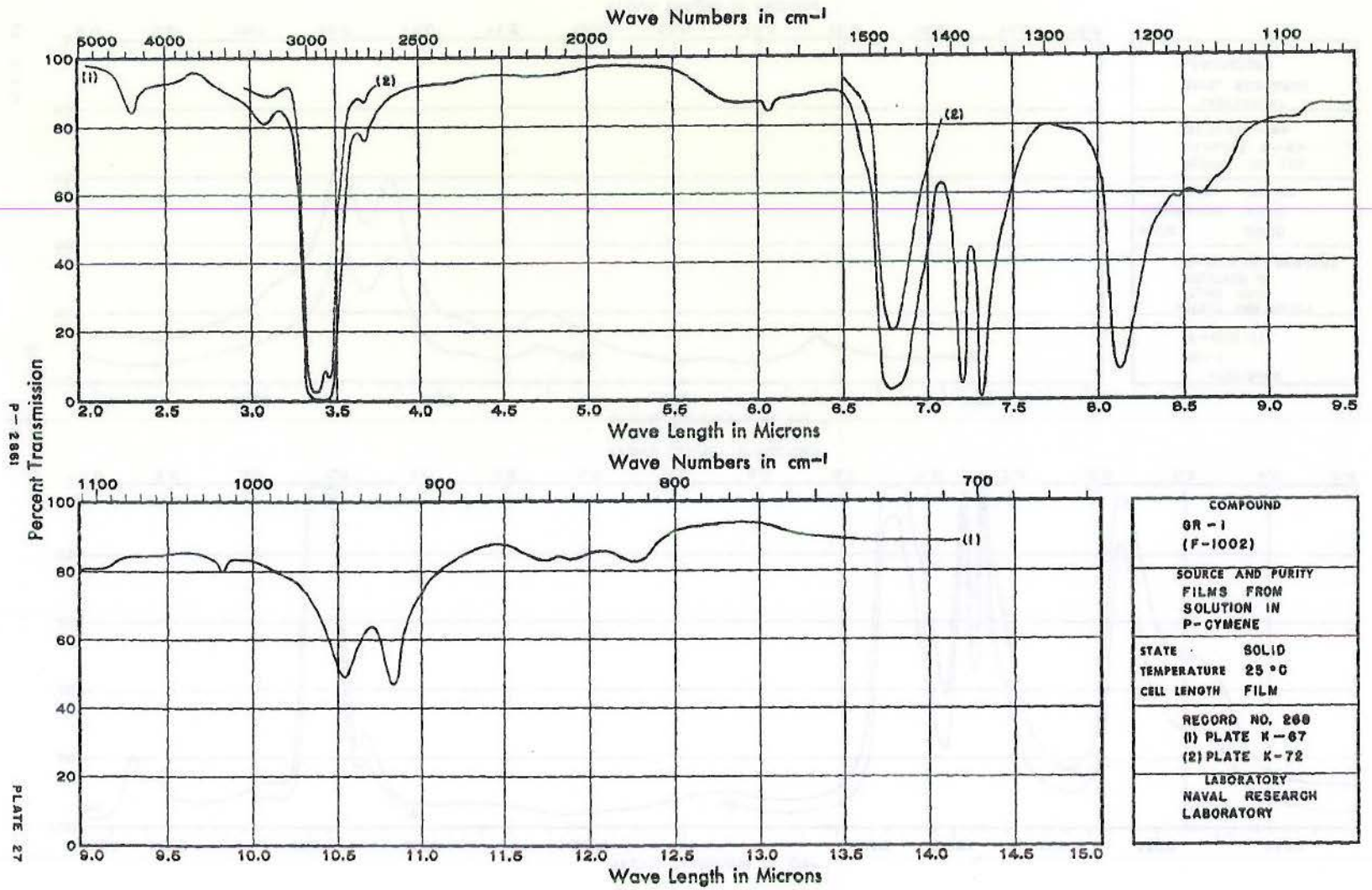


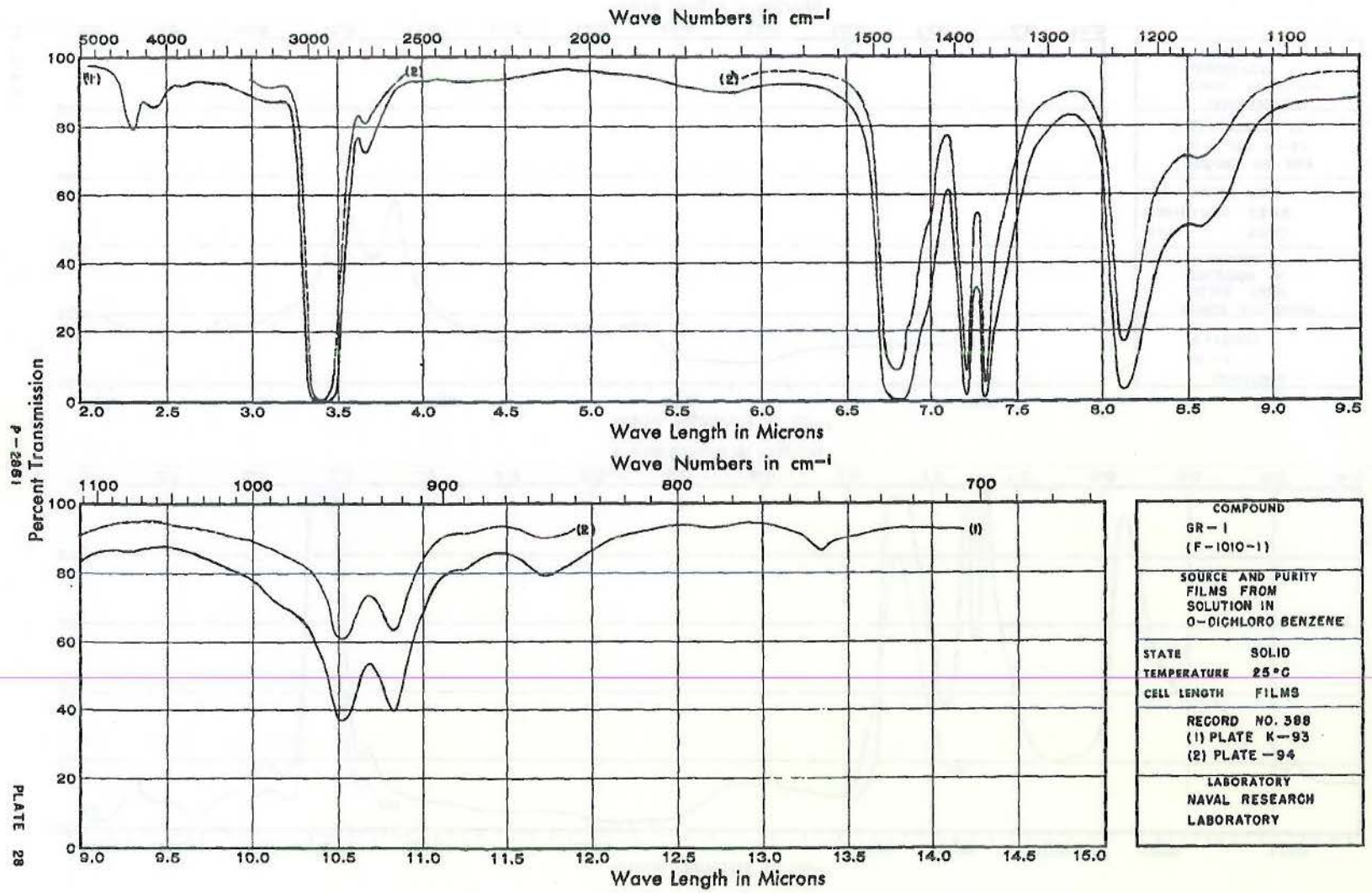
P — 2861

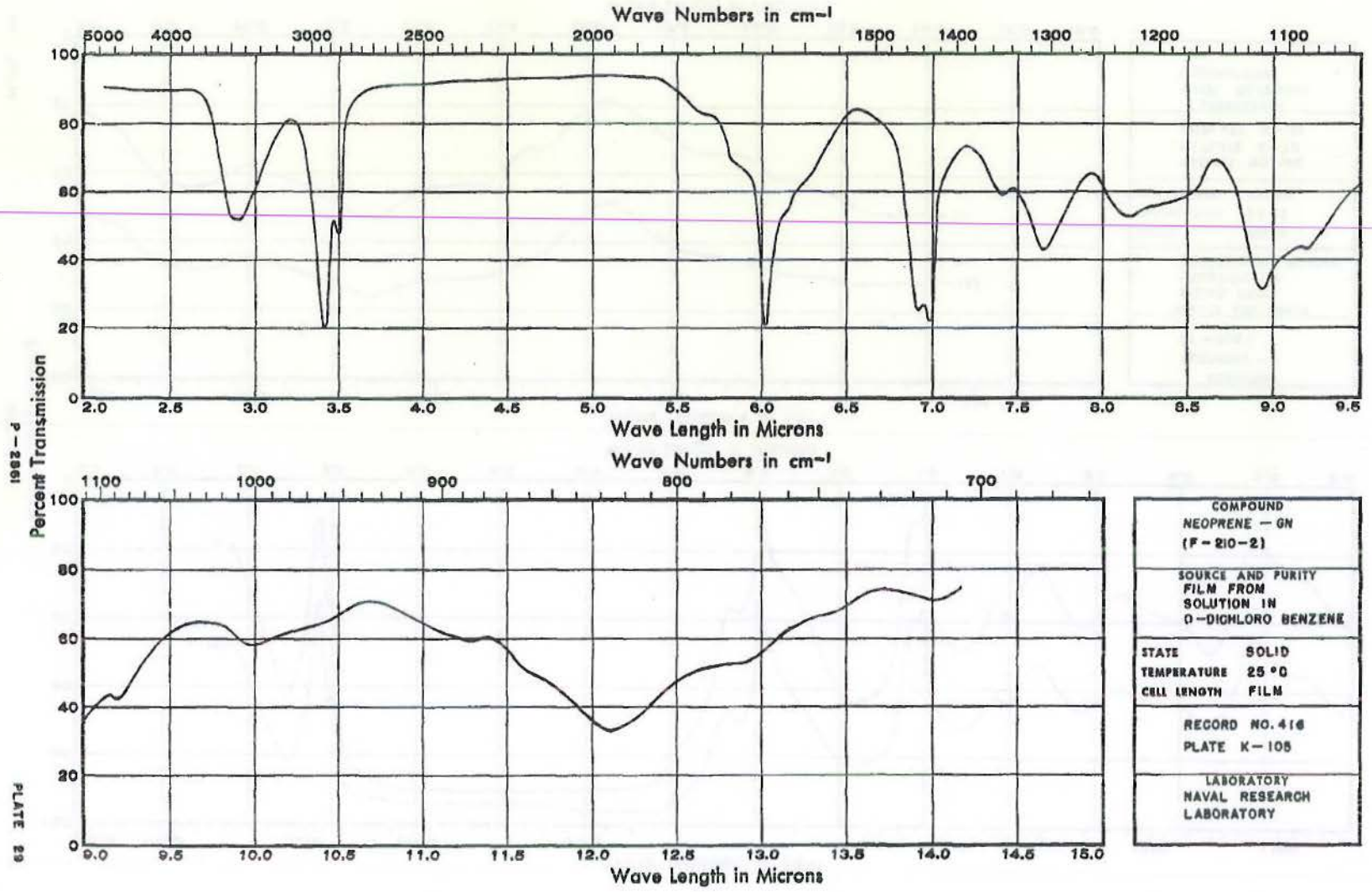
PLATE 24

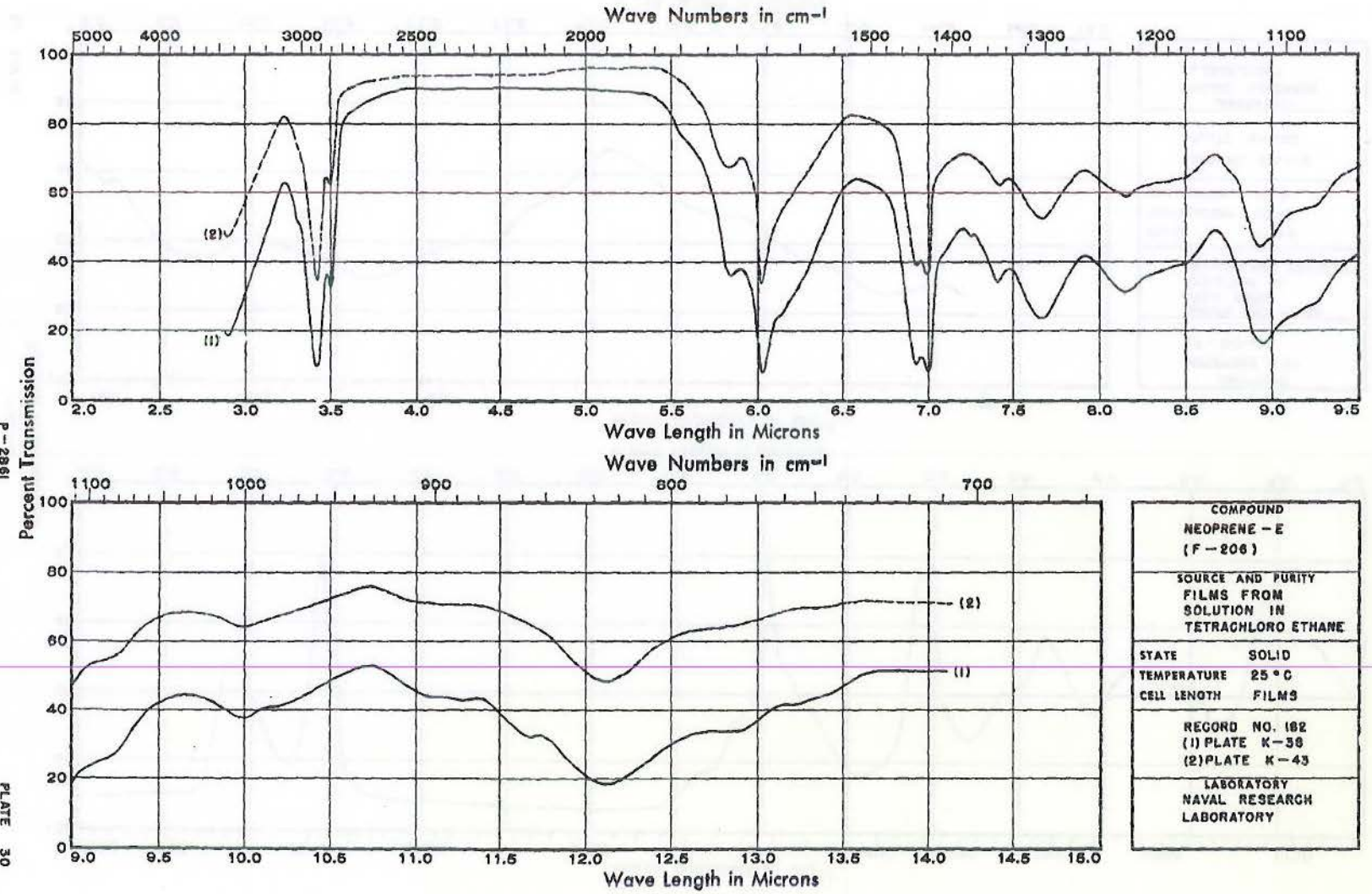

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
1983 – d
PLATE 23
COMPOUND
TUBE RECLAIM
REVULCANIZED
SOURCE AND PURITY
FILM FROM
SOLUTION IN
P-CYMENE
STATE VISCOUS LIQUID
TEMPERATURE 25 °C
CELL LENGTH FILM
PLATE K-29
RECORD NO. 164
LABORATORY
NAVAL RESEARCH
LABORATORY

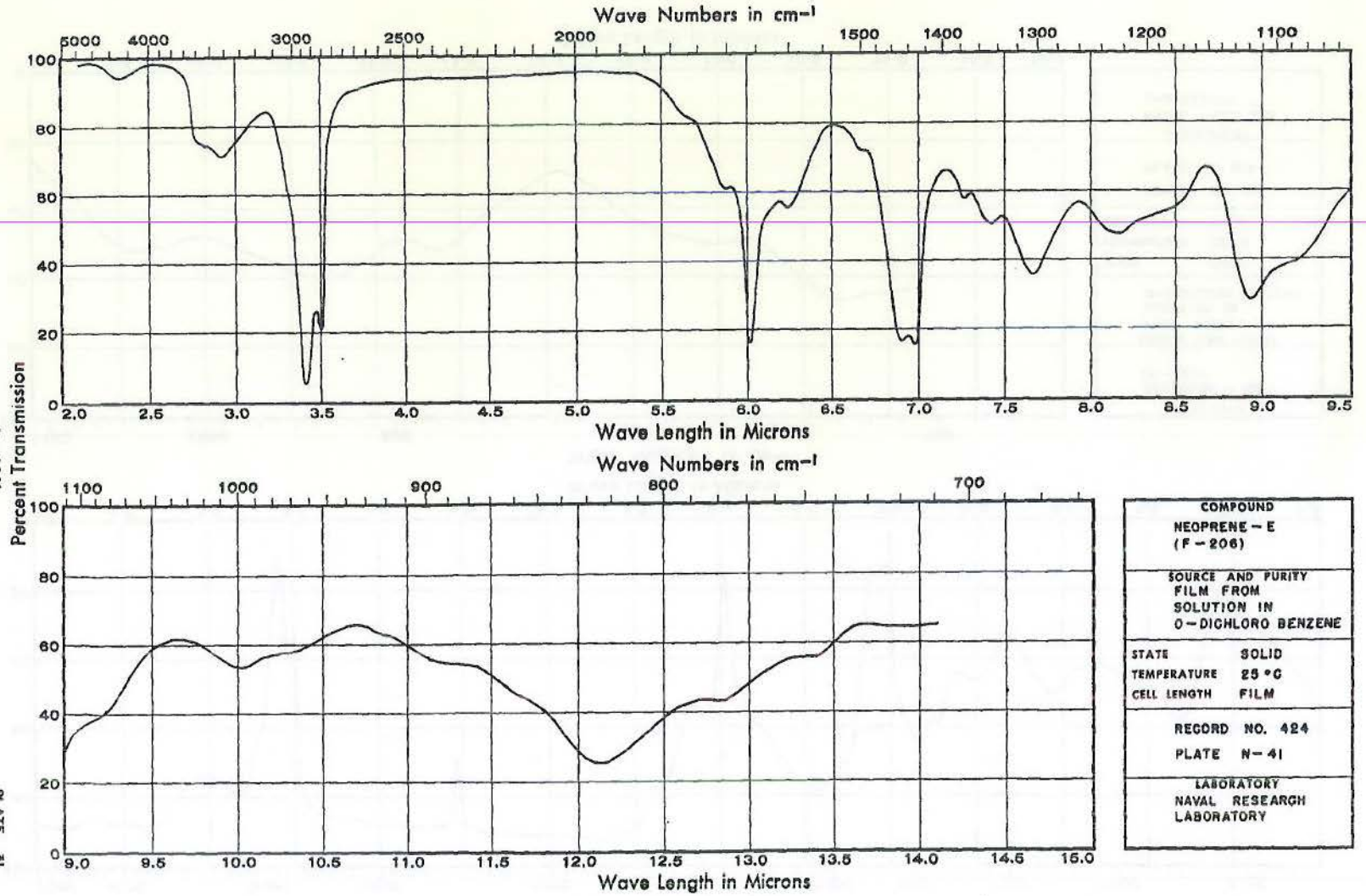

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
(2)
(1)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
GR — 1
(F — 1002)
SOURCE AND PURITY
FILMS FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 211
(1) PLATE N-30
(2) PLATE K-52
LABORATORY
NAVAL RESEARCH
LABORATORY
P - 2861
PLATE 26

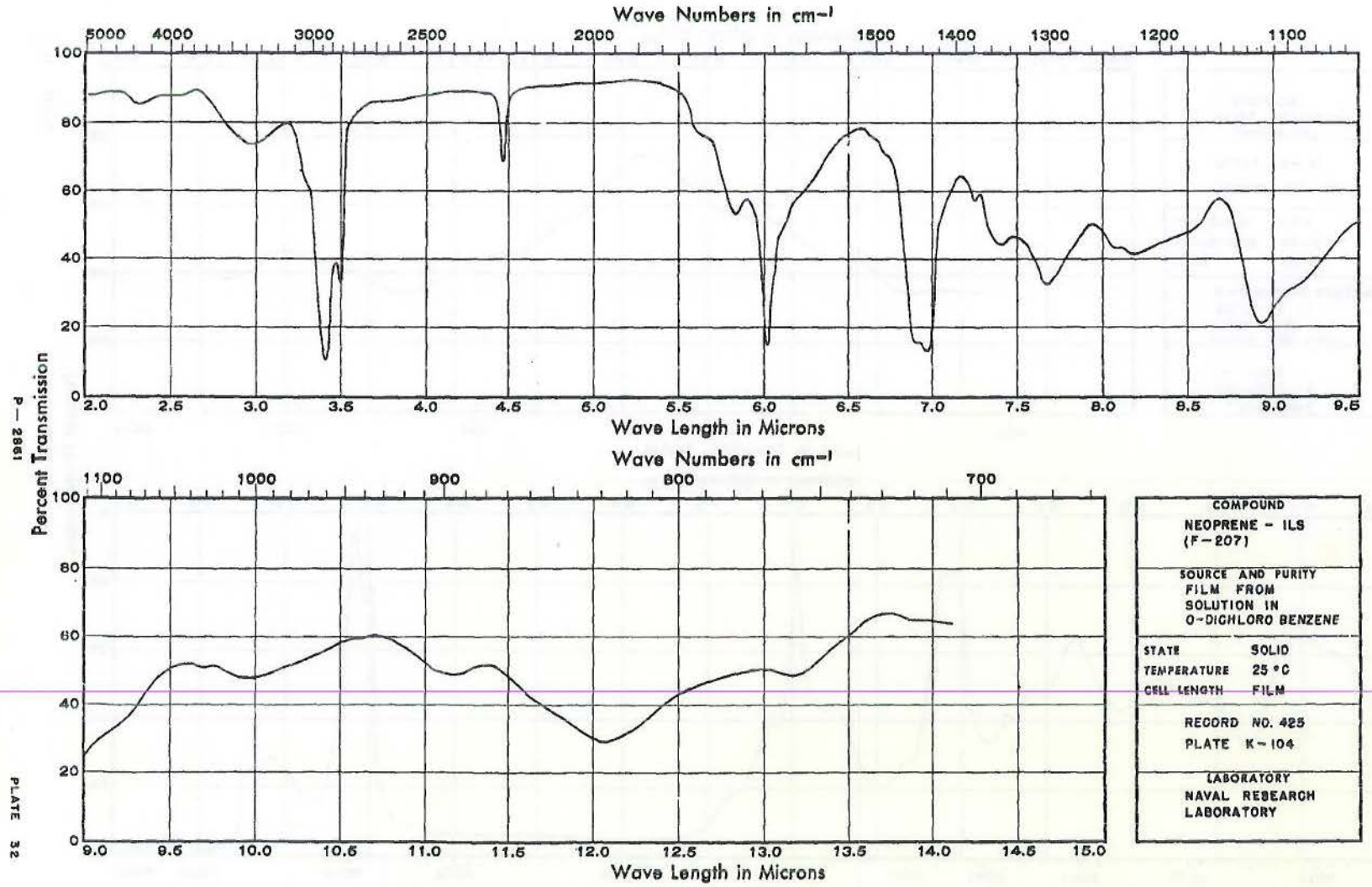

Wave Numbers in cm-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
(1)
(2)
(2)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm-1
1100 1000 900 800 700
100 80 60 40 20 0
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
GR - I
(F-1002)
SOURCE AND PURITY
FILMS FROM SOLUTION IN P-CYMENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 268
(1) PLATE K-67
(2) PLATE K-72
LABORATORY
NAVAL RESEARCH LABORATORY
P - 2861
PLATE 27


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
(1)
(2)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
(2)
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
P-2881
PLATE 28
COMPOUND
GR-I
(F-1010-1)
SOURCE AND PURITY
FILMS FROM
SOLUTION IN
O-DICHLORO BENZENE
STATE SOLID
TEMPERATURE 25°C
CELL LENGTH FILMS
RECORD NO. 388
(1) PLATE K-93
(2) PLATE -94
LABORATORY
NAVAL RESEARCH
LABORATORY


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
P-2861
PLATE 23
COMPOUND
NEOPRENE — GN
(F-210-2)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
O-DICHLORO BENZENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 416
PLATE K-105
LABORATORY
NAVAL RESEARCH
LABORATORY

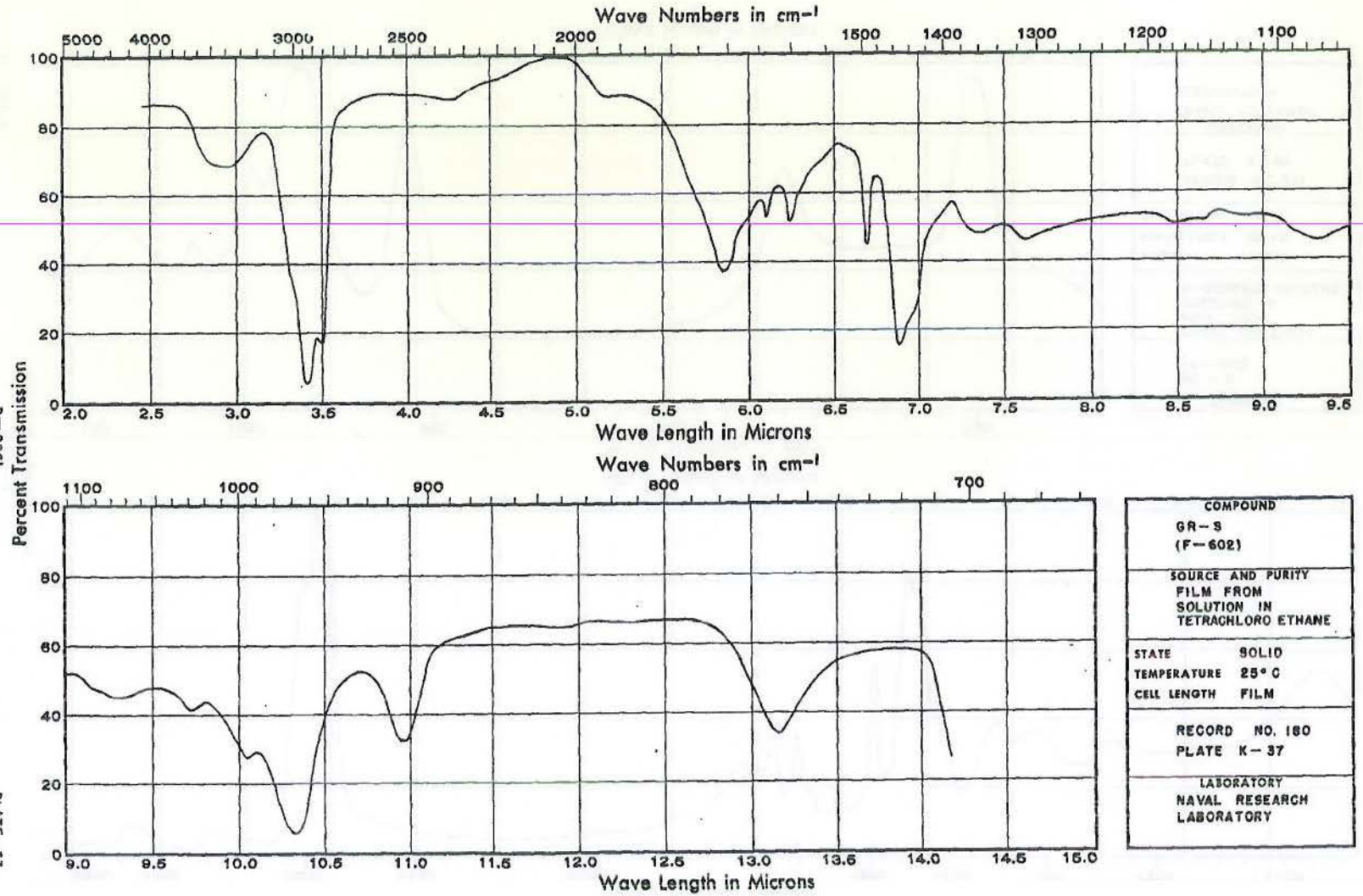

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
(2)
(1)
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
(2)
(1)
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
NEOPRENE – E
(F – 206)
SOURCE AND PURITY
FILMS FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE SOLID
TEMPERATURE 25 ° C
CELL LENGTH FILMS
RECORD NO. 182
(1) PLATE K – 36
(2) PLATE K – 43
LABORATORY
NAVAL RESEARCH
LABORATORY
P – 2861
PLATE 30

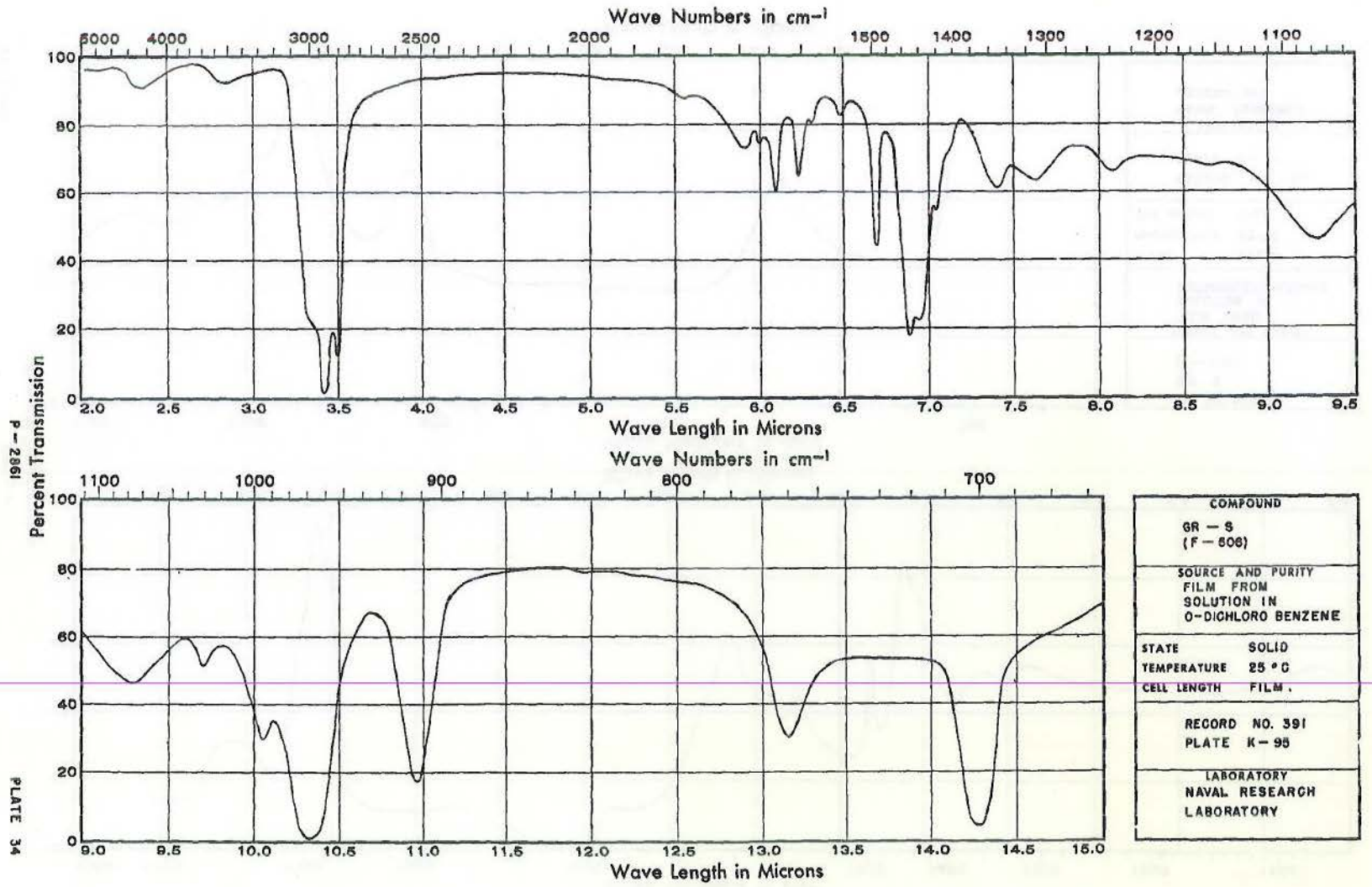

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
NEOPRENE – E
(F – 206)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
O – DICHLORO BENZENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 424
PLATE N – 41
LABORATORY
NAVAL RESEARCH
LABORATORY
A – 2861
PLATE 31



P - 2861

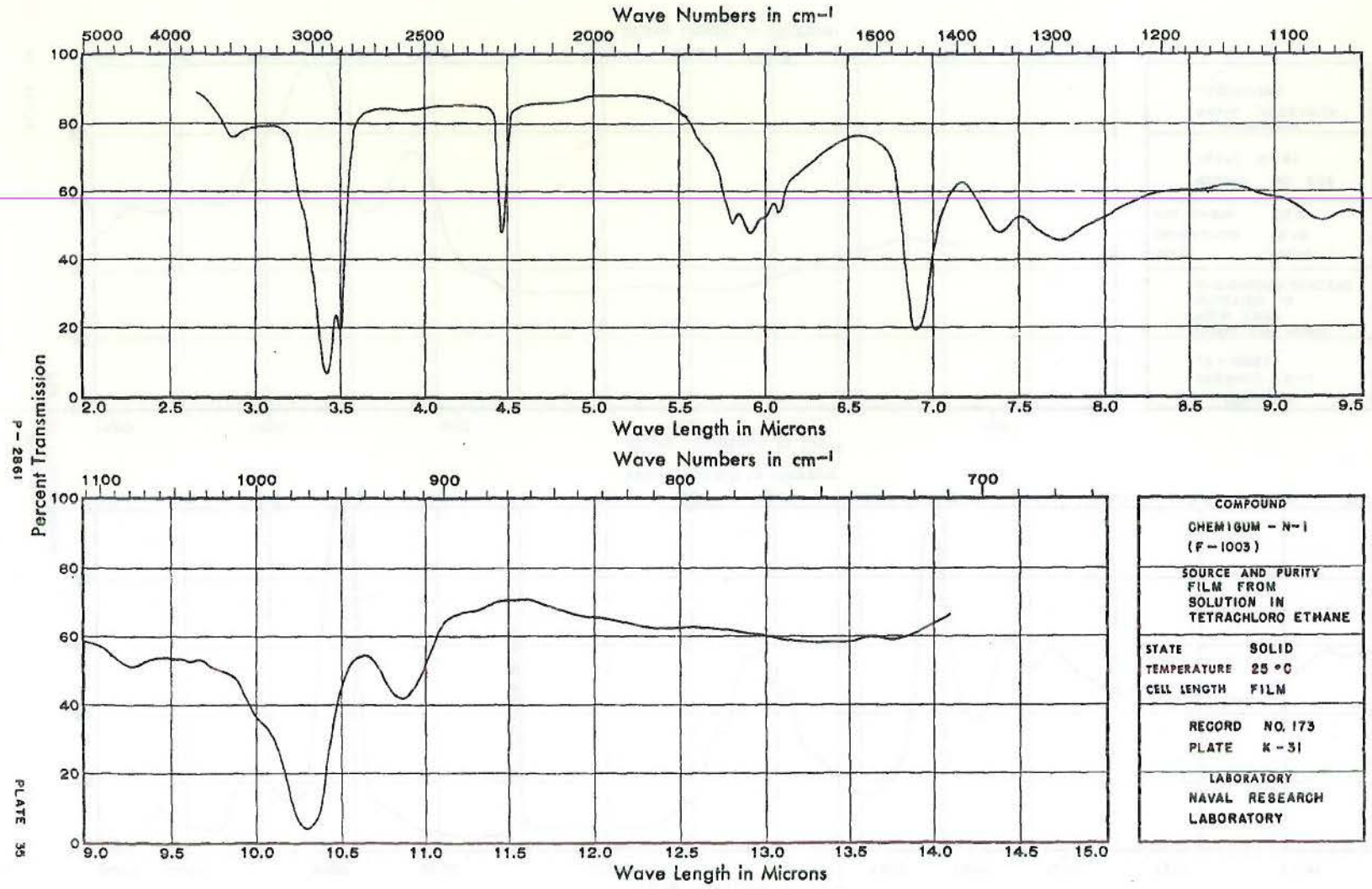
PLATE 32

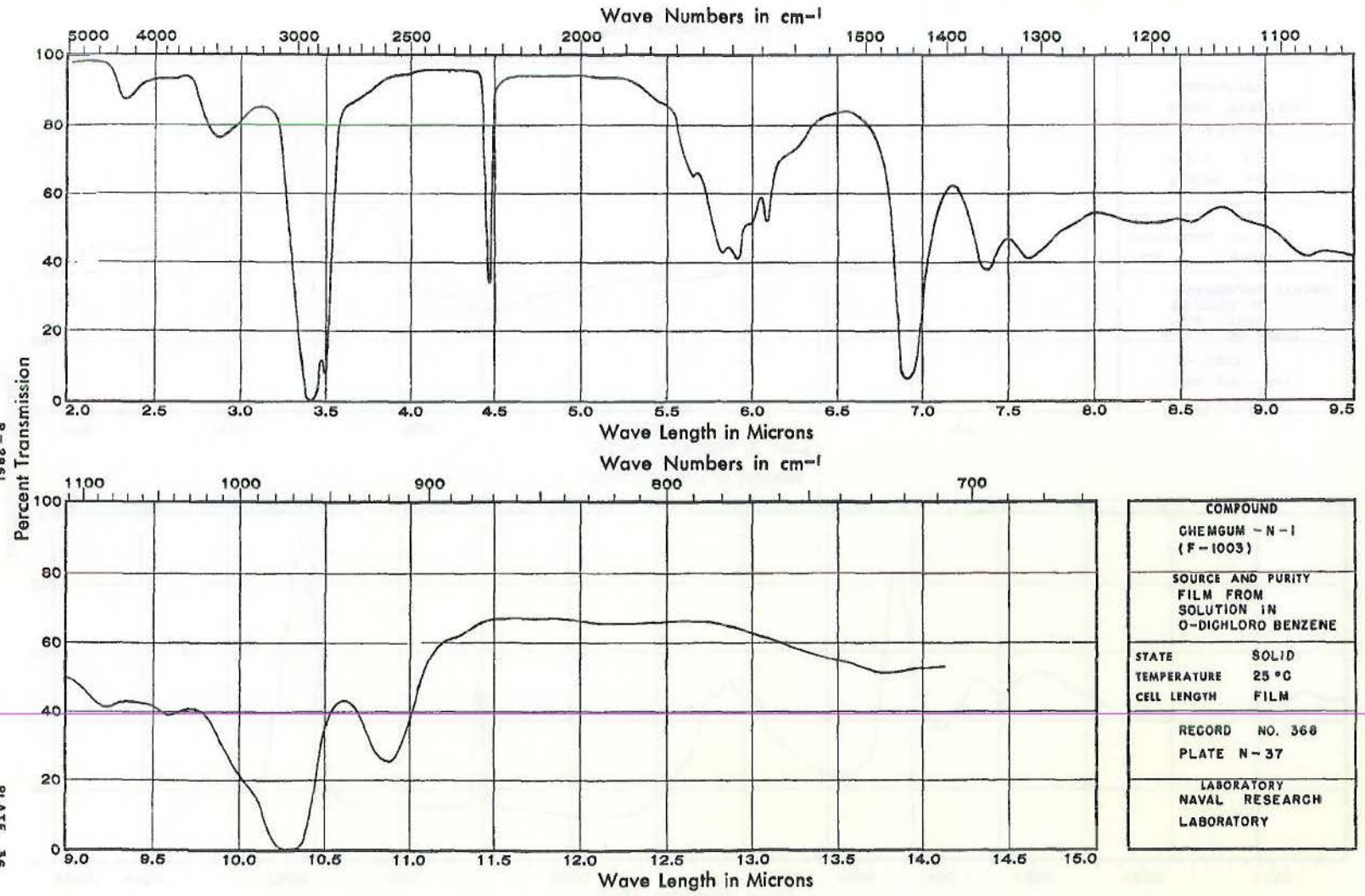

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
P—2881
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
PLATE 53
COMPOUND
GR—S
(F—602)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE SOLID
TEMPERATURE 25° C
CELL LENGTH FILM
RECORD NO. 180
PLATE K—37
LABORATORY
NAVAL RESEARCH
LABORATORY

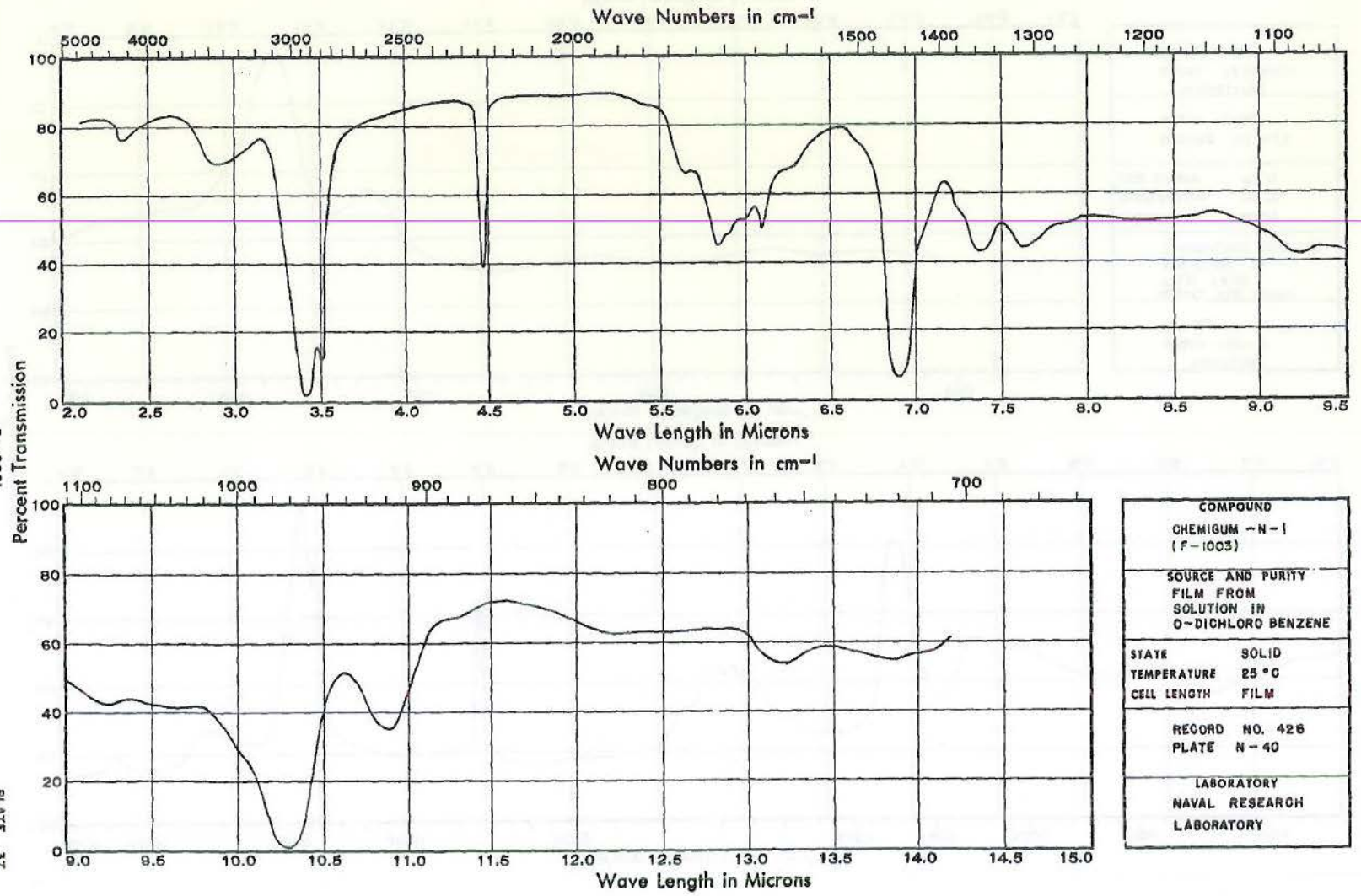


1982 — P

PLATE 34

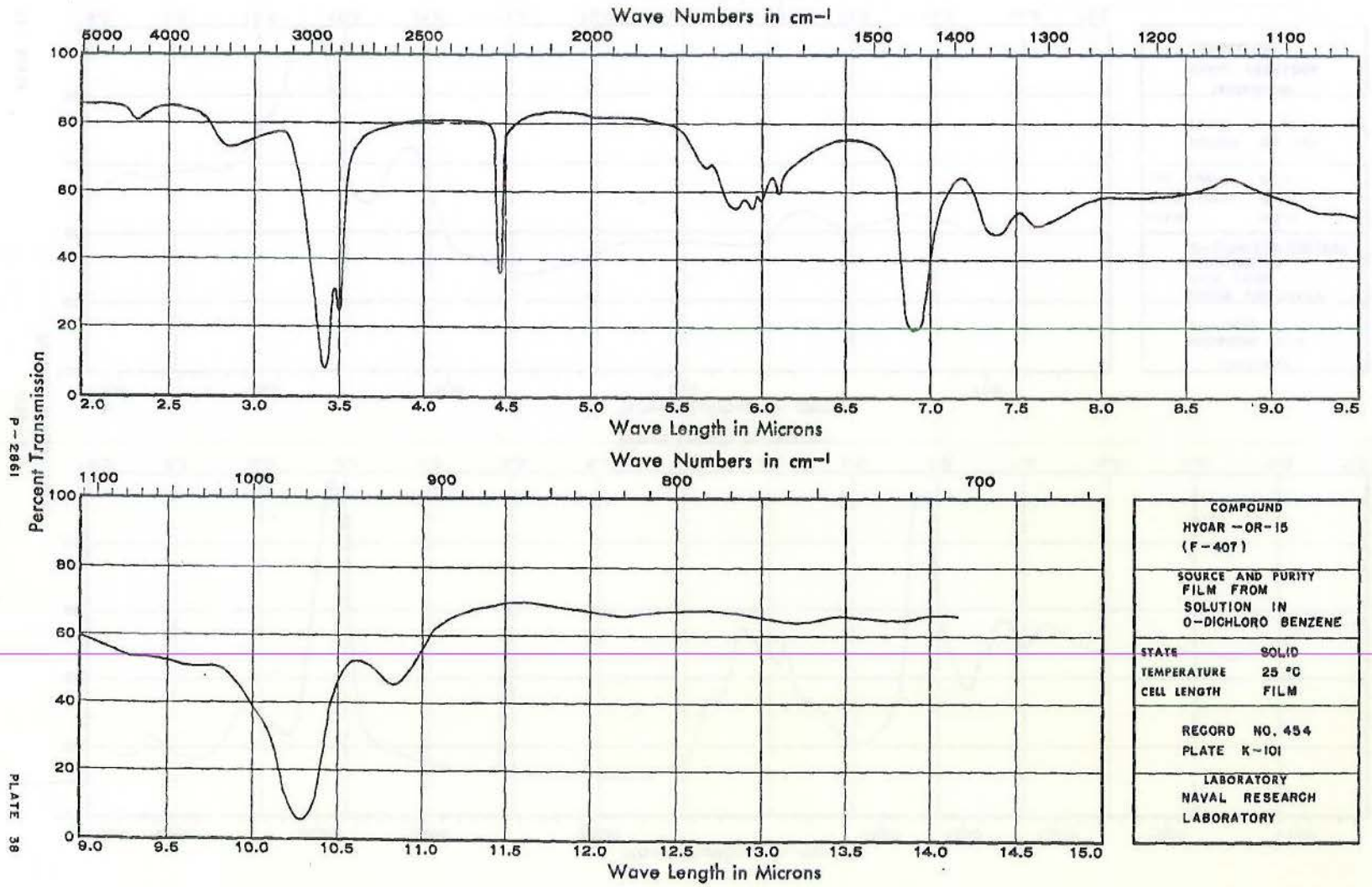

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
P - 2861
PLATE 36
COMPOUND
CHEMIGUM - N-1
(F-1003)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 173
PLATE K-31
LABORATORY
NAVAL RESEARCH
LABORATORY


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
Percent Transmission
COMPOUND
CHEMGUM - N - 1
(F - 1003)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
O-DICHLORO BENZENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 368
PLATE N - 37
LABORATORY
NAVAL RESEARCH
LABORATORY
P - 2861
PLATE 36



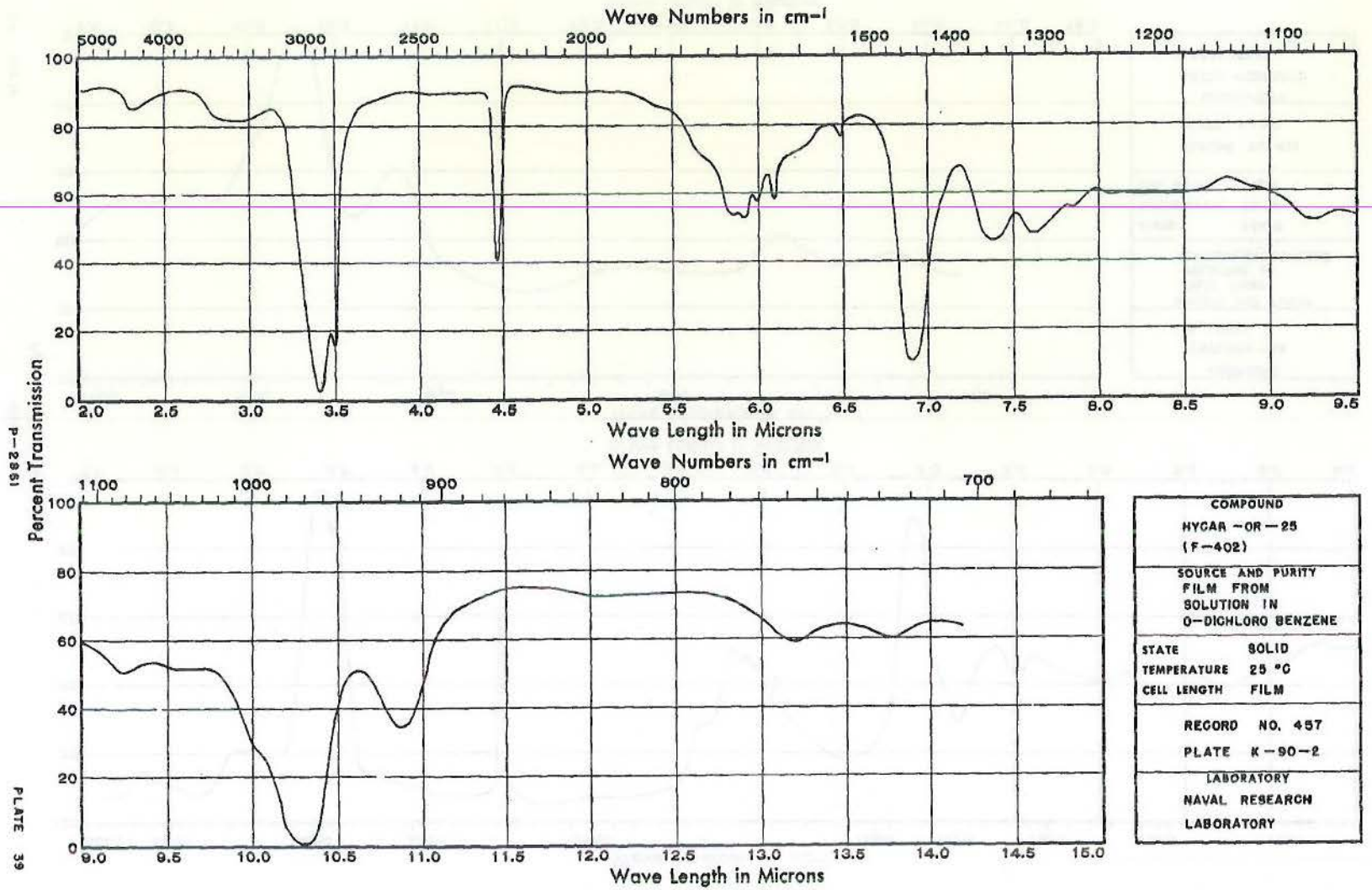
P-2681

PLATE 37



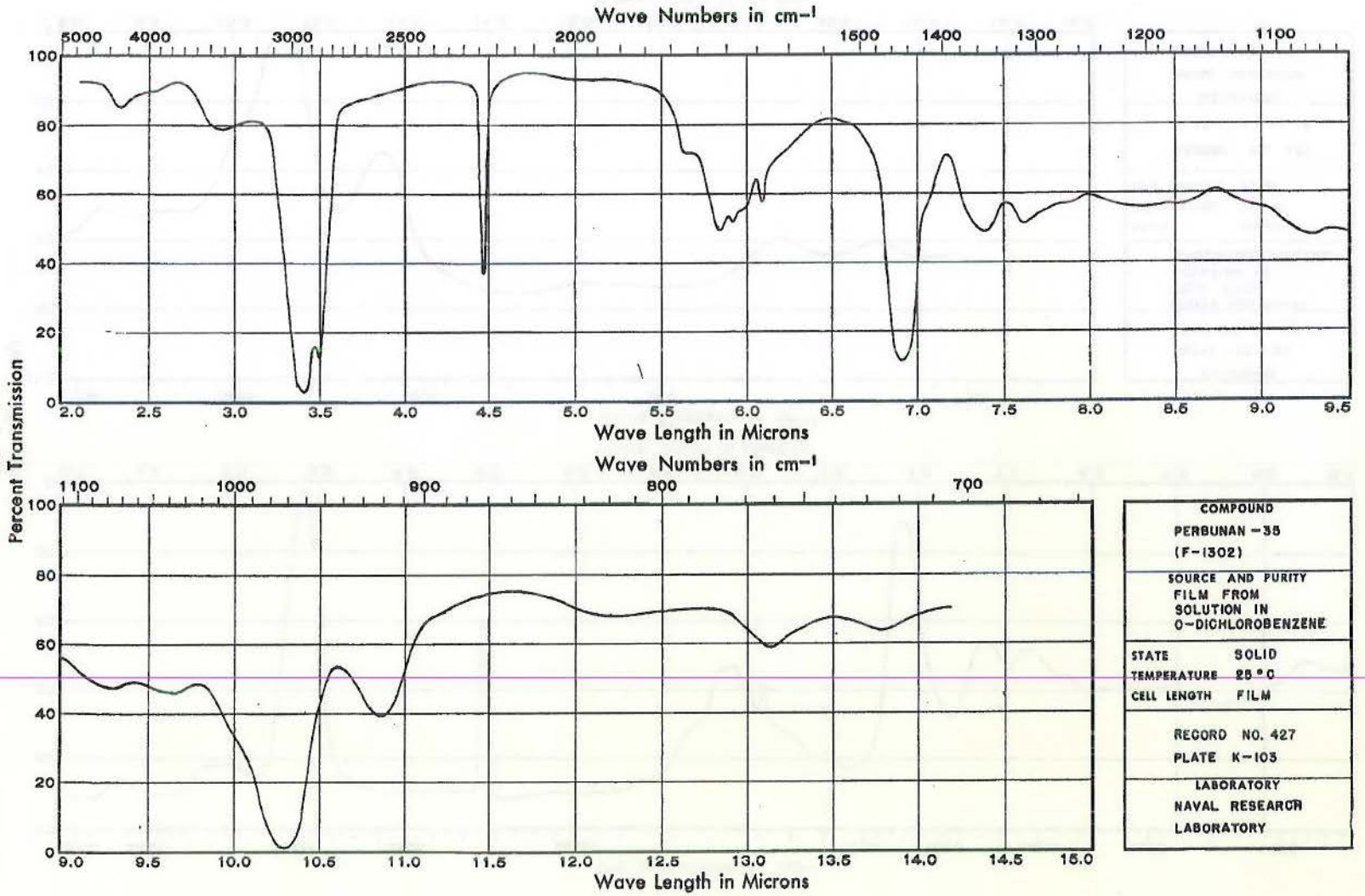
P-2861

PLATE 38



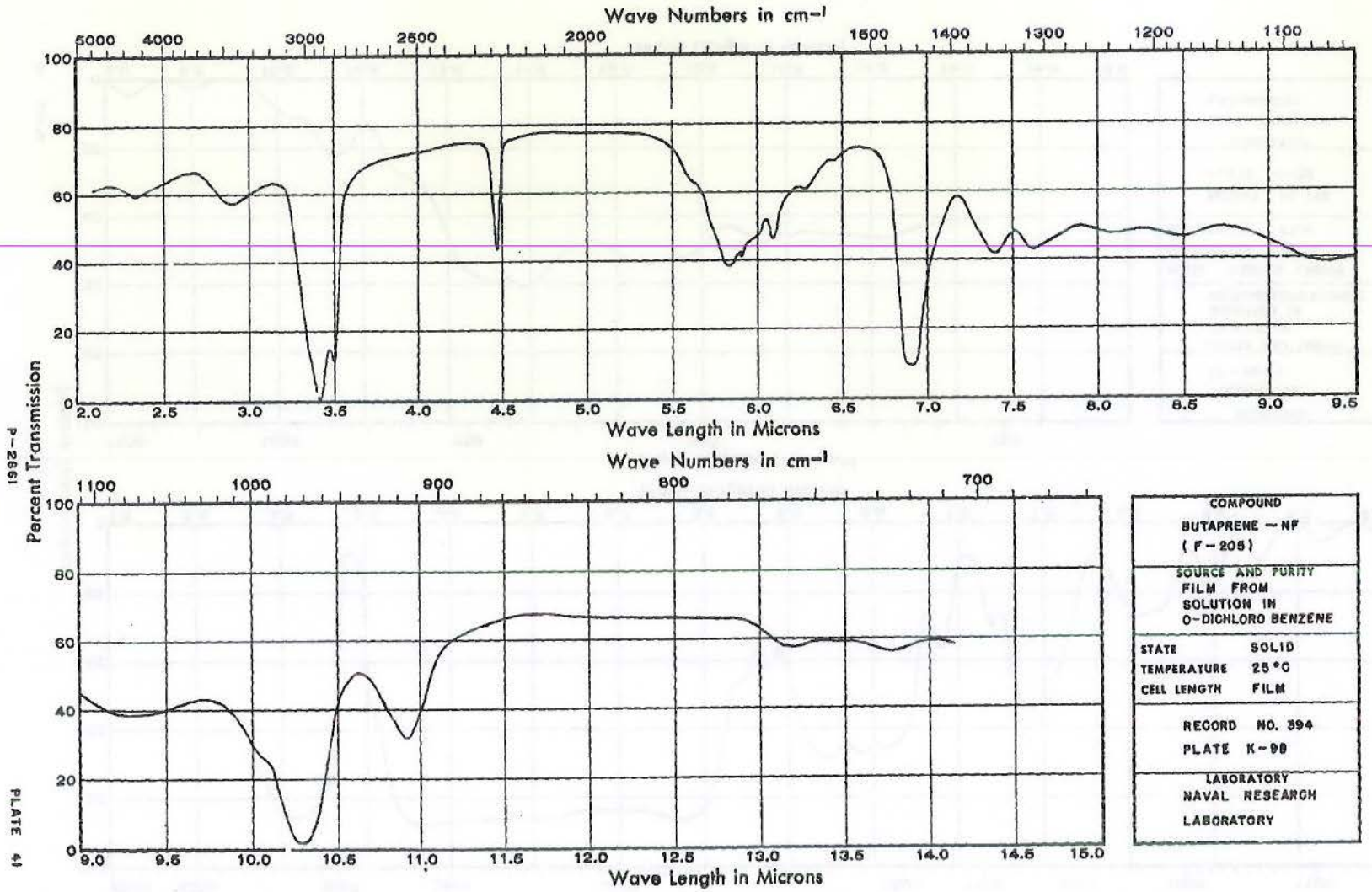
P-2861

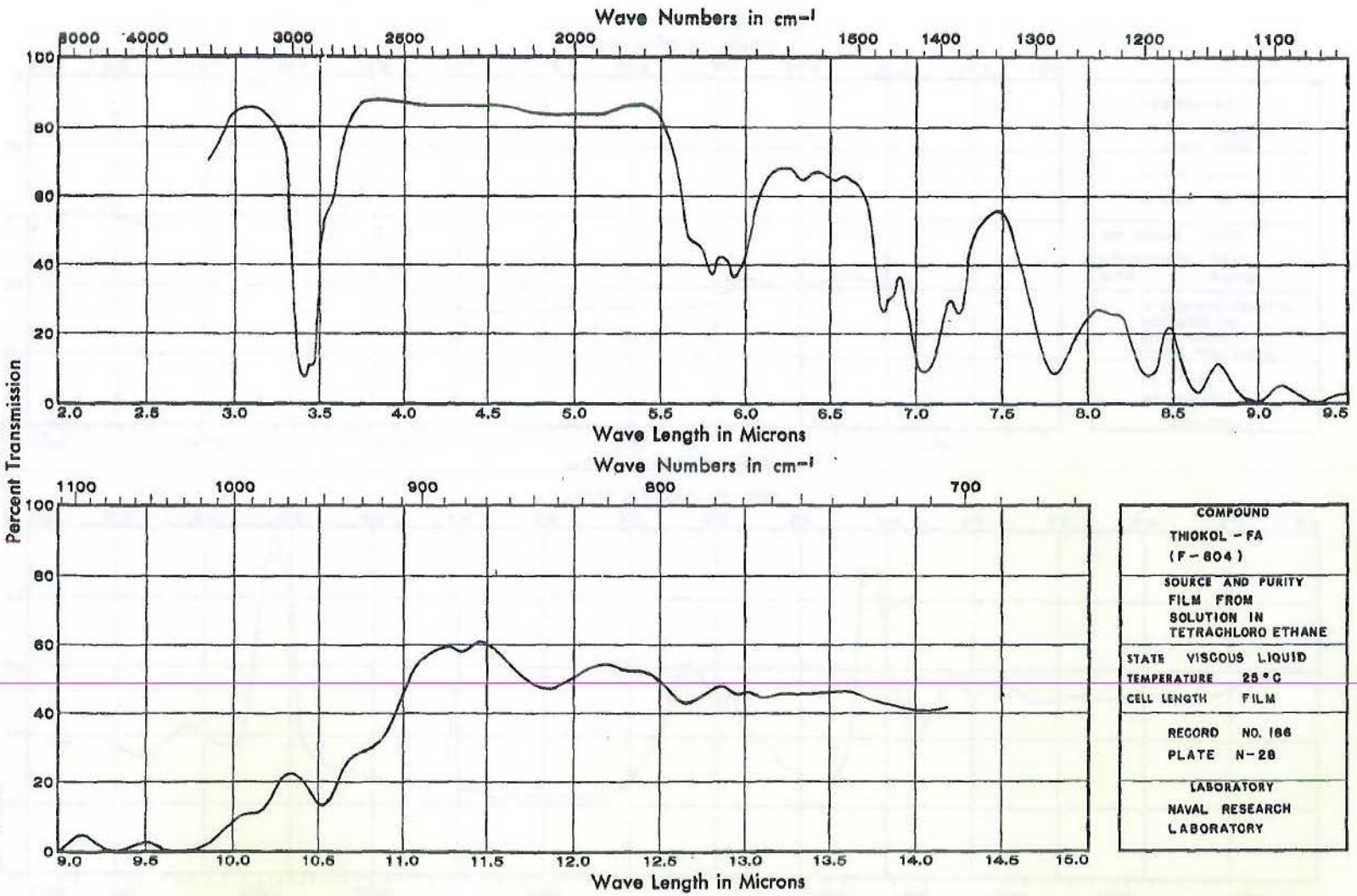
PLATE 39

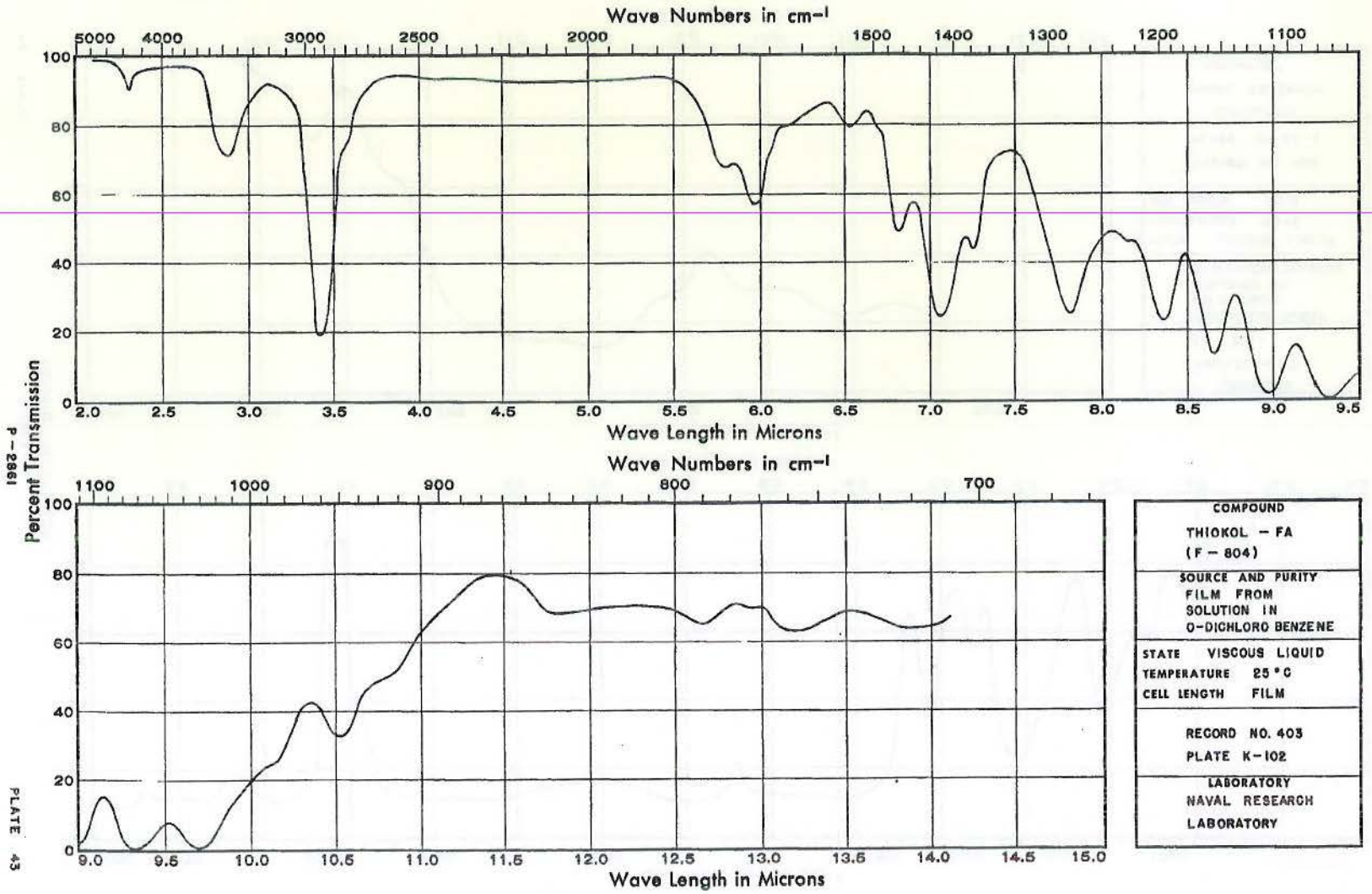


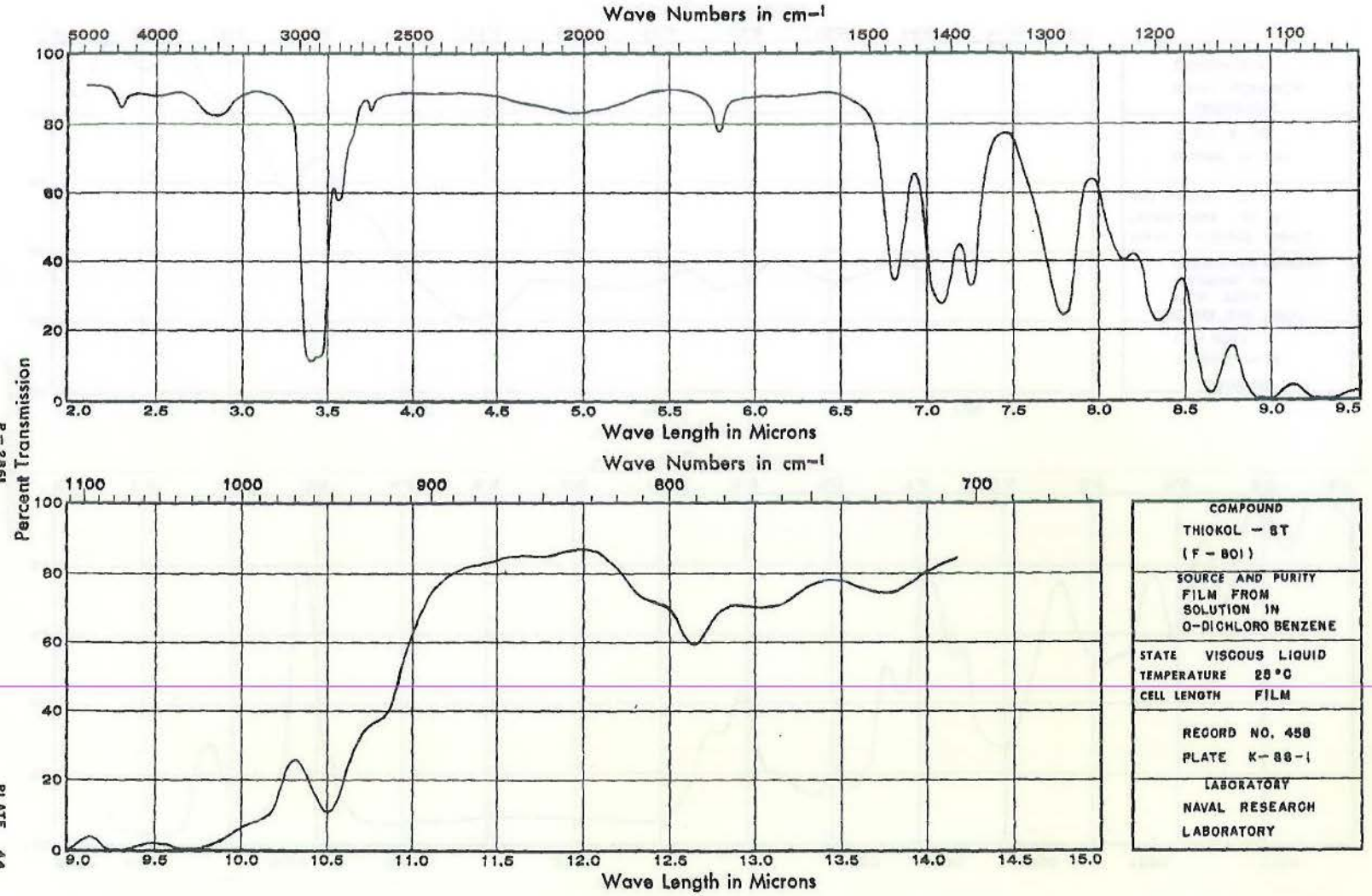
P - 2861

PLATE 40


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1600 1400 1300 1200 1100
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Percent Transmission
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
BUTAPRENE — NF
(F — 205)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
O-DICHLORO BENZENE
STATE SOLID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 394
PLATE K-98
LABORATORY
NAVAL RESEARCH
LABORATORY
P-2861
PLATE 41

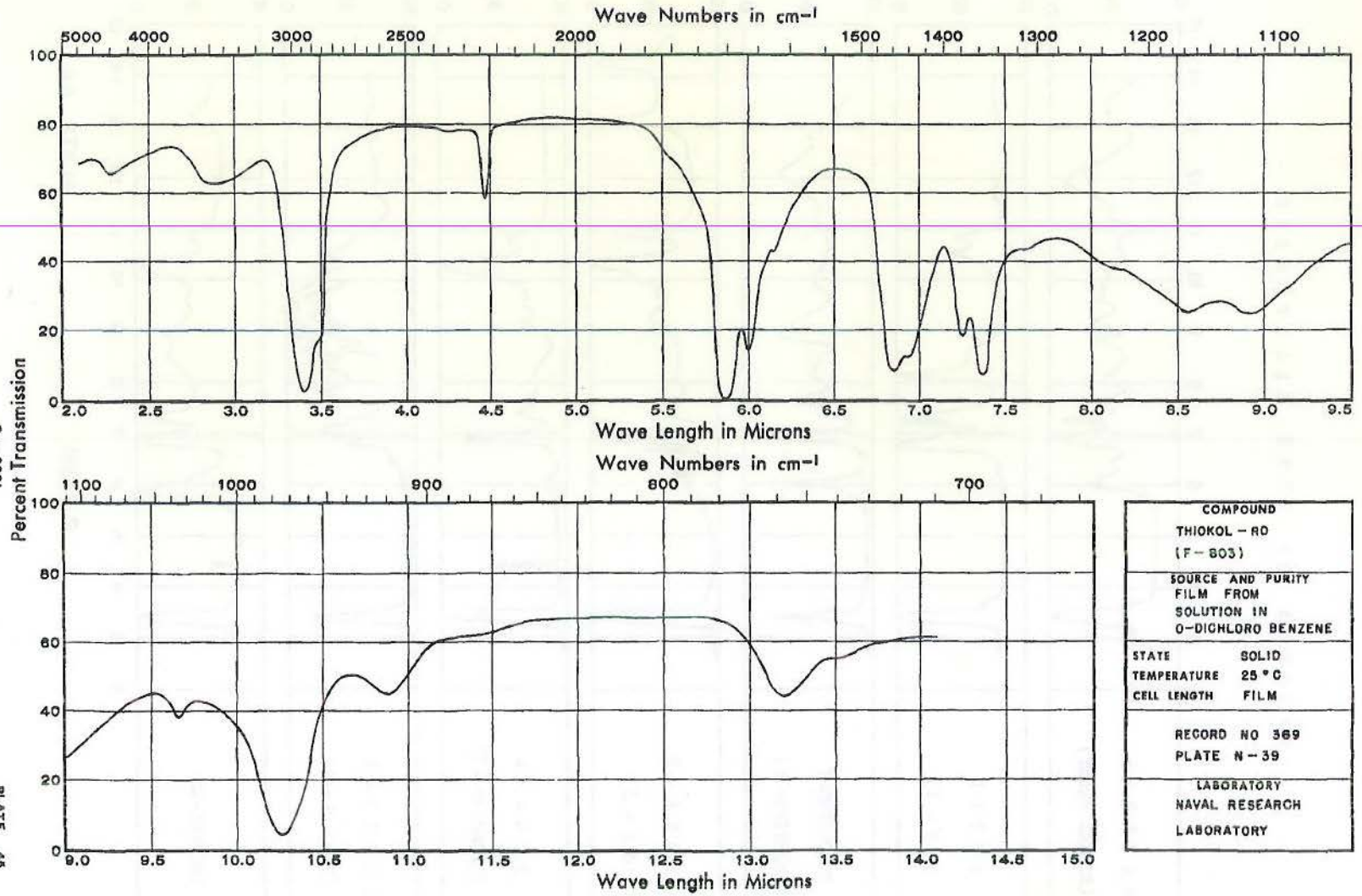

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
THIOKOL - FA
(F - 804)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
TETRACHLORO ETHANE
STATE VISCOUS LIQUID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 186
PLATE N-28
LABORATORY
NAVAL RESEARCH
LABORATORY
P-2861
PLATE 42


Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
THIOKOL – FA
(F – 804)
SOURCE AND PURITY
FILM FROM
SOLUTION IN
O-DICHLORO BENZENE
STATE VISCOUS LIQUID
TEMPERATURE 25 °C
CELL LENGTH FILM
RECORD NO. 403
PLATE K-102
LABORATORY
NAVAL RESEARCH
LABORATORY
P – 2861
PLATE 43



P-2281

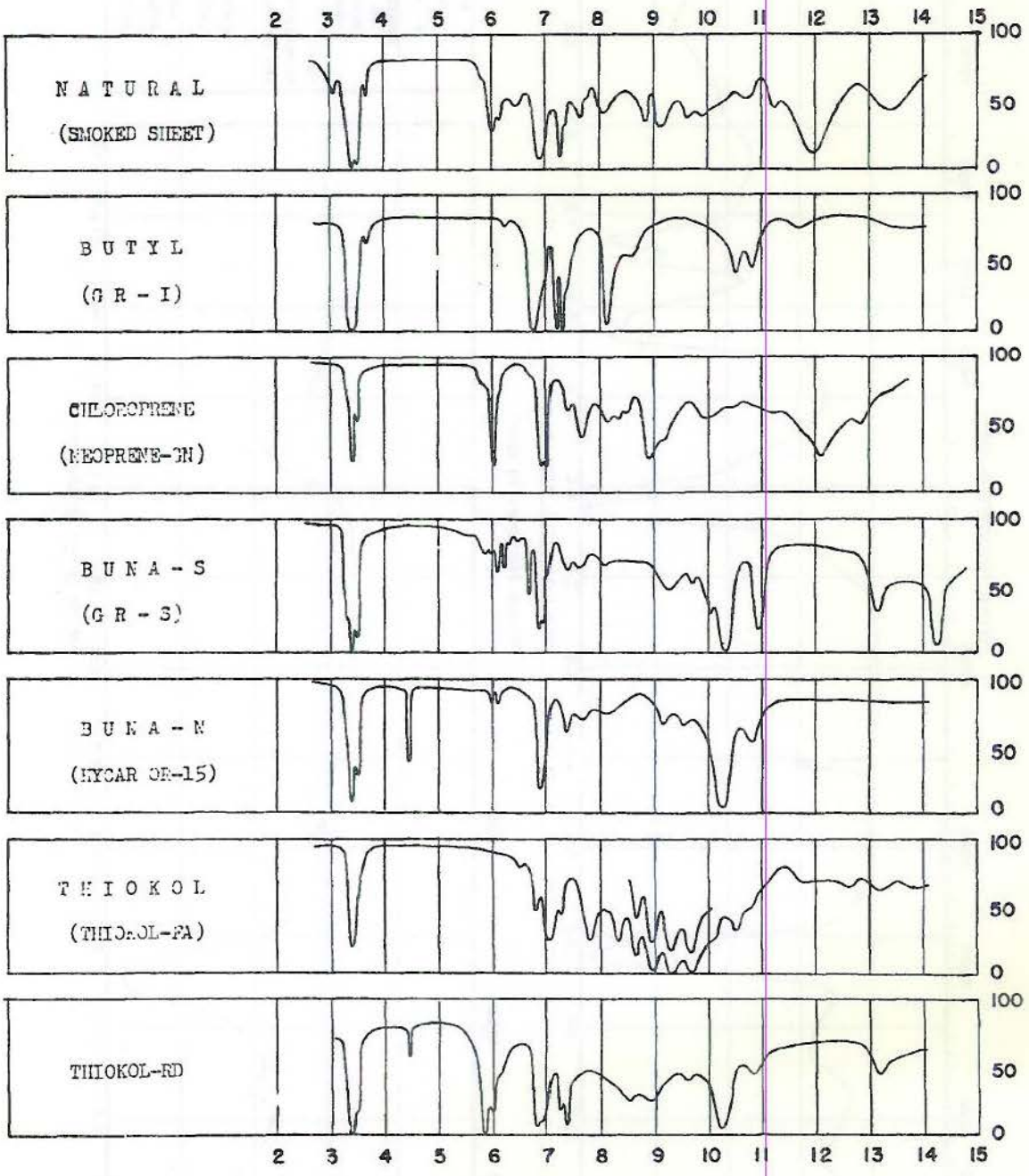
PLATE 44



API – 1982

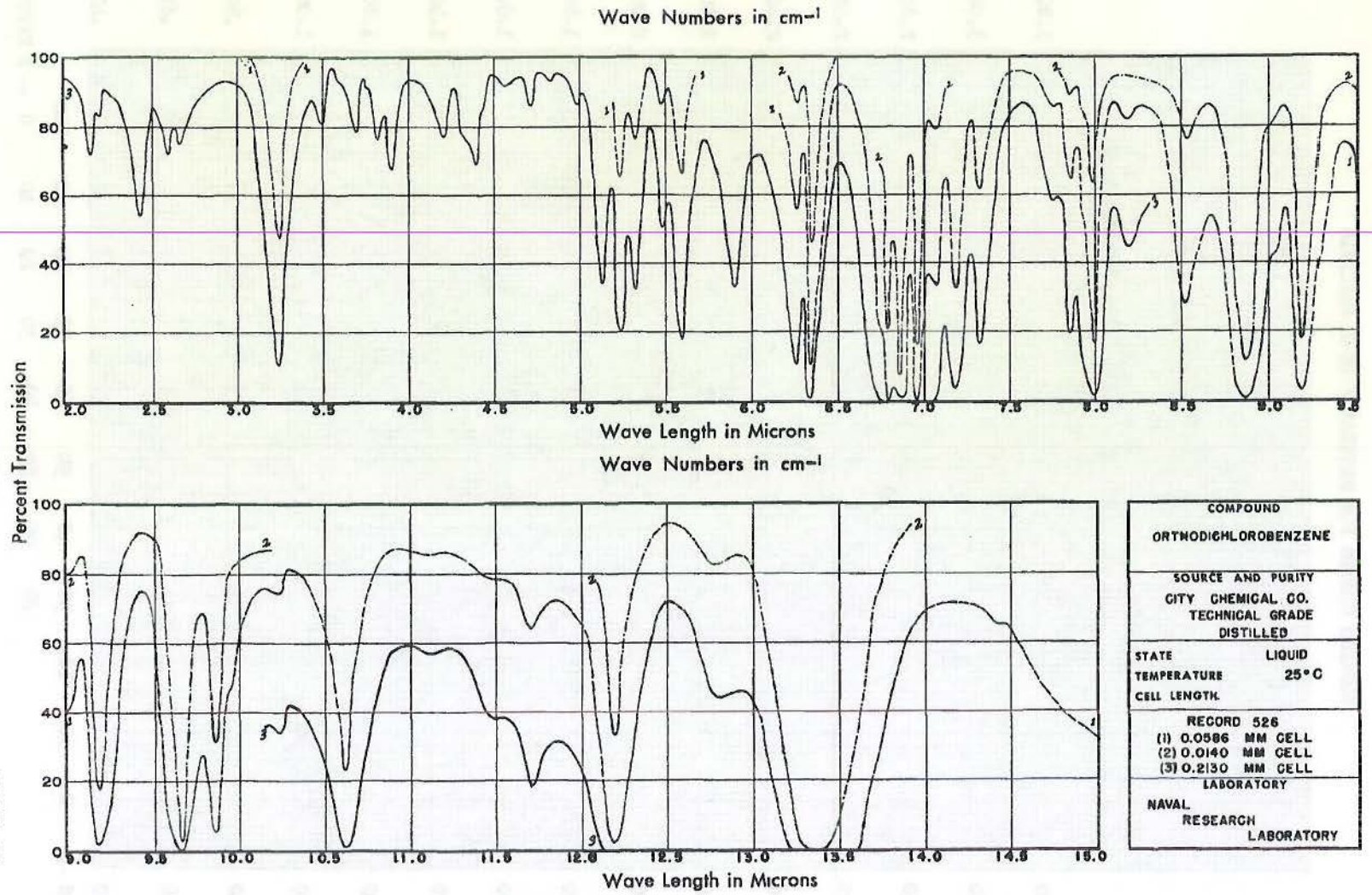
PLATE 45

SPECTRA OF PURE ELASTOMERS



P-2861

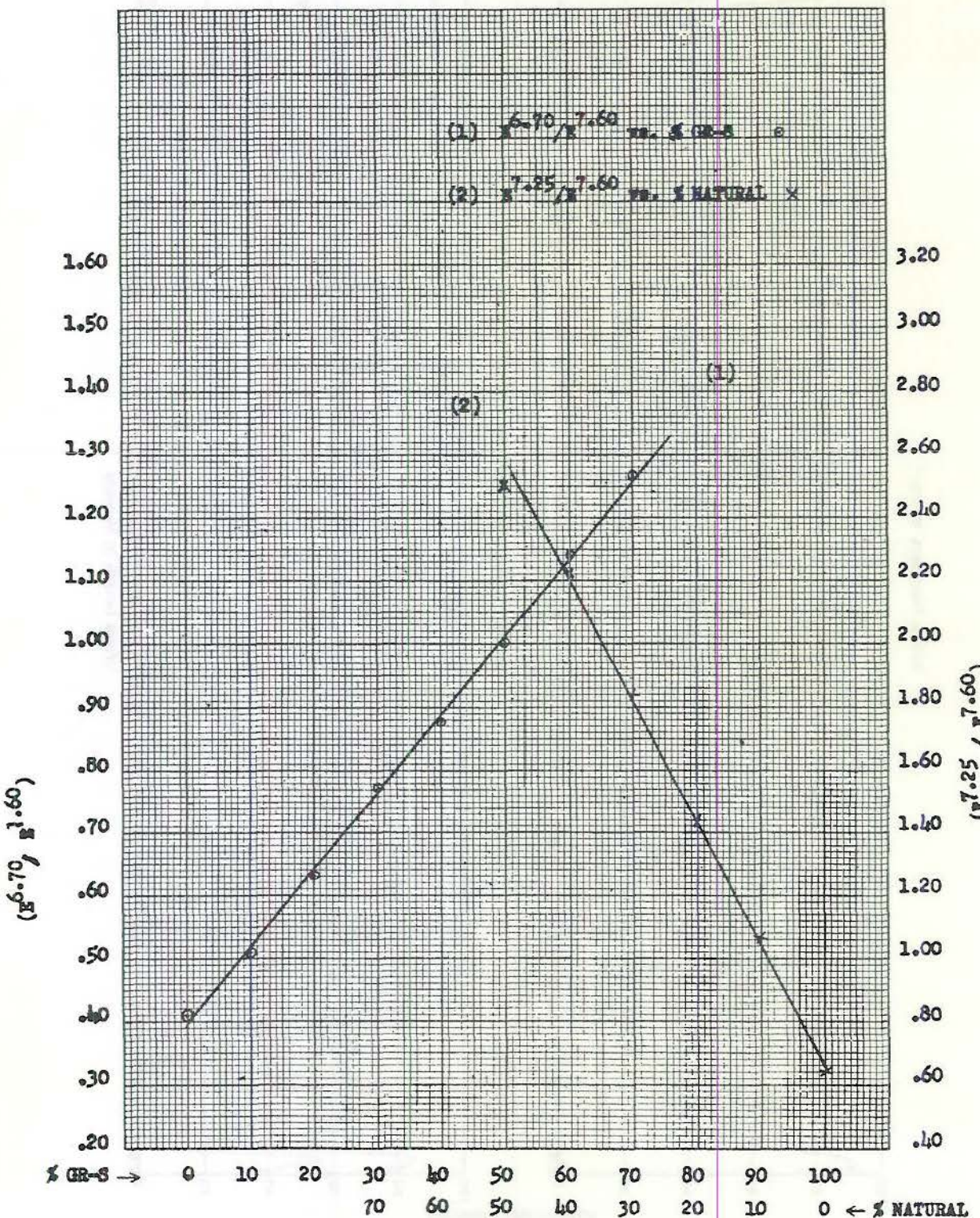
PLATE 46



P-2861

PLATE 47

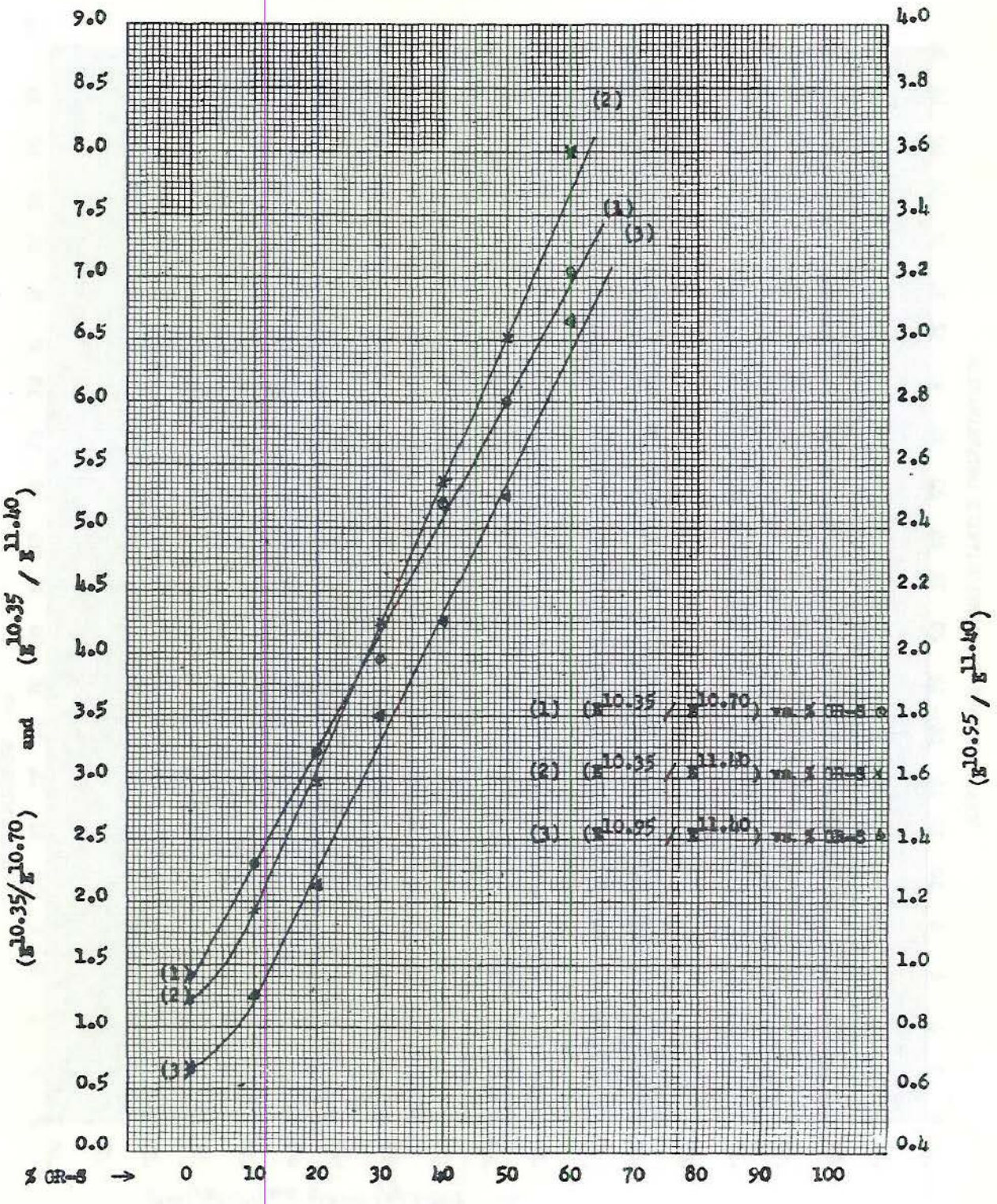
WORKING CURVES FOR NATURAL / GR-S ANALYSIS



P-2861

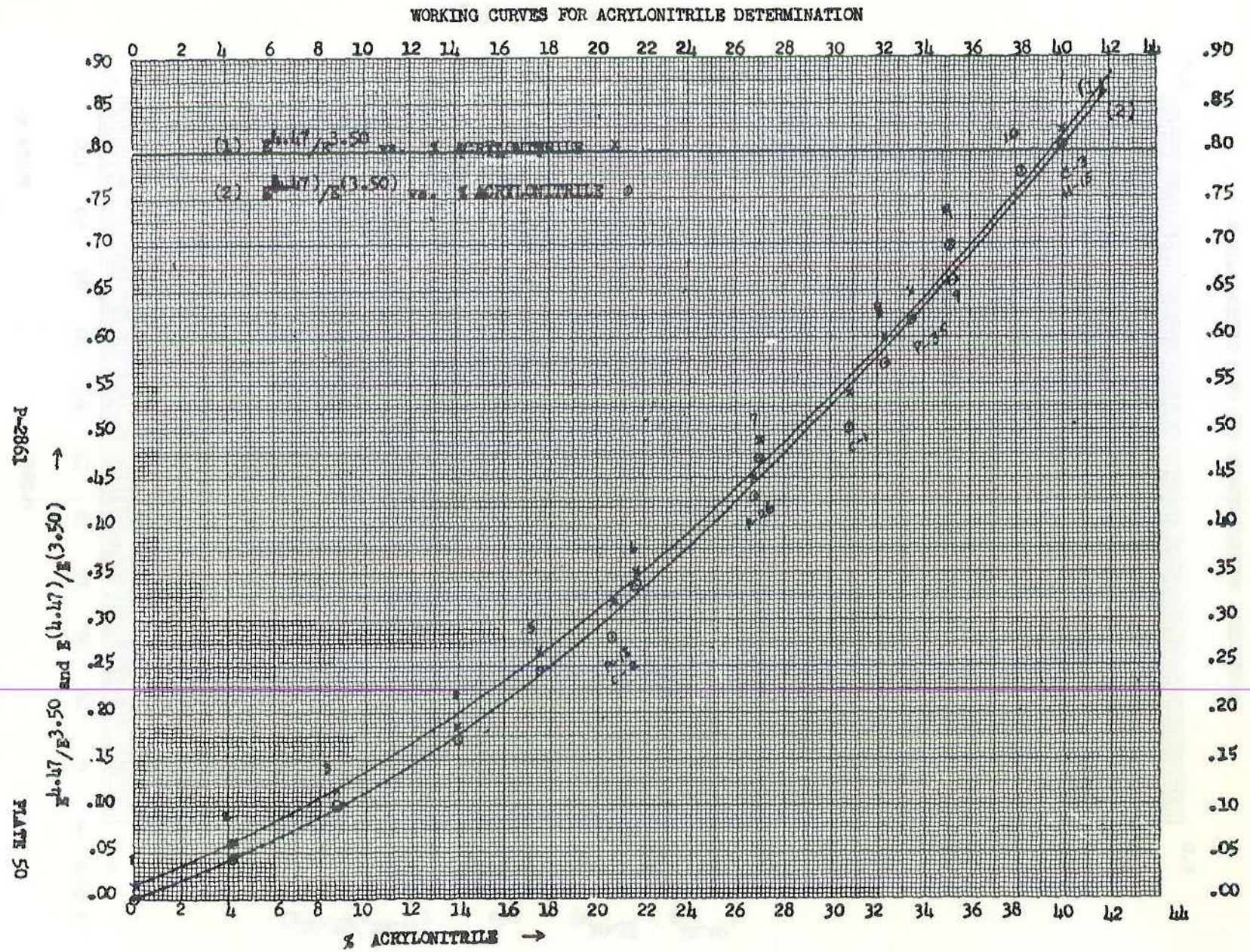
PLATE 48

ADDITIONAL WORKING CURVES FOR GR-S DETERMINATION



P-2861

PLATE 49


WORKING CURVES FOR ACRYLONITRILE DETERMINATION
(1) E4.47/E3.50 vs. % ACRYLONITRILE
(2) E(4.47)/E(3.50) vs. % ACRYLONITRILE
E4.47/E3.50 and E(4.47)/E(3.50) →
% ACRYLONITRILE →
PLATE 50
P-2861

DISTRIBUTION

15	BuShips
5	BuAer
5	BuOrd
5	ONR
2	BuStand
2	University of Minnesota
2	Rubber Reserve