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Reviewer's name(s): A. THOMPSON,
P. HANNA

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THE ABSORPTION SPECTRA
OF SILICONE FLUIDS

By: D. C. Smith, J. M. French
and J. J. O'Neill

- Report P-2746 -

~~CONFIDENTIAL~~
15 SEP 1953
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Approved by:

D. C. Smith, Head, Chemical Spectroscopy Section
William A. Zisman, Head, Lubrication Section

Dr. P. Borgstrom
Superintendent, Chemistry Division

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

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ABSTRACT

This report concerns the application of infrared and ultra-violet absorption spectroscopy to the determination of composition and molecular structure of silicone fluids. The spectra of a number of pure reference compounds of open-chain, cyclic and branched dimethyl siloxanes have been obtained for the first time. The spectral data have been correlated with molecular structure and several useful relationships have been determined.

These relationships have been used in a partial interpretation of the spectra of several commercial silicone fluids. The types of polymer structures in each of the silicones examined has been determined, but in some cases the exact structure of the polymer has not been deduced.

One silicone fluid, a Dow Corning 500 Series sample composed of open-chain dimethyl siloxanes, was studied extensively for change of structure produced by polymerization. Evidence concerning the mechanism of polymerization produced by several methods of treatment has been obtained and the results are discussed.

INTRODUCTION

A. Authorization

1. This investigation was authorized by Bureau of Ships Project Order No. 193/46 dated 1 July 1945 and by Bureau of Ships letter JJI4(350) dated 19 October 1942.

B. Statement of the Problem

2. The development of silicone polymers under the impetus of World War II has resulted in the production of several products which have found important applications during the war. Most of these applications have been due either to the unusually low temperature coefficient of viscosity or to the unusual high-temperature thermal oxidation stability of these polymers. These characteristics are responsible for the effectiveness of silicone fluids as instrument oils and in hydraulic and dash-pot systems, for example, and for the effectiveness of silicone varnishes and resins as insulation for electrical power equipment. The war-time applications of these products will undoubtedly continue to develop and multiply in the post-war period and it may be assumed confidently that silicone products will be encountered frequently both in naval and industrial use in the future. It is imperative, therefore, that methods for determining the composition of these materials be developed.

3. Regardless of the especially desirable characteristics of silicone polymers their utilization in certain applications frequently has been limited and even prohibited by other undesirable properties of the polymers. For example, the lubricating properties required in certain instruments and hydraulic systems prohibit the utilization of the unusually good temperature-viscosity characteristics of the silicone fluids in these applications. This difficulty, in particular, now has been partially overcome as a result of extensive research and testing and frequently can be avoided by careful specification of system components and conditions. (See NRL Report P-2227 and NRL letter report C-JJ76(458-HS) dated 24 May 1945). The ultimate explanation of such difficulties, however, and the key to the formulation of remedies for these difficulties must depend at least partly on a fundamental interpretation of the molecular structure and properties of the materials. In view of the importance attached to the problem it seemed desirable to apply the methods of absorption spectroscopy to an examination of silicone polymers in the hope of deriving data of a fundamental nature which would assist in the formulation of molecular concepts leading to the solution of some of the problems arising in the applications of silicone polymers.

4. In addition to such fundamental considerations it was considered desirable to develop a method of examination of commercial silicone products which could be used to check the identity or non-identity of batch samples from the same or different sources and, in general, to analyze for silicone polymer content in unknown samples originating in the course of work at this Laboratory or elsewhere. Because of the chemical inertness of these polymers and the ensuing difficulty of chemical analysis, measurement of absorption spectra seemed a logical choice in view of the uniqueness of this physical property for analytical purposes.

C. Previous Work

5. The application of silicone polymers to naval usage has been extensively investigated at this Laboratory and the results are to be found in NRL Reports P-2481, P-2530, P-2499, P-2681 and in other reports being prepared. Full discussions of the applications of these polymers, of their peculiar characteristics and the problems resulting therefrom are given in these reports and will not be repeated here.

6. Previous work on the spectroscopic examination of silicone polymers has not been published. The General Electric Company has indicated in conference that infrared measurements have been made at their Schenectady Laboratories on various silicon compounds. Their work, however, has been limited to the analysis and control of the reactants used in the production of the silicone polymers, and no work has been done on the products.

7. The Dow Corning Corp. at Midland, Michigan has examined a large number of silicon compounds, including some silicone polymers. It has been indicated that the spectroscopic data obtained at the Dow Chemical Company will eventually be published by Dr. Wright of that company. These data have not been made available generally although the infrared spectrum of one Dow Corning commercial fluid was forwarded to this Laboratory. The detail of the spectral data forwarded was so incomplete, however, that it was impossible to evaluate the possibilities of infrared investigation from it. In addition, it was indicated in conference that the course of the spectroscopic investigations at Dow Chemical was not directed along the lines desired at this Laboratory and could not be expected to provide information useful to this Laboratory for correlation with work on the lubricating properties of silicone fluids.

8. In view of these facts it was considered desirable to investigate the absorption spectra of silicone products independently, utilizing the superior infrared facilities at this Laboratory.

D. Method of Attack

9. The application of absorption spectroscopy to the problems outlined in the preceding paragraphs involves the interpretation of spectroscopic data in terms of the molecular structures of the sample. The numerous absorption bands in the spectrum of a compound are determined by the configuration or arrangement of the atoms comprising the molecule: Certain bands may be correlated with specific atomic linkages or valence bonds while other bands may be correlated with a particular configuration of a group of atoms within the molecule or with the structure of the molecule as a whole. When such relationships are known the spectrum of an unknown sample can be interpreted and information concerning the composition of the sample can be derived. Similarly, spectral changes which develop during treatment of a sample can often be interpreted in terms of a change in structure or composition, and these changes may be correlated with other changes in the properties of the sample. The applicability of absorption spectroscopy to a particular problem is usually dependent both upon the spectral characteristics of the materials involved in the investigation and upon the completeness with which the spectral absorptions can be interpreted.

10. Since spectroscopic data for the siloxanes which comprise the silicone fluids had not been obtained previously, it was necessary first to procure and examine a number of pure compounds of known molecular structure in order to establish basic relationships between molecular structure and spectral absorptions for this new class of compounds. The information derived from the examination of these pure reference compounds was then applied to the interpretation of spectral data obtained for the various silicone fluids.

EXPERIMENTAL

A. Description of Samples

11. All samples studied were obtained from industrial laboratories. Summary description of the purified dimethyl silicone samples which were used as standard reference compounds in obtaining basic spectral data is given in Table I. These samples were supplied in 5 ml. quantities, and it was requested that data relative to the samples be held confidential.

12. The reference compounds available constituted two homologous series, one composed of open-chain dimethyl siloxanes and the other of cyclic or closed-chain dimethyl siloxanes. In addition, two branched-chain structures were available.

13. The commercial products investigated, with one exception, were obtained from the Dow Corning Corporation and are described in Table II. They are typical of commercial fluids available and were supplied in small quantities by the Lubrication Section of this Laboratory.

B. Infrared Equipment & Measurements

14. A large research-type infrared spectrometer was used for this investigation. This instrument utilizes the double dispersion of a 15-cm rocksalt prism in Wadsworth-Littrow mounting and has high resolving power over the range 2 - 15 microns covered in this work. Liquid samples were measured as thin films between rocksalt plates. A set of cells of different thickness was used in order to obtain transmission values between 20 and 80% at all wavelengths. The same set of cells has been used throughout the investigation so that in most cases it is possible to compare the relative intensities of the absorptions of different samples without considering cell thickness. In regions of strong absorption the samples were studied in carbon disulfide solution. Concentrations are given in weight-percent and film thickness in millimeters. One sample (hexamethylcyclotrisiloxane) is a solid at room temperature and was studied in C S_2 solution over the range 7 - 15 μ and in C Cl_4 solution in the 2 - 7 μ range. The instrument recordings were converted into percent transmission curves plotted on a linear wavelength scale. Correction has been made for the absorption cell and "background" radiation effects. The spectra are given in Plates II to XXVII.

15. In general the wavelength measurements are accurate to $\pm 0.01 \mu$ and the transmission values are thought to be accurate to ± 1 to ± 2 percent over the range 20 to 80 percent. For the $C S_2$ solutions the reproducibility is not as good because of the errors in concentration resulting from the volatility of the solvent.

C. Ultraviolet Equipment & Measurements

16. A National Technical Laboratories Model DU Quartz Spectrophotometer was used to measure the ultraviolet spectra of some of the samples over the range 4000 to 2200 Å. A low-pressure hydrogen discharge lamp served as the source of continuous radiation, and the samples were studied in purified iso-octane solution in 1 cm matched quartz cells. For each curve the concentration is given by the volume ratio of sample to solution. The spectra are presented in Plate I where extinction is plotted vs. wavelength in millimicrons. Extinction is defined by $E = \log_{10} (1/T)$ where T = percent transmission.

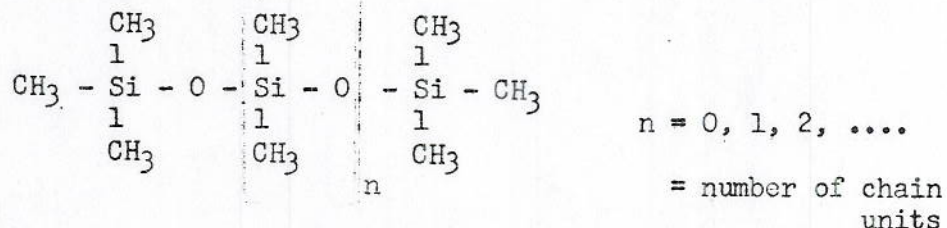
DISCUSSION OF RESULTS

A. Open-Chain Dimethyl Siloxanes

17. The characteristic absorptions of the homologous series of open-chain dimethyl siloxanes are given in Table III. The siloxanes exhibit several very intense absorptions beyond 7.5μ where an equivalent film thickness of only .001 mm or less is required to bring the intensity of the absorption in a measurable range. Such intense bands are general characteristics of polar molecules in contrast to non-polar compounds, such as hydrocarbons, where a film thickness 10 to 100 times greater is required. The siloxanes, then, in general lend themselves favorably toward detection and measurement by infrared and unfavorably toward the detection of admixed compounds.

18. As in most cases of a homologous series, these compounds all have the same general spectral characteristics. There are at least nine bands which are constant in both wavelength and intensity and may therefore be used in identifying a compound or mixture of compounds regardless of molecular weight. The other bands exhibit change in position and/or intensity with change in molecular weight and these bands may be used to identify a particular member of the series. This will be discussed more fully after considering the origins of some of the absorption bands.

19. In proceeding through a series of siloxanes having the structure



certain spectral changes may be correlated with molecular structure and useful information may be deduced without resorting to mathematical vibrational analyses which, for molecules of sizes considered here, would be

extremely difficult and only approximate at best. Some of the absorption bands correlated with molecular structures are summarized in Table V.

20. The strong band at 8 μ is associated with the carbon-silicon bond and is probably a valence vibration. For the first member of the series which contains only trimethyl-substituted silicon atoms (end groups) this band center is at 8.00 μ . With an increase in molecular weight this band decreases rapidly in intensity and a new band appears around 7.94 μ . The 7.94 μ band apparently has its origin in the dimethyl-substituted silicon atoms of the chain units.

21. Absorption in the 9 - 10 μ region is characteristic of ether-oxygen linkages and here is due to the Si - O - Si structure. With the appearance of chain units this band splits and the separation increases with increasing molecular weight.

22. The bands at 11.35 and 13.25 μ decrease with increasing m.w. and are correlated with the $(\text{CH}_3)_3\text{Si} - \text{O}$ end group structure.

23. The band at 12.5 μ (absent for the first member and split for the second member) increases in intensity with increasing m.w. and is associated with the $-\text{Si}(\text{CH}_3)_2\text{O}-$ structure of chain units.

24. These changes in absorption which are correlated with increasing molecular weight are measurable functions of the relative abundancies of chain units and end groups of the polymer sample. While neighboring lower members of the series have marked differences in absorption, these differences become smaller as one proceeds to higher members. Hence, while it is possible to identify any one of the homologs studied here by its infrared absorption, the analysis of mixtures is largely confined to the first two or three members where the spectral differences are unique and relatively large. For higher members only the average composition can be determined, it being impossible to distinguish accurately between adjacent members or to distinguish between a given member and a mixture of members adjacent to it. The ratio of the intensity of the 12.5 μ band to that of the 11.84 μ band is probably the most sensitive function of molecular weight and could be used to determine the average m.w. of a sample of open-chain dimethyl siloxanes such as would be obtained in a distillation cut. This method of molecular weight determination appears to have no advantage over other simpler methods such as viscosity determination, provided the polymer type of the sample is known.

B. Cyclic Dimethyl Siloxanes

25. The characteristic absorptions of the first five members of the homologous series of cyclic dimethyl siloxanes are summarized in Table IV. This series also has at least nine or ten short-wavelength bands which are constant in position and intensity. Most of these bands are common to both the open-chain and cyclic series and are characteristic of dimethyl siloxanes in general. One band at 4.71 μ , a weak one, occurs only in the cyclic series and another weak band at 4.78 μ occurs only in the open-chain series. These are the only two bands in the region below 7.5 μ which enable a positive differentiation between the two types of structure, and because of their low intensity are not very useful. Other differences in the region of 6 μ

are not useful because of their dependence upon molecular weight.

26. In the longer wavelength region, where the absorptions are generally characterized by the structure of the whole molecule or of groupings within the molecule, the spectrum of cyclic members of higher molecular weight would be expected to be essentially identical to that of the higher members of the open-chain series where the absorption of the end groups becomes negligible. In the cyclic series the Si - C (methyl) vibration appears at 7.94 μ and agrees with that of the corresponding structure in the open-chain series. This band is constant in position and intensity in accordance with the equivalence and constant population of this linkage in the various members of the series.

27. The Si-O-Si vibration is displaced to 9.74 μ for the first member, a six-atom ring, and apparently results from a distortion of the valence angles. This vibration occurs at 9.30 μ in the succeeding members of the series and splits into a doublet for the 14 atom ring. For still higher members this absorption would undoubtedly become identical with that of the high molecular weight open-chain structures.

28. Similarly, the absorption at 12.45 μ resulting from vibrations of the chain unit structure occurs at the same position for the higher members of both the open- and closed-chain series. For lower members this band is displaced toward longer wavelengths in the open-chain series and toward shorter wavelengths in the cyclic series. In polymers of more than six Si atoms this absorption occurs at 12.45 μ and indicates that the chain units of both series are equivalent.

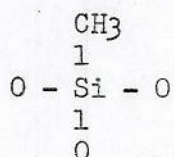
29. The only really significant difference between the spectra of the open-chain and cyclic series is the absence of the bands at 11.88 μ and 13.25 μ which originate in the vibrations of the end groups of the open-chain series. For the higher polymers such as are found in all but the lowest viscosity commercial fluids the spectra of the open and closed-chain species become identical except for these end-group absorptions which themselves tend to become weak due to the low concentration of such groups.

30. The detection of end groups by infrared absorption, then, may be used to differentiate between open-chain and cyclic polymers of the dimethyl siloxanes. Difficulty is encountered in its application, however, since the concentration of end groups is dependent upon molecular weight. If the molecular weight distribution in a sample is known, say by viscosity or solubility measurements, and the material is known to consist of dimethyl siloxanes by its infrared spectrum, then the bands at 11.88 μ and 13.25 μ may be used to differentiate between open and cyclic polymers.

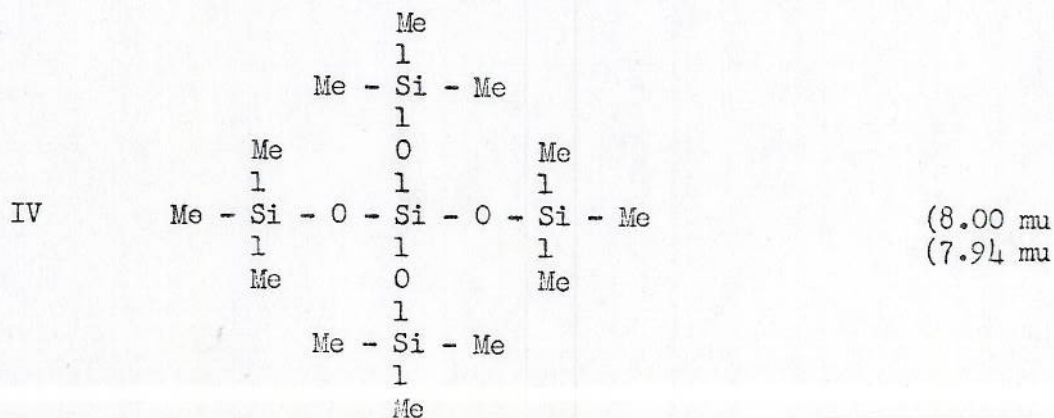
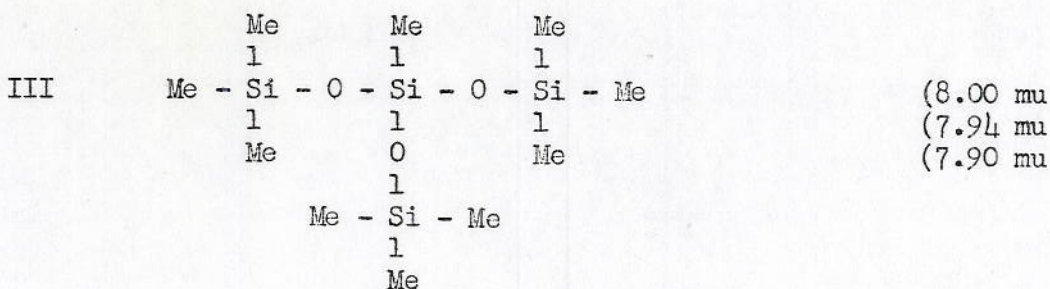
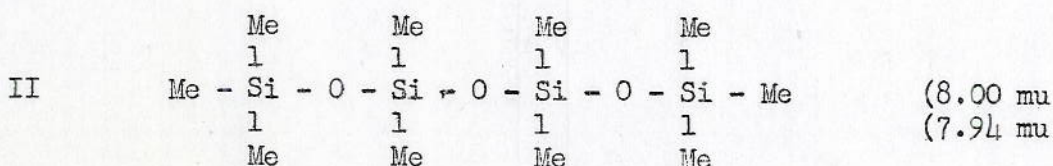
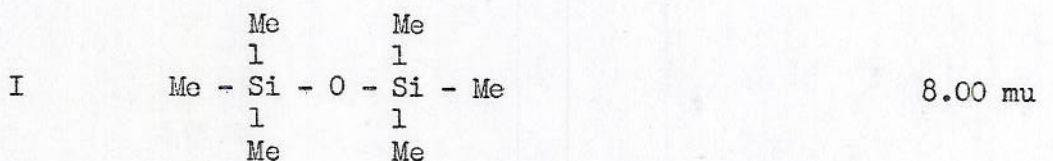
C. Branched Dimethyl Siloxanes

31. The study of the spectral changes which occur when branching is present in a dimethyl siloxane was somewhat limited since it was impossible to obtain a homologous series of branched polymers. However, the data on the two compounds available permit some conclusions.

32. The presence of branching would be expected to introduce additional absorption bands into the spectrum due to the structure



of branching centers and to change the intensity of other bands due to a higher proportion of end groups for a given molecular weight. For a large molecule containing this structural unit the most important new absorption is probably that due to the Si - CH₃ linkage where the Si atom is attached to three O atoms. The spectral data seem to confirm this conclusion. The position of this absorption is indicated by a comparison of the 8 mu bands for the following four compounds.



The complete spectra of these compounds are shown in Plates II, IV, XIV and XV. It is not clear why compound IV should have an absorption band at 7.94 mu unless it is due to isomeric impurities of type II in the sample. Regardless of the origin of this band which occurs in both compounds III and IV, the band at 7.90 mu which occurs in compound III must be due to the branching structure under consideration. Since the end groups are two atoms removed from this C-Si linkage an increase in molecular weight would not affect this absorption and it may, therefore, be used to identify branching in polymeric siloxanes of this type.

33. It may be mentioned in considering these branched siloxanes that their spectra in general are very similar to the isomeric open-chain and cyclic compounds. Most bands in the short wavelength range are the same although some differences are observed around 5 to 6 mu. The ether-like oxygen absorptions around 9.5 mu are slightly displaced, the end group absorptions around 11.84 mu and 13.25 mu are slightly displaced and proportionately stronger, and the chain unit vibration at 12.5 mu is displaced for compound III and entirely absent for compound IV. Except for the last case these differences would not be observed for compounds of high molecular weight. The sharp band at 14.34 mu found for compound IV may be due to the central Si atom attached to four O atoms.

34. In summarizing the above considerations, it is concluded that, for samples in the liquid state, branching is to be detected by the appearance of a band at 7.90 mu. Since this band is not completely isolated from neighboring bands and will tend to be masked when it is low in intensity, it would be impossible to measure the percentage of Si atoms participating in branching structures if the fraction of such branching centers is less than a few percent of the total Si atoms in the sample. Since only a small fraction of one percent of branching centers in a commercial polymer is known to produce large effects on the physical properties of the polymer, this method of detection will in general be too insensitive to be useful.

D. Composition of Commercial Fluids

35. Industrial organizations have not been inclined to state the composition and structure of their commercial products and this has somewhat hampered certain phases of the silicone research at this Laboratory. Considerable confusion also was introduced by changes in the company designations of their products. In addition, the uncertainty of identity in repeat batches during the early stages of commercial production development and the question of identity of product from different sources warranted consideration. For these reasons several commercial samples representative of those available and of interest in other investigations at this Laboratory were examined from the standpoint of composition and structure determination. The conclusions developed from the spectra are presented in the following paragraphs.

(a) Dow Corning 500 Series Fluids

36. One member of this series having a viscosity of 100 centistokes at 25°C, a sample obtained in volume for extensive tests at this Laboratory, was examined and the spectrum is presented in Plate XXV. All of the characteristic bands of the open-chain dimethyl siloxanes are present in this spectrum and no additional bands are found. The fluid definitely consists of open-chain dimethyl siloxanes. No branching is indicated by the absence of a band at 7.90 μ . The low intensity of the trimethyl end group bands at 11.9 and 13.25 μ indicates that the polymer chains contain considerably more than 7 silicon atoms in agreement with the higher molecular weight indicated by the viscosity. A relatively large molecular weight is also indicated by the separation of the bands at 9.5 μ and by the loss of identity of the 8.00 μ band. No attempt was made to derive quantitative data on the molecular weight. The absence of the band at 4.71 μ indicates that no cyclic structures are present, but, as it has already been pointed out, the sensitivity of the detection of cyclic structures is not great due to the low intensity of this band.

37. This fluid has no spectrum in the ultraviolet region from 4000 \AA to 2300 \AA in accordance with the conclusion that the fluid is composed entirely of saturated dimethyl siloxanes.

(b) Dow Corning 700 Series Fluids

38. This series is composed of mixed methyl-phenyl siloxanes. The ratio of phenyl to methyl substitution is not constant but varies irregularly with increasing viscosity of the different members. The exact structure of the polymers has not been deduced from the spectral data due to the lack of reference data.

39. Throughout the spectra of the series (see Plates XVI to XXIV) the bands which are characteristic of the dimethyl siloxanes (see par. 17 and 25) are always present. This includes the 7.94 μ band of the silicon-methyl vibration and shows that, in part, the structures involved in all members of this series are identical in type with the dimethyl (500) series.

40. In addition to these bands, most of which fall in the short wavelength region below 9 μ , there are 21 distinct absorption maxima which are characteristic of the 700 series fluids and which have not been observed in any dimethyl siloxane. The strongest of these new bands are present in all members of the series examined but their intensities vary for the different members. Some of the weaker bands are not detected in two of the samples.

41. The band at 3.29 μ is invariably found for aromatic hydrocarbons and is due to the aromatic C-H vibration. This indicates the presence of phenyl groups in this series of fluids. In addition, the band at 6.28 μ is characteristic of phenyl groups and the four bands in the region of 5.1 to 5.7 μ as well as the band at 13.7 μ are characteristic bands of monosubstituted benzenes. It is fairly conclusive from this evidence that the 700 series siloxanes have phenyl substitution.

42. This conclusion is confirmed by the ultraviolet spectra of this series presented in Plate I. Absorption in this region of the spectrum must originate in the presence of unsaturated chemical structures and the characteristics of the absorption spectra are typical of phenyl structures.

43. The intensity of phenyl bands in the infrared may be used to calculate the relative phenyl contents of the samples. These calculations could be made on an absolute concentration basis if the proper pure reference compounds were available and values accurate to at least +2% or better could probably be obtained with careful spectral measurements. Since this investigation was confined to a general survey of the method and possible applications, no attempt has been made toward quantitative analyses. Values taken directly from the curves, however, can be used to obtain rough, relative values of the phenyl content. The choice of bands for this is important since the intensity of some of the phenyl bands varies with the type of phenyl substitution. For these samples the choice of different phenyl bands leads to different values of relative phenyl content and indicates, in fact, that the phenyl groups are substituted differently in the different samples. The best values are probably obtained by measuring the ratio of the absorption at 3.29 μ (phenyl) to that at 3.37 μ (methyl) since no other bands fall in this region and since these absorptions are probably almost independent of the type of phenyl and methyl substitutions involved in this series of siloxanes. Using this ratio as a measure of the relative phenyl-to-methyl substitution of the various members of the 700 series, fair correlation with the refractive index is obtained and the infrared measurements indicate that for this series phenyl content can be estimated from refractive index measurements. (See column six, Table II).

44. The spectra of the 700 series silicones beyond 8 μ indicate that the structures involved in the various members are not identical. It is believed that if reference data were available the spectra could be interpreted and the essential differences in structure could be deduced from the data presented. A careful study of these spectra, however, has not revealed any correlations which enable the differentiation between phenyl substitution on chain units and phenyl substitution on end groups. It is quite probable when phenyl substitution is involved that for both chain units and end groups the silicon atom concerned is not completely phenyl-substituted but has both phenyl and methyl groups attached to it. Such random substitution of phenyl groups would result in the presence of several structures, i.e., three types of chain units and four types of end groups, for linear polymers and would make interpretation difficult. If, on the other hand, phenyl substitution occurred only as triphenyl end groups and diphenyl chain units, interpretation probably could have been effected by correlations in this series of samples. Until such interpretations are made, however, the infrared spectra serve only to establish the identity or non-identity of the structures of the various samples, but for this purpose it has considerable effectiveness.

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45. The information deduced from the spectral data is presented in summary form for each sample of the D.C. 700 series fluids listed in Table II. The first four samples cover the viscosity range of the commercial samples studied. The other samples will be compared to one of the first four having similar viscosity.

(1) 416 - III - 292 (3.5 centistokes)

This sample contains the following structures:

- (C-H Bonds (Aromatic)
- (C-H Bonds (Paraffinic, methyl)
- * (Si-O-Si Structure
- (Si-CH₃ Structure
- (C₆H₅- X Structure, where X is probably silicon.

(* These structures are present in all samples of this series.)

The ratio of the phenyl to methyl absorption is .60, the highest of the first four samples.

No dimethyl chain units detected.

No trimethyl end groups detected.

No cyclic dimethyl siloxane structure detected.

The structure(s) of the polymer units produces absorption in the 11 to 14 mu range which is different from all other samples. This may be due to the combination of low molecular weight and considerable phenyl substitution. Apparently all silicon atoms of this sample are attached to at least one phenyl group.

(2) 416-IV-78 (25 c.s.)

The ratio of phenyl to methyl absorption is .37, lowest for the first four samples.

Dimethyl chain units in high concentration.

Trimethyl end groups not positively detected.

Cyclic dimethyl siloxane structure is positively indicated by a band at 4.71 mu.

This sample is probably composed of cyclic siloxanes with mixed methyl and phenyl substitution.

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(3) 416-IV-71 (50 c.s.)

The ratio of phenyl to methyl absorption is .53, not quite as great as for sample (1).

Dimethyl chain units are indicated.

No trimethyl end groups are detected.

No definite indication of cyclic structures.

All of the structures existing in sample (1) are present in this sample, but to a lesser extent.

The sample is probably composed largely of open-chain polymer with phenyl substitution occurring both on chain units and on end groups, but some chain units have only methyl substitution.

(4) 416-IV-75-76 (102 c.s.)

The ratio of the phenyl to methyl absorption is .49, intermediate between the two preceding samples.

Dimethyl chain units are detected.

Trimethyl end groups also detected.

No positive indication of cyclic structure is detected.

The 12.65 mu band found in sample (1) is also detected in this sample and indicates that one of the structures involved in sample (1) is also present here. It may be a diphenyl chain unit.

The chief components of this sample are probably open-chain dimethyl siloxanes with phenyl substitution largely confined to the chain units.

(5) 405A-IV-28 (25 c.s.)

The ratio of phenyl to methyl absorption is .12, the lowest of all samples of this series and considerably lower than most of the samples.

Dimethyl chain units are present in high concentration.

No trimethyl end groups are detected.

Cyclic dimethyl siloxane structure is positively indicated by absorption at 4.71 mu.

This sample is composed almost entirely of cyclic dimethyl siloxanes with only a small amount of phenyl substitution. It is essentially the same as sample (2) (having the same viscosity) except that much less phenyl substitution is present.

(6) 700-26 (50 c.s.) Now designated D.C. 510

The ratio of phenyl to methyl absorption is 0.14, nearly as low as sample (5) and considerably lower than the other samples.

Dimethyl chain units are detected in high concentration.

Trimethyl end groups are also detected.

No positive indication of cyclic structure is detected.

This sample is composed essentially of open-chain dimethyl siloxanes but has a small amount of phenyl substitution. The similarity of the composition of this sample with that of the 500 series fluids probably accounts for the new 510 designation. This sample differs from sample (3) (same viscosity) in that it has much lower phenyl content.

(7) 405A-IV-30 (100 c.s.) Now designated D.C. 550

The ratio of phenyl to methyl absorption is .51, indicating the presence of considerable phenyl content.

Dimethyl chain units are indicated, although not too definitely.

Trimethyl end groups are definitely indicated.

The 12.65 μ band found in sample (1) is also detected in this sample and indicates that one of the structures involved in the first sample is also present here. It may be that of a diphenyl chain unit.

The chief components of this sample are probably open-chain dimethyl siloxanes with phenyl substitution largely confined to the chain units.

This sample is quite similar to sample (4) (same viscosity) except that it has slightly higher phenyl content. As for the previous sample, the new 550 designation probably arises from its similarity to the 500 series. Low phenyl content was found for the 510 designation and much higher phenyl content is found for the 550 designation.

(8) 408A-III-33 (27 c.s.) Designated D.C. 702

The ratio of phenyl to methyl absorption is .63, higher than for all preceding samples.

Dimethyl chain units are not definitely indicated; the characteristic 12.45 μ band is slightly displaced and the significance of the displacement is not clear.

Trimethyl end units are definitely indicated.

No definite indication of cyclic structure is detected.

The 702 designation of this sample may have its origin in a phenyl content higher than has been found for any of the 700 series compounds.

(9) 408A-III-44 (60 c.s.) Designated D.C. 703

The ratio of the phenyl to methyl absorption is .68, the highest of all samples examined.

Dimethyl chain units are not detected.

Trimethyl end groups are detected.

No cyclic structure is detected.

This sample is similar to the preceding sample, designated D.C. 702, except that it has higher phenyl content. The spectra of both of these samples differ from the 700 series in the 9.5 μ region (Si-O-Si vibration) and the structure of these two samples has not been determined. In addition to high phenyl content, branching may also occur in these samples. This has not been definitely established.

(c) G.E. A-249 Fluid

46. This was the only General Electric Company commercial fluid examined. It was a special fluid developed for improved lubricating performance and supplied in 25 ml. volume. The sample composition corresponds to the Dow Corning 700 Series fluids, and it is noted that both commercial organizations selected mixed methyl and phenyl substituted siloxanes for improved lubricating properties.

47. All of the characteristic absorption bands of methyl substituted siloxanes and phenyl substituted siloxanes are present in the spectrum of this sample (Plate XXVII) as in the D.C. 700 series samples. The ratio of phenyl to methyl absorption is .20, a value intermediate between the D.C. 510 and 550 series. Dimethyl chain units are detected and trimethyl end groups are detected. A weak absorption at about 4.70 μ may indicate some cyclization. The sample is essentially composed of open-chain dimethyl siloxanes

but has some phenyl composition. The phenyl structure involved differs somewhat from that of the D.C. samples and produces an absorption at 13.95 μ . The phenyl absorption in the ultraviolet also differs from that of the D.C. series and the exact structure(s) involved has not been ascertained. It is interesting to note that the phenyl structure of this sample is present to some extent in only one D.C. sample, 405A-IV-28. This is evident from the u.v. spectra in Plate I. The essential difference between these two fluids, however, is that the D.C. fluid is composed essentially of cyclic dimethyl siloxanes, while the G.E. sample is composed essentially of open-chain dimethyl siloxanes.

(d) D.C. 400 Series

48. Although the infrared spectrum (Plate XXVI) of this fluid has the general characteristics of siloxanes, the main bands which characterize the dimethyl series are absent. No methyl substitution is present and no phenyl substitution is detected. Alkyl groups are present, however, and these are composed of both methyl and methylene groups. The absorption of the silicon-carbon band is displaced toward longer wavelength in this sample (8.077 μ) and it is almost certain that this is the result of ethyl substitution. The D.C. 400 series is undoubtedly composed of alkyl siloxanes and the alkyl group is very probably the ethyl group. It is not known whether this polymer is of the open-chain or cyclic type, or whether branched structures are present.

E. Polymerization of Open Chain Dimethyl Siloxanes

49. Additional tests were made on a sample of D.C. 500 Series fluid in an attempt to obtain information concerning the anomalous behavior of the fluid in certain systems. (See par. 3). This sample, designated 369-62-67 in Table II, has been shown to be composed of open-chain dimethyl siloxanes without branching. (Par. 36). It was tested extensively by the NRL Lubrication Section and several tested samples were furnished for spectroscopic examination.

50. An explanation of gelling which occurred in several of these tests was sought. In particular, it was desired to determine whether polymerization was the result of a simple increase in length of the polymer chains or whether branching and cross-linking also occurred. In addition, any other changes in molecular structure which occurred in the polymerization or simultaneously with it might also be detected.

51. In all of the samples examined, where polymerization was indicated by an increase of viscosity or gelling, an increase in length of the polymer chains was shown by an increase in the concentration of chain units and a decrease in the concentration of end groups. This change was readily detected by the method described in par. 24.

52. The formation of branched or cross-linked structures is not easily detected spectroscopically. (See par. 34). It is measured by the appearance of a band at 7.90 μ originating in the Si - CH₃ structure at branching centers. Considerable interference is encountered due to another strong band at 7.94 μ originating in the Si - CH₃ structure of the dimethyl chain units. These bands can be only partially resolved even with good equipment and a few percent of branching centers are probably required for definite detection.

53. The tested samples, some of which were treated drastically in order to enhance the concentration of branching centers which might be formed, were examined accurately in the 8.0 μ region. The samples included thickened fluid and small quantities of gel formed by treatment in a journal bearing, viscous oils and gelatinous material formed by bubbling dry air or nitrogen thru samples held at 200-225°C both with and without metallic catalysts, totally gelatinous material formed by heating in a pyrex beaker over a burner or hot plate, and hard lacquer-like films formed by exposure in air to ultraviolet radiation. The results from these samples follow a definite pattern. Two spectroscopic effects were found and are discussed in the following paragraphs.

54. First, a gradual shift of position of the 8 μ absorption band occurred upon polymerization and is associated with the transition from the liquid to the solid state. For example, the position of this band for the untreated fluid is 7.933 μ ; treated samples which are liquid and gelatinous samples soluble in CS₂ absorb from 7.933 to 7.929 μ ; gelatinous material insoluble in CS₂ but soluble in benzene absorbs at 7.929 μ ; gelatinous material insoluble in both CS₂ and benzene absorbs from 7.929 to 7.921 μ ; and hard lacquer-like films absorb from 7.907 to 7.861 μ . This shift in position appears to be independent of the method of polymerization. The progressive shift has been shown in a single sample which was examined periodically during exposure to ultraviolet radiation. At one point in the course of the treatment the position of the 8 μ band corresponds precisely to that which has been associated with branching in the liquid state, but in this case the sample has solidified and the correspondence of absorption position is entirely accidental and of no significance. The method for determining branching by absorption at 7.90 μ applies only to liquid samples and cannot be used in this case because of the change of state of the sample and its related shift of absorption position.

55. The second effect is a change in the shape of the 8 μ band upon polymerization. For the untreated fluid this band is practically symmetrical except for a slight distortion on the long wavelength side which results from an absorption of the end groups at slightly longer wavelength. This distortion is barely observable due to the low concentration of end groups in this particular fluid and to the weakness of the end group absorption at this position. For samples in the liquid state the appearance of a similar distortion on the short wavelength side (7.90 μ) would indicate the presence of branching centers. In all the liquid samples examined no such change in shape of the 8 μ band was observed and for these samples it is concluded that if branched structures were formed during the polymerization, the concentration of such structures was too low to be detected by these observations.

56. Considering, for the moment, the concentration of branching centers which might be required for detection by this method, it is pointed out that the intensity of the absorption of the branching centers in this spectral region is of the same order of magnitude as the intensity of the absorption of end groups. Since the effect of end groups was just barely observable in the untreated fluid, it is concluded that if branching is to be detected the concentration of branching centers formed during polymerization must be approximately as great as the concentration of end groups in the unpolymerized fluid. This is probably of the order of one or two percent in this fluid, and when branching centers are formed to this extent during polymerization it is almost certain that the physical state of the sample will change from a liquid to a gel or solid state. In view of these considerations it is not surprising that branching was not detected in polymerized samples which remained in the liquid phase.

57. Samples of gel which were examined showed a shift in position associated with a change of state, as described in par. 54, but showed no change in the shape of the band. Only in the case of the hard lacquer-like films formed by ultraviolet irradiation was any change in shape of the 8 μ band observed. Upon continued irradiation this band shifts from 7.933 μ toward shorter wavelength until it finally reaches 7.900 μ . At this point the band becomes distorted on the short wavelength side by a weak absorption of 7.861 μ . At this point the film was very hard by scratch test. (Because of the extremely thin films required for spectroscopic study no measurement of hardness was considered significant). Upon still further irradiation of the sample the intensity of this weak absorption at 7.861 μ increases and eventually becomes the maximum of the band while the intensity of the band at 7.900 μ becomes less and tends to disappear.

58. The character of this change in shape of the 8 μ band is that which would be expected upon formation of branching or cross-linking. If this explanation is correct, the formation of branching does occur during polymerization of open-chain dimethyl siloxanes, and when the polymerization is carried to an extreme the branched structure becomes predominant. The evidence supporting this explanation cannot be considered conclusive, however, since there exists a possibility that the observed change in shape of the 8 μ silicone band is not due to the formation of branching centers but to the change in state of the sample or possibly to some other cause.

59. This uncertainty encountered in spectroscopic detection of branching is due to the change of state which accompanies polymerization and cannot be avoided when working with a sample of initially high viscosity (100 centistokes) such as was used here. Efforts were accordingly directed toward the polymerization and study of low molecular weight siloxanes where an appreciable concentration of branching centers might possibly be built up before a change of state occurs. Because of effects of volatility on the extremely thin films required for study, siloxanes of less than six silicon atoms could not be studied. A pure sample of hexadecamethylheptasiloxane (7 Si atom chain) was polymerized by ultraviolet radiation and examined periodically. No change in shape of the 8 μ band was observed until after the position of the band had shifted and it is concluded that even for this low molecular weight polymer sufficient branching for spectroscopic detection does not occur before a change of state is evoked.

60. In addition to the measurements in the region of 8 mu described in the preceding paragraphs, most of the treated samples were studied over the complete spectral region from 2 to 15 mu. In the region from 11.85 to 13.25 mu it was observed that an increase of viscosity and gelling were accompanied by small intensity changes resulting from a decrease in the concentration of end groups and an increase in the number of chain units. This indicates that the polymerization is the result of an increase in length of the polymer units but does not outlaw the possibility that the increase in molecular weight is partly due to branching. Some cyclization may also occur but no evidence of cyclic structure was detected.

61. No other spectral changes were detected in any of the samples of the treated fluid. If any chemical reactions such as oxidation or reaction with the metallic catalyst occur during thickening or gelling by any of the methods used, the reaction products were present in such low concentrations they were not detected.

62. Interesting results were obtained from examination of the volatile condensates obtained when this fluid was aerated at 200 to 225°C with dry air and nitrogen. The condensate in each case was a mixture of crystalline solid and liquid material which was identified as a mixture of cyclic siloxanes containing three and four silicon atoms. The spectra of the condensates showed all the bands of the cyclic trimer and tetramer (see Plates IX and X) and no additional bands. This indicates that at 200°C with gaseous agitation cracking is not limited to the removal of methyl groups from the polymer chains but segments of the chain also are broken off and form cyclic structures. The cyclic trimer and tetramer are both volatile at the temperature used and constitute the volatile condensate obtained. Although none of the other lower molecular-weight cyclic structures was detected in the treated fluid, it would seem logical that they might be formed by the same mechanism and might be present in low concentration.

CONCLUSIONS

A. Spectra of Dimethyl Siloxanes

63. Open-chain dimethyl siloxanes are characterized by numerous absorption bands from 2 to 15 μ in the infrared. Several of these bands are independent of molecular weight and may be used to identify a polymer of this type; other bands vary with size of the polymer chains and may be used to identify individual compounds, particularly those of low molecular weight.

64. The spectra of cyclic dimethyl siloxanes have fewer bands than the open-chain isomers and the missing bands are those due to the end groups of polymer chains. Except for this difference the spectra are nearly identical, especially for polymers of more than ten units in length. Weak bands at 4.71 and 4.78 μ are of some use in distinguishing between cyclic and open-chain polymers.

65. For samples in the liquid state, branched structures may be detected by a band at 7.90 μ . A strong band at 7.94 μ interferes, however, and renders this means of detection insensitive. The methods of infrared are not well adapted to the determination of branching.

B. Commercial Fluids

66. It has been shown that the methods of infrared are useful in determining the type of polymer structure of commercial fluids, especially when reference compounds of known structure are available for examination.

67. The methods of ultraviolet are useful for the detection of certain types of impurities in alkyl-substituted siloxanes such as the Dow Corning 400 and 500 series silicones and for the detection of phenyl-substituted siloxanes such as the Dow Corning 700 series silicones.

68. The Dow Corning 500 series commercial fluid has been shown to consist of open-chain dimethyl siloxanes.

69. The Dow Corning 700 series commercial fluids have been shown to consist of siloxanes with mixed methyl and phenyl substitution. The ratio of phenyl to methyl substitution is not constant for the series and does not vary uniformly with viscosity. Some samples are predominantly cyclic while others are predominantly of the open-chain type.

70. The Dow Corning fluids now designated 510 and 550 are similar to the D.C. 500 series fluids but have some phenyl substitution. The 510 fluid has low phenyl content while the 550 fluid has correspondingly higher phenyl content.

71. The Dow Corning 702 and 703 series fluids have greater phenyl content than the 700 series fluids. The structure of these polymers may also differ from that of the 700 series fluids.

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72. The G.E. A-249 commercial fluid is similar to the Dow Corning 700 series fluids but the structure of the polymer is different in some way. It consists of mixed methyl and phenyl-substituted siloxanes.

73. The Dow Corning 400 series fluid is composed of alkyl-substituted siloxanes and the alkyl group is probably ethyl.

C. Polymerization

74. In all cases of polymerization by thermal treatment or ultraviolet irradiation of open-chain dimethyl siloxanes examined, an increase in length of the polymer chains was detected spectroscopically. In each case no indication of branching was detected previous to gelling and solidification of the sample. Upon solidification and hardening of the sample by ultraviolet irradiation two spectral effects were observed in the region of 8 μ : One effect, a shift in the position of the absorption, is due to the change from the liquid to solid phase; the other effect, a change in the shape of the absorption band, may be due to the formation of branching.

75. The absorption spectra of silicone fluids have revealed no evidence useful for interpretation of the peculiar lubricating properties of these fluids. Except for polymerization, no evidence of chemical reaction or other changes in molecular structure was found for any of the samples studied.

RECOMMENDATIONS

76. The method of infrared absorption is not well adapted to the determination of molecular weight or to the determination of the extent of branching of silicone fluids and is not recommended for these purposes.

77. The infrared spectrum is useful in distinguishing between silicone polymers with different substitution on the polymer chains and is recommended for identification of methyl-, ethyl-, and phenyl-substituted siloxanes.

78. It is recommended that the methods of absorption spectroscopy be included in the examination of commercial silicone fluids and in all investigations in which the structure of the silicone fluid may affect the results.

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TABLE I

Reference Samples of Pure Dimethyl Siloxane Compounds

Serial No.	Compound	Structural Type	(e) Source	(f) Purity %	(g) n_D^{25}	(g) Boiling Point °C	(g) Viscosity 25°C (Centistokes)
		(a)					
56	Hexamethyldisiloxane	Open-chain	G.E.	98+			
65	"	"	D.C.		1.3748	99	0.65
57	Octamethyltrisiloxane	"	G.E.	98+			
66	"	"	D.C.		1.3822	150	1.04
58	Decamethyltetrasiloxane	"	G.E.	98+			
67	"	"	D.C.		(Contained toluene impurity)		
154	"	"	D.C.		1.3872	192	1.53
59	Dodecamethylpentasiloxane	"	G.E.	98+			
68	"	"	D.C.		1.3902	114/20 mm	2.06
69	Tetradecamethylhexasiloxane	"	D.C.		1.3922	70/1 mm	2.63
70	Hexadecamethylheptasiloxane	"	D.C.		1.3940	87/0.5 mm	3.24
71	Octadecamethyloctasiloxane	"	D.C.		1.3952	103/0.5 mm	3.88
60	Hexamethylcyclotrisiloxane	Cyclic	G.E.	98+			
157	"	"	D.C.			133	m.p.=64°C
61	Octamethylcyclotetrasiloxane	"	G.E.	98+	1.3921*		
158	"	"	D.C.			171	m.p.=17.4
62	Decamethylcyclopentasiloxane	"	G.E.	98+			
159	"	"	D.C.			205	m.p.= -45
63	Dodecamethylcyclohexasiloxane	"	G.E.	98+			
160	"	"	D.C.			236	m.p.= -3
64	Tetradecamethylcycloheptasiloxane	"	G.E.	98+			
161	"	"	D.C.			147/20mm	m.p.= -32
162	Hexadecamethylcyclooctasiloxane	"	D.C.			168/20mm	m.p.=31.5
72	Decamethylisotetrasiloxane	Branched	D.C.		(Contained toluene impurity)		
155	"	"	D.C.		1.3851	60/6 mm	1.57
73	Dodecamethylneopentasiloxane	"	D.C.		(Contained toluene impurity)		
156	"	"	D.C.		1.3865	90/9 mm	2.97

(a) Structural formula $(CH_3)_3Si-O-[Si(CH_3)_2O]_n-Si(CH_3)_3$ $n = 0, 1, 2, \dots$

(b) Structural formula $[Si(CH_3)_2O]_n$ $n = 1, 2, 3, \dots$

(c) Structural formula $CH_3Si[OSi(CH_3)_2]_3$

(d) Structural formula $Si[OSi(CH_3)_2]_4$

(e) Samples by courtesy of Dr. Patenode at General Electric Laboratory and Mr. A. Kauppi at Dow Corning Corporation.

(f) Determined by G.E. at time of preparation in 1943.

(g) Data from Dr. M. J. Hunter, courtesy of Dow Corning Corporation.

(*) n_D^{30} measured at NRL.

TABLE II

Commercial Silicone Fluids

Commercial Designation	Sample Designation	Viscosity (c) Centistokes/25°C	n_D^{30} (c)	Boiling Point °C (d)	Aromatic-Aliphatic Ratio (e)
D.C. 700 Series	L16-III-292	3.5	1.5124		.60
D.C. 700 Series	L16-IV-78	25	1.4834		.37
D.C. 700 Series	L16-IV-71	50	1.5076		.53
D.C. 700 Series	L16-IV-75-76	102	1.4955		.49
D.C. 700 Series	L05A-IV-28	25	1.4180		.12
D.C. 700 Series (a)	700-26	50	1.4287		.14
D.C. 700 Series (b)	L05A-IV-30	100	1.5078		.51
D.C. 702	L08A-III-33	27	1.5063	160/0.2 mm	.63
D.C. 703	L08A-III-44	60	1.5200	190/0.2 mm	.68
D.C. 500 Series	369-62-69	100	1.4009	Above 250/25 mm	-
D.C. 400 Series	L05A-2-54	60			-
G.E. Fluid	A-249	25	1.4462 (23.5°C)		.20

(a) Now designated D.C. (510)

(b) Now designated D.C. (550)

(c) Measured by NRI Lubrication Section

(d) Manufacturer's Data

(e) Ratio of the Intensity of Aromatic Absorption to the Intensity of Paraffinic Absorption (see Par. 41).

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TABLE III

Characteristic Absorptions of Open-Chain Dimethyl Siloxanes

Absorption Maxima (μ)	Effect of Increasing Molecular Weight	
	Position	Intensity
2.28	Constant	Constant
2.37	"	"
~ 2.47	"	"
2.68	"	"
2.75	"	"
3.37	"	Approx. constant
~ 3.46		Decreases rapidly
~ 3.55(shoulder)	"	Decreases (?)
~ 3.76	"	Constant
~ 4.01	"	"
4.78	"	Decreases
4.87	"	Increases, initially absent
~ 5.00	Apparently shifts to 5.05	Decreases rapidly
5.16	Constant	Approx. constant
5.36	Shifts rapidly toward 5.25	Decreases
5.80	Shifts toward 5.70, broadens	Approx. constant
6.35	Shifts toward 6.25, develops broad triplet structure	
6.63(weak)		Disappears rapidly
6.92	Constant	Decreases (?)
7.09(strong)	"	Increases (?)
~ 7.14(shoulder)	"	?
7.66(weak)	Shifts toward 7.55	Decreases
7.94(strong)	Approx. constant	Increases, absent in dimer
8.00(strong)	Constant	Decreases rapidly
9.55(strong)	Splits, maxima separate toward 9.15 and 9.78	Approx. constant
11.35(weak)	Approx. constant	Initially absent, broadens
11.84	Shifts toward 11.88	Decreases
~ 12.13(weak)	Shifts toward 12.24	Approx. constant
~ 12.50	Initially absent, doublet in trimer, shifts toward 12.45	Increases
13.25	Constant	Decreases
~ 14.17	Approx. constant	Develops in higher members
~ 14.50	Approx. constant	Approx. constant

TABLE IV

Characteristic Absorption of Cyclic Dimethyl Siloxanes

Absorption Maxima (μ)	Effect of Increasing Molecular Weight	
	Position	Intensity
2.28	Constant	Constant
2.37	"	"
~ 2.48	"	"
2.68	"	"
2.75(shoulder)	Constant	"
3.37	"	"
~ 3.44(shoulder)	"	?
3.55(shoulder)	"	Approx. constant
~ 3.77	"	Constant
4.00	"	"
4.71	"	Decreases slowly
4.88	"	Decreases (?)
5.04(weak)	"	Decreases rapidly
5.15	"	Approx. constant
5.48	Shifts toward 5.65	Increases
~ 5.85	Varies	Varies
~ 6.2	Changes position and shape	
6.44	Shifts toward 6.56	Decreases
6.90	Constant	Approx. constant
7.09	"	Approx. constant
7.16(shoulder)	"	?
7.35 - 7.50	Varies	Varies
7.99(strong)	Constant	Constant
~ 9.3(strong)	Displaced to 9.84 in trimer, splits	Approx. constant
11.40	Shifts to 11.65	Approx. constant (?)
12.30	Shifts toward 12.45	Approx. constant
14.55	Shifts toward 14.15	Increases

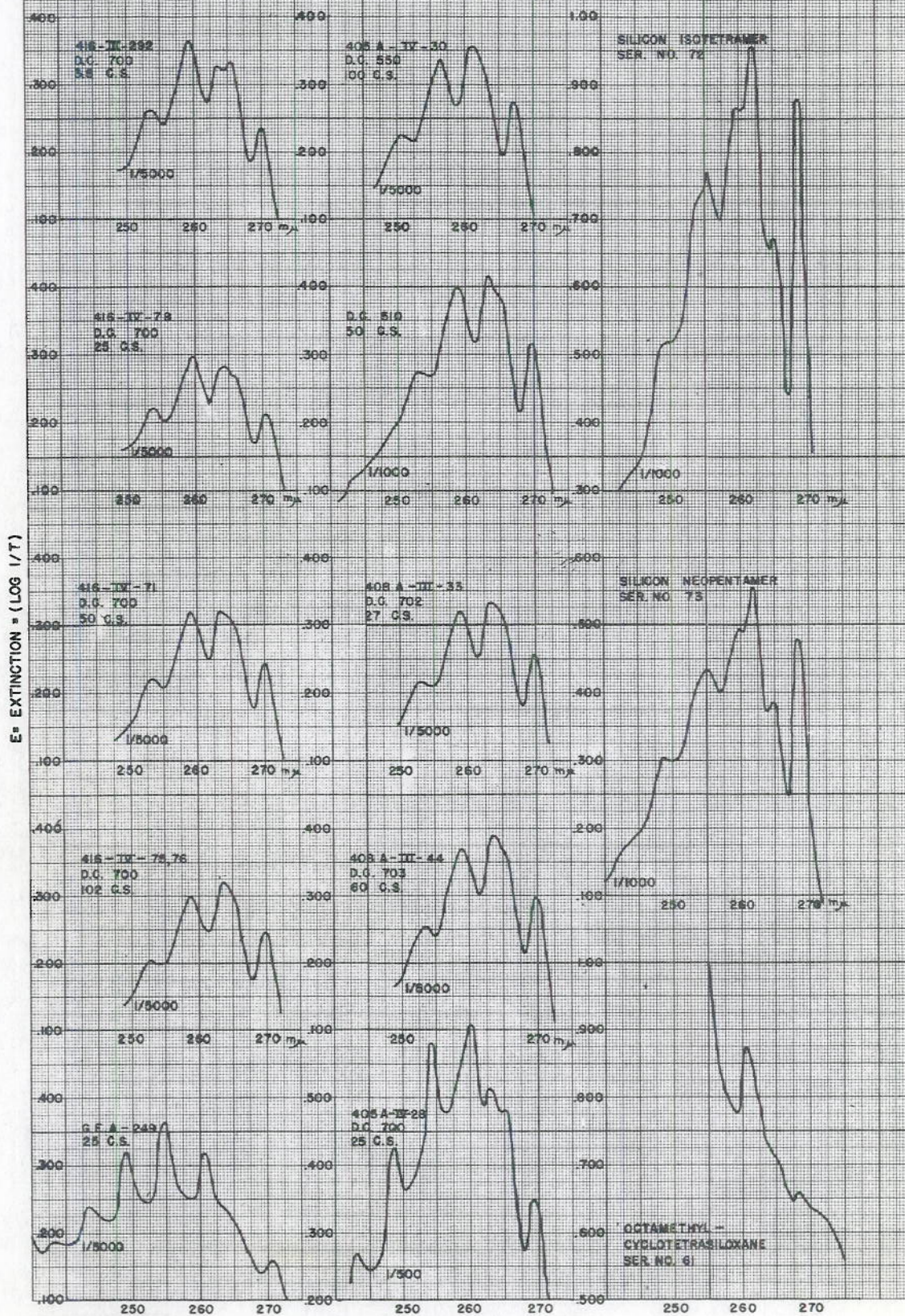
TABLE V

Correlation of Absorption with Molecular Structure

<u>Band Position (Mu)</u>	<u>Molecular Structure</u>
3.37.	C-H bond (Methyl groups)
7.94.	C-Si bond in $\begin{array}{c} \text{CH}_3 \\ \\ \text{O-Si-O} \\ \\ \text{CH}_3 \end{array}$ structure
8.00.	C-Si bond in $\text{O-Si(CH}_3)_3$ structure
9-10.	Si-O-Si structure
11.84.	O-Si(CH ₃) ₃ end groups
12.45.	O-Si(CH ₃) ₂ -O chain units
13.25.	O-Si(CH ₃) ₃ end groups

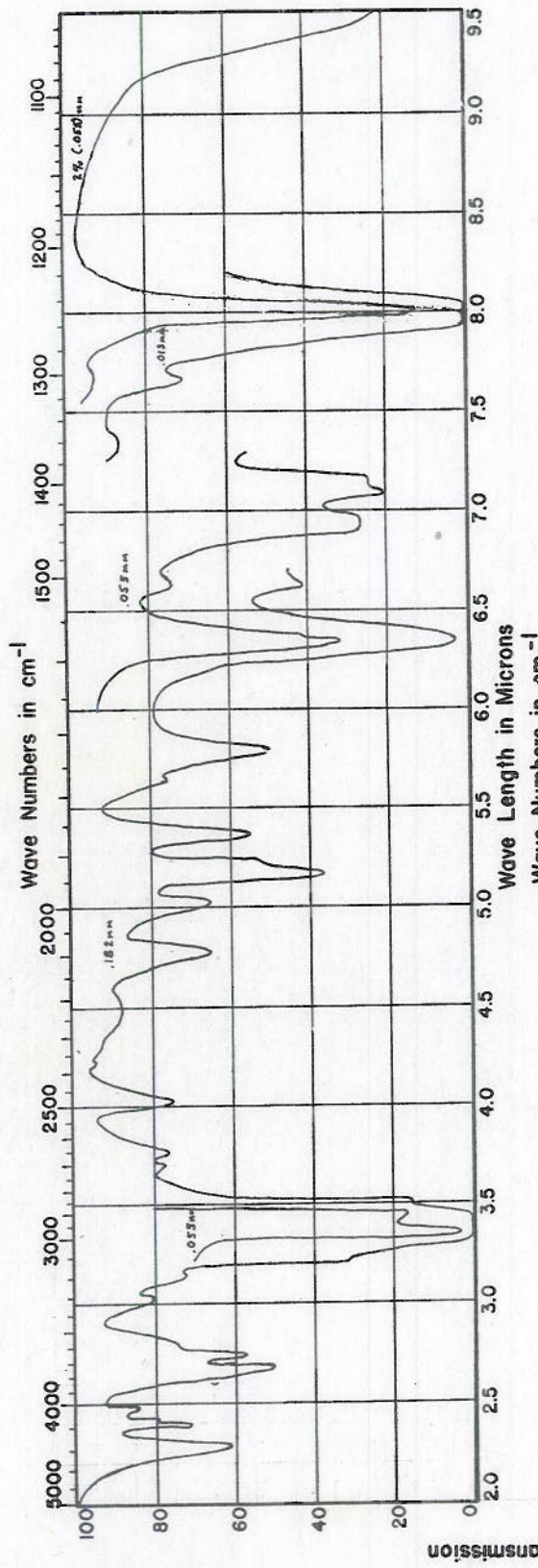
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ULTRA-VIOLET ABSORPTION SPECTRA OF SILICONE FLUIDS

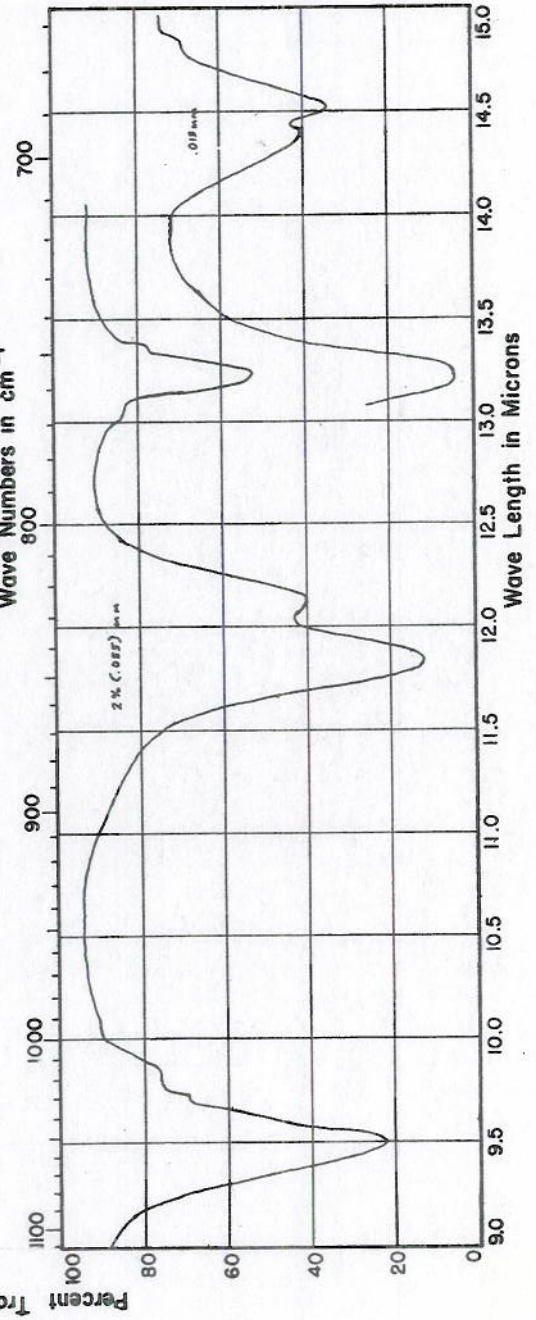


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PLATE I



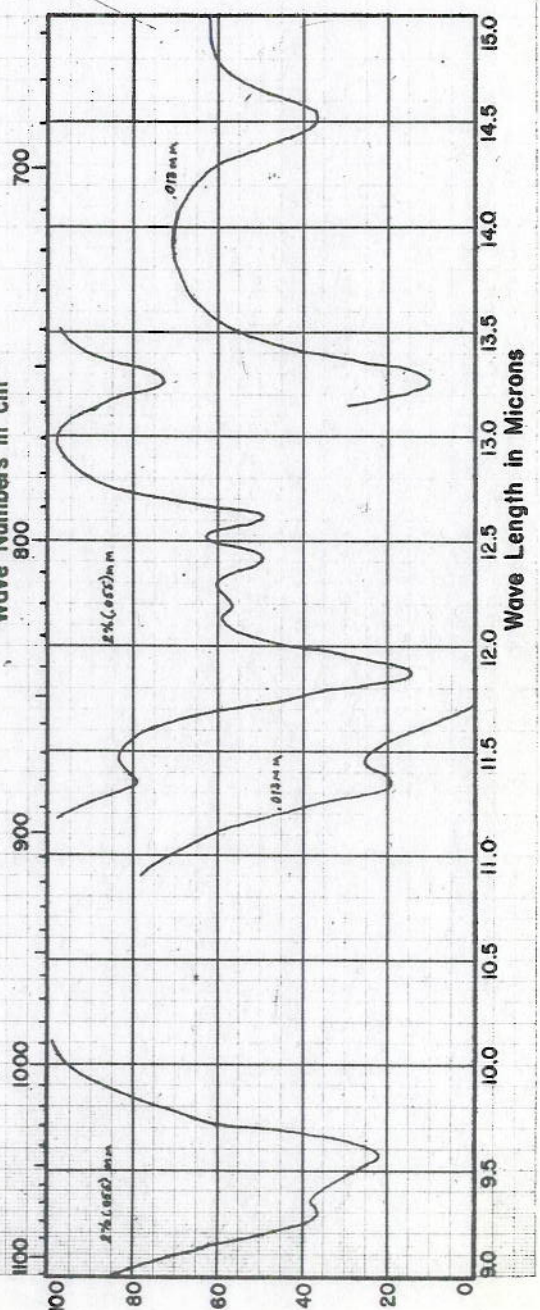
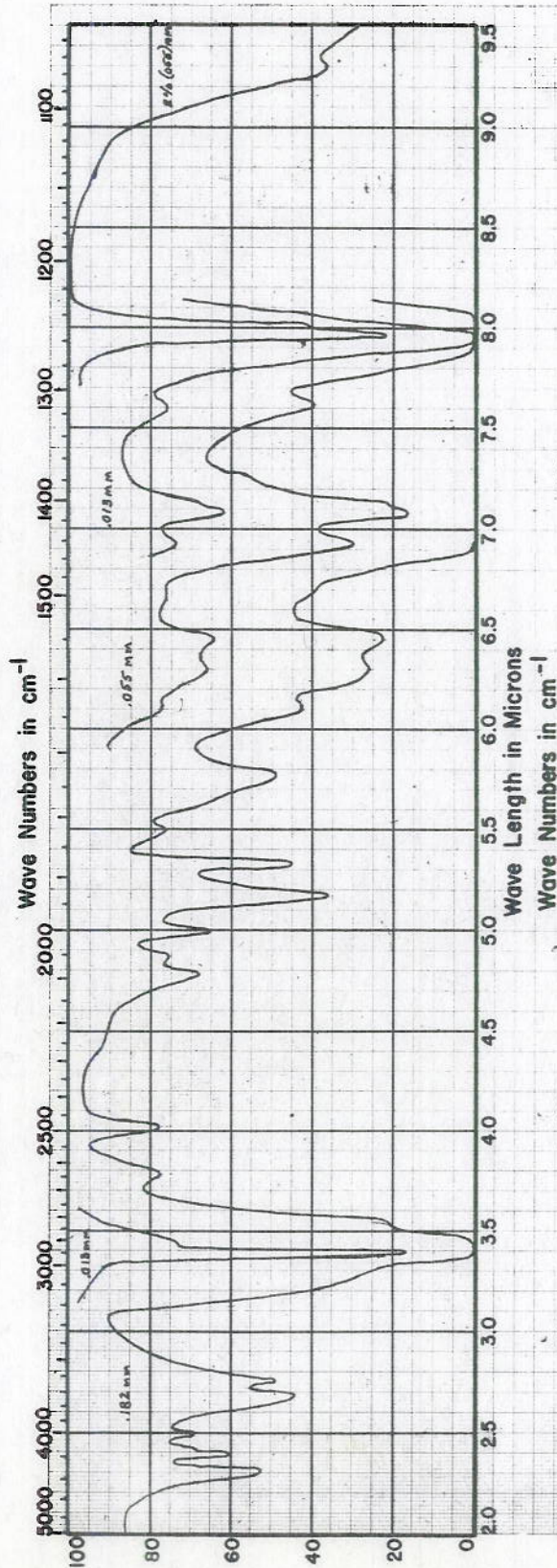
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SOURCE AND PURITY	SERIAL # 56
STATE	LIQUID
TEMPERATURE	GENERAL ELECTRIC
CELL LENGTH	
RECORDS	307 - 310
LABORATORY	
CHEMICAL	
SPECTROSCOPY	



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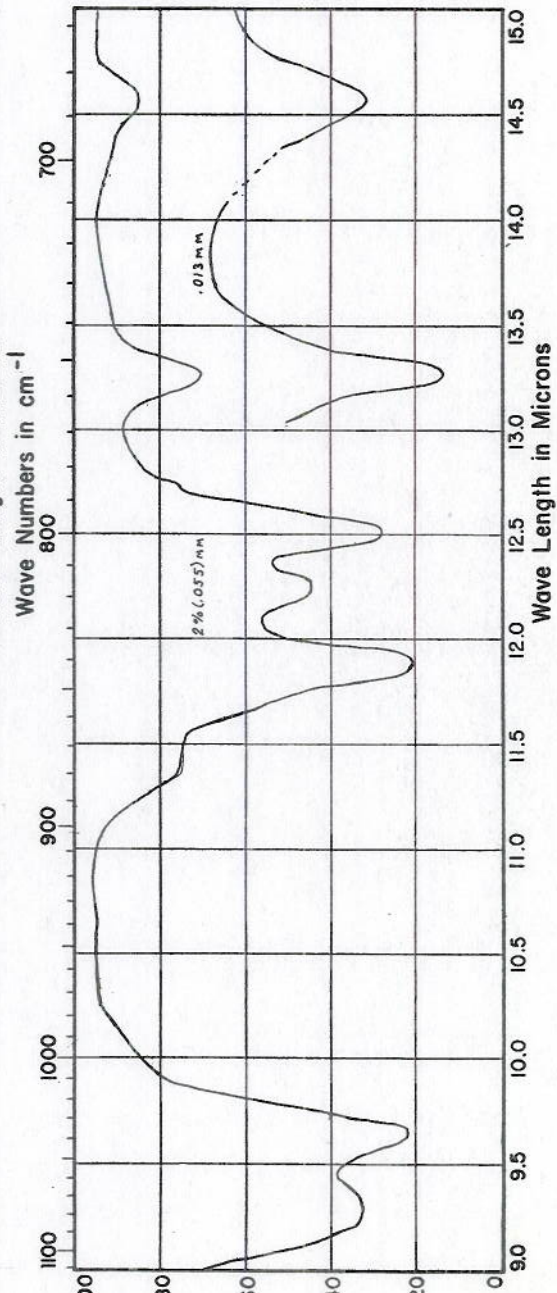
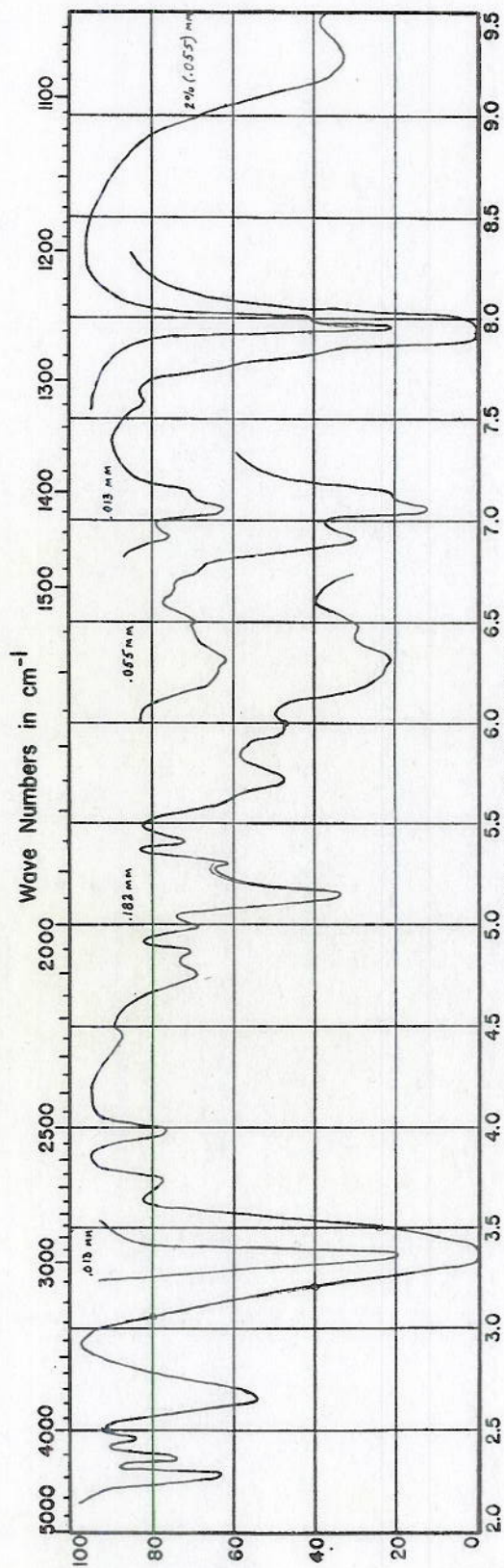
P-2746

PLATE 2



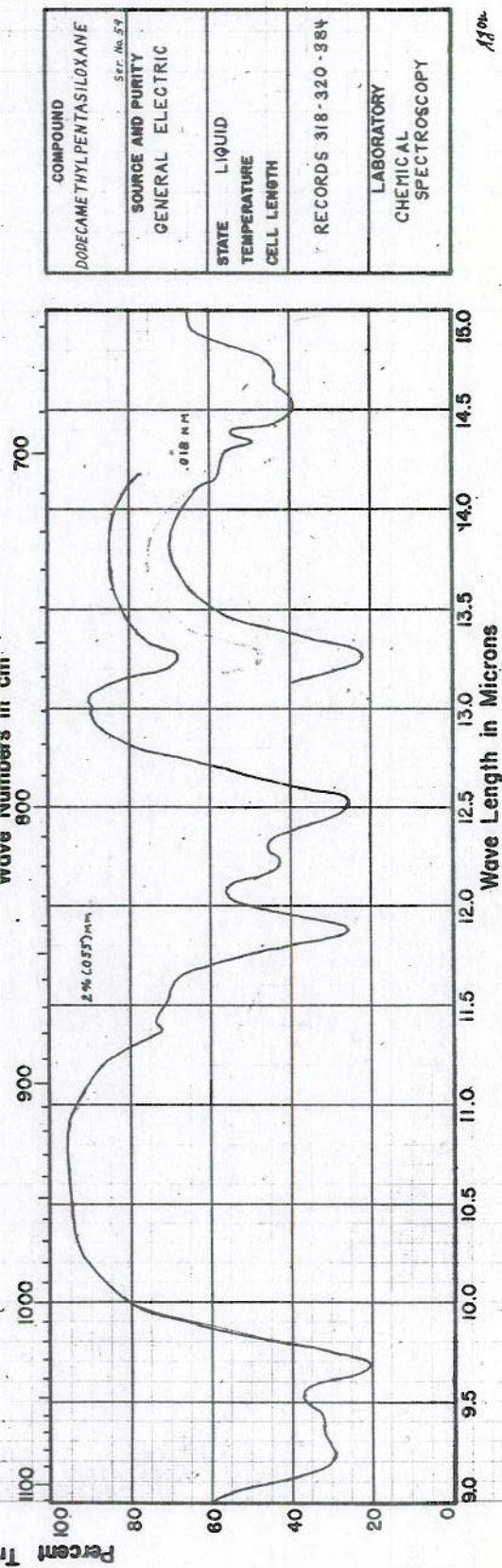
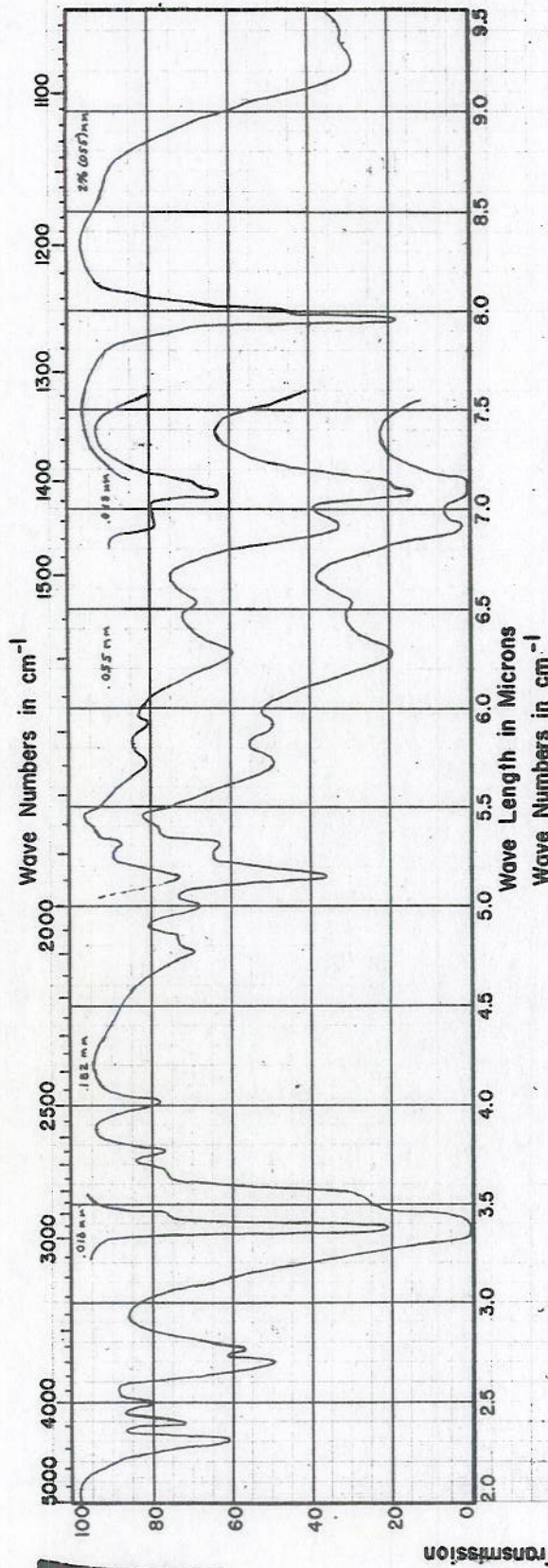
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SOURCE AND PURITY	SER. # 57 GENERAL ELECTRIC
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	334-385
LABORATORY	CHEMICAL SPECTROSCOPY

8/90



COMPOUND	DECAMETHYL TETRASILOXANE
SOURCE AND PURITY	GENERAL ELECTRIC
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	315-317
LABORATORY	CHEMICAL SPECTROSCOPY

11/46



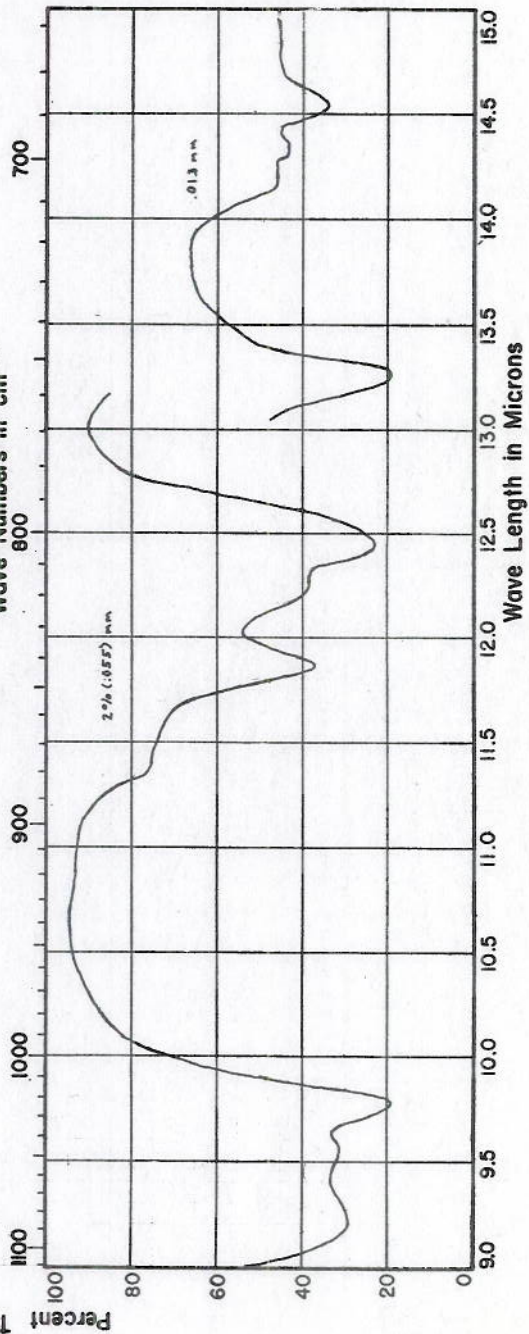
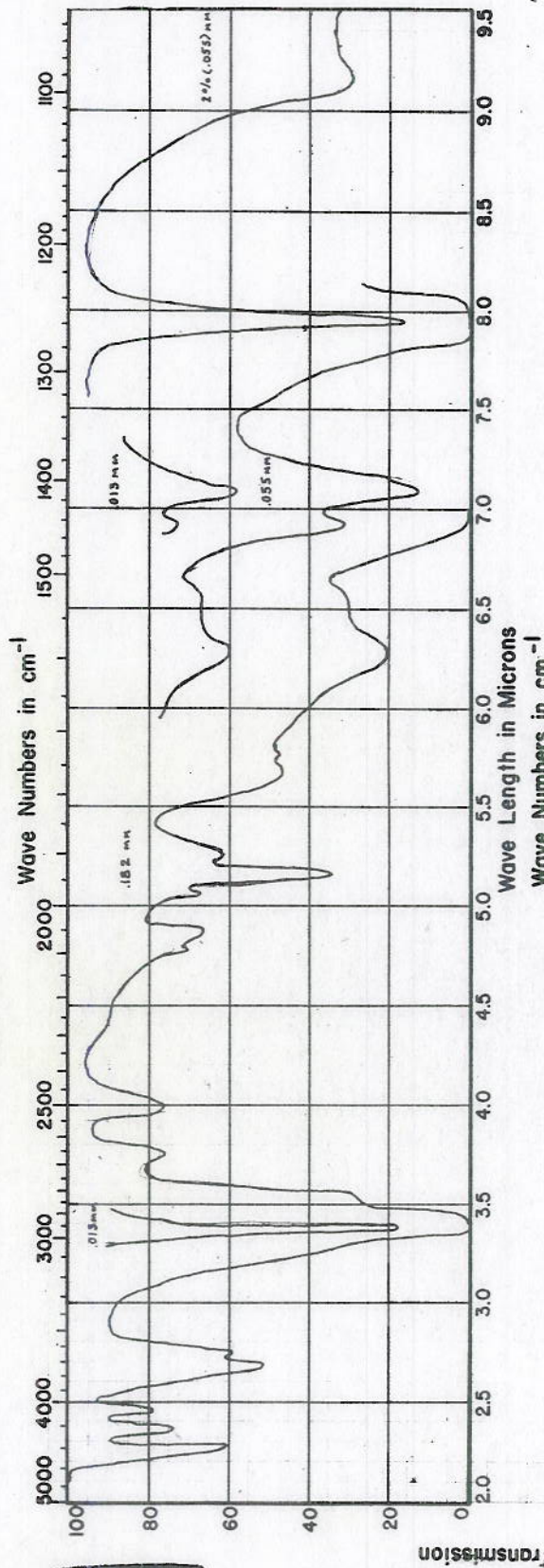
COMPOUND	DODECAMETHYLPENTASILOXANE
SOURCE AND PURITY	GENERAL ELECTRIC
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	318-320-384
LABORATORY	CHEMICAL SPECTROSCOPY

1394

P-2746

PLATE 5

DECLASSIFIED



COMPOUND	TETRADECAMETHYLHEXA SILOXANE
SOURCE AND PURITY	DOW CORNING
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	361 + 363
LABORATORY	CHEMICAL SPECTROSCOPY

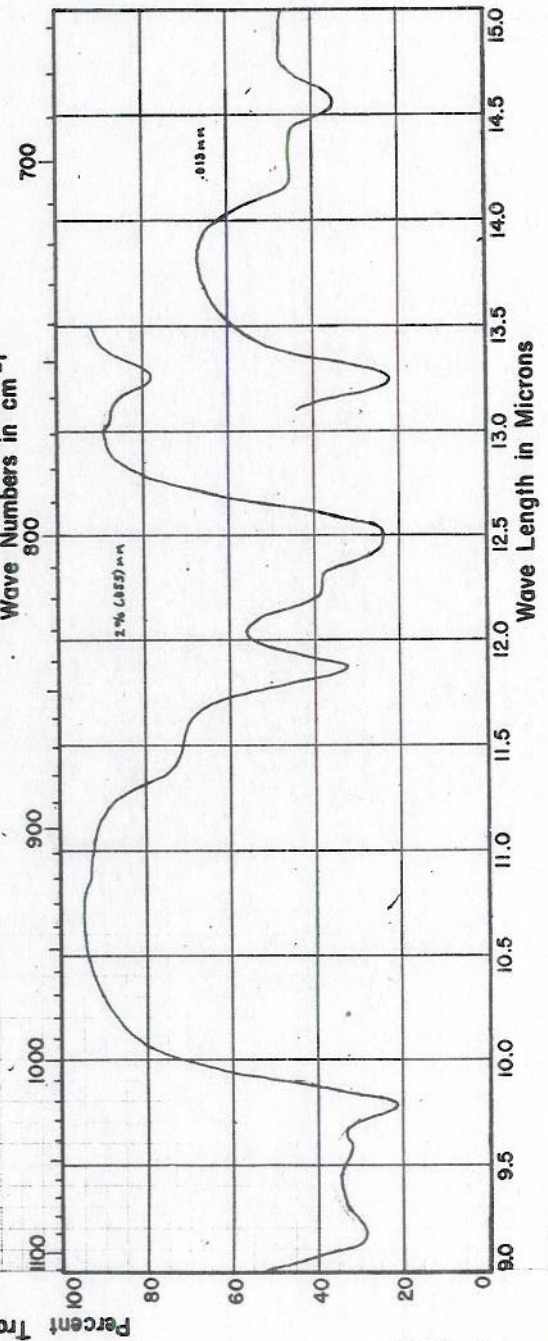
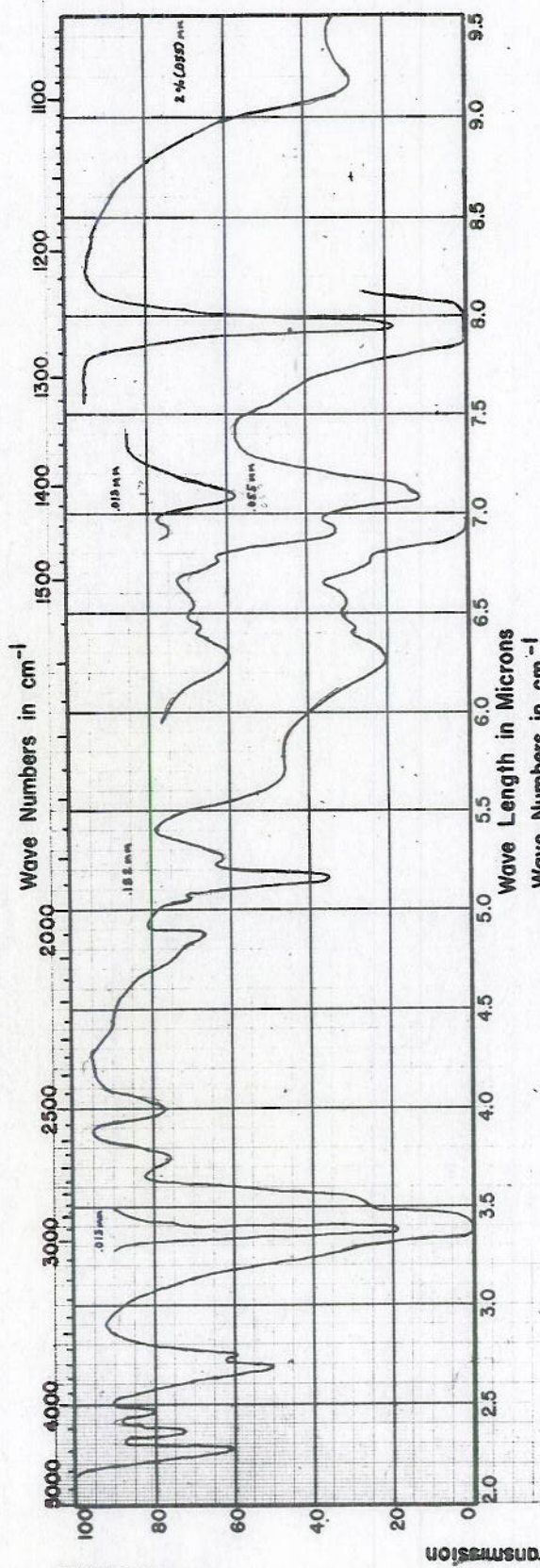
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P-2746

PLATE 6

DECLASSIFIED



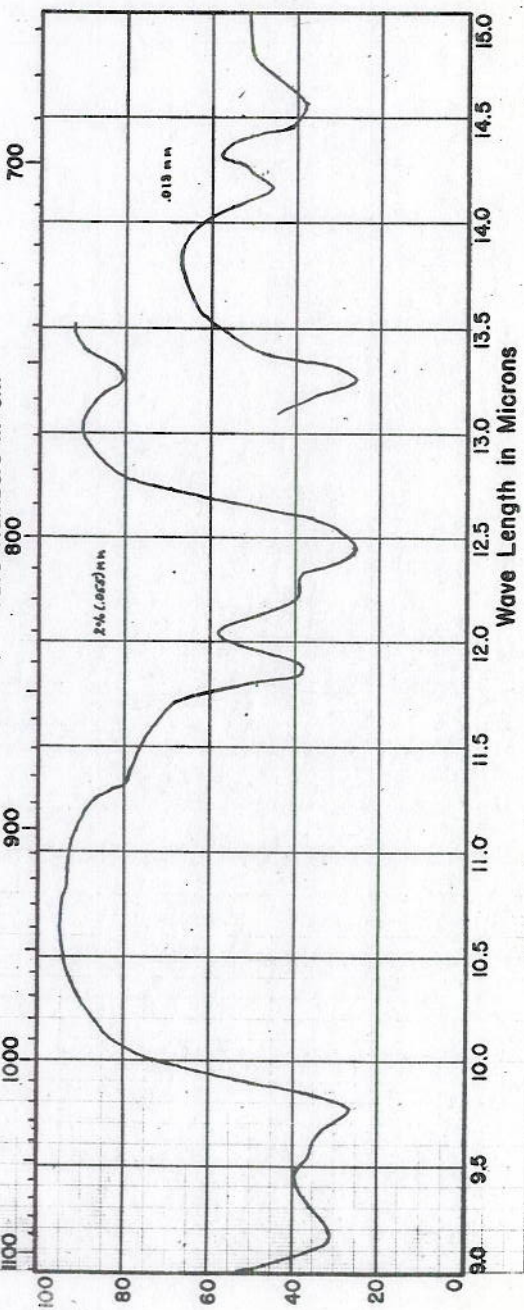
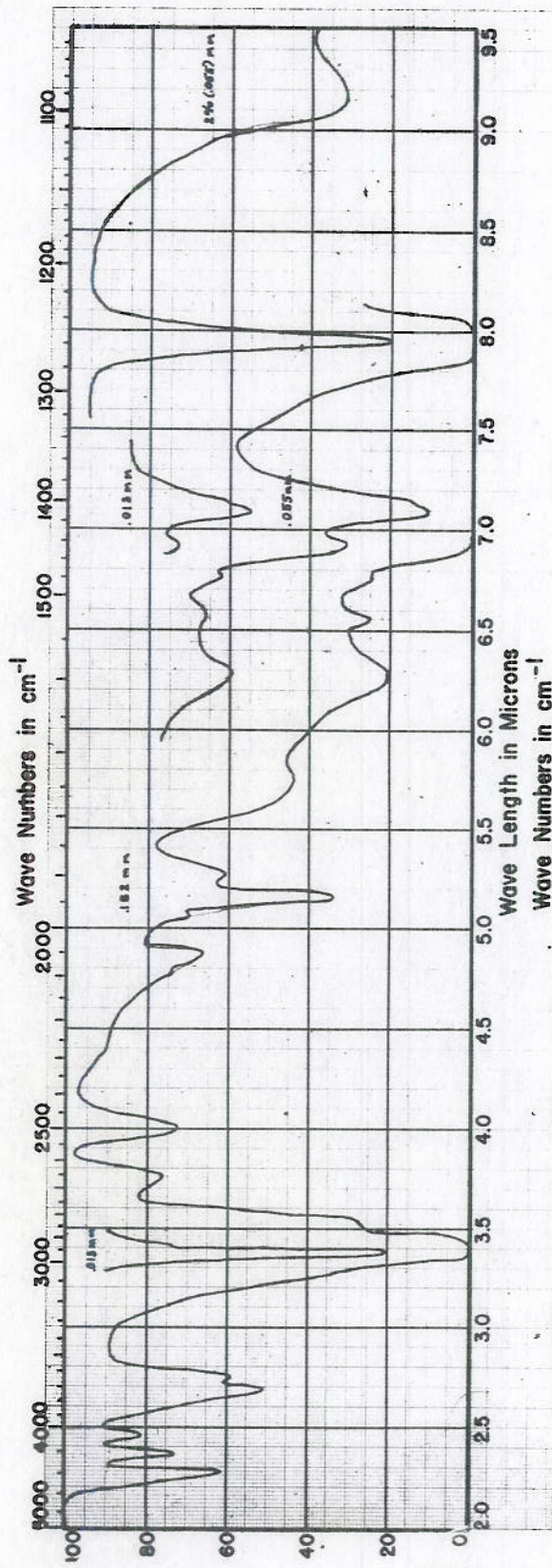
COMPOUND	HEXADECAMETHYLHEPTA SILOXANE
SOURCE AND PURITY	DOW CORNING
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	359-260
LABORATORY	CHEMICAL SPECTROSCOPY

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PLATE 7



COMPOUND	OCTADECAMETHYLOCTA SILOXANE
SOURCE AND PURITY	DOW CORNING
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	35G-857
LABORATORY	CHEMICAL SPECTROSCOPY

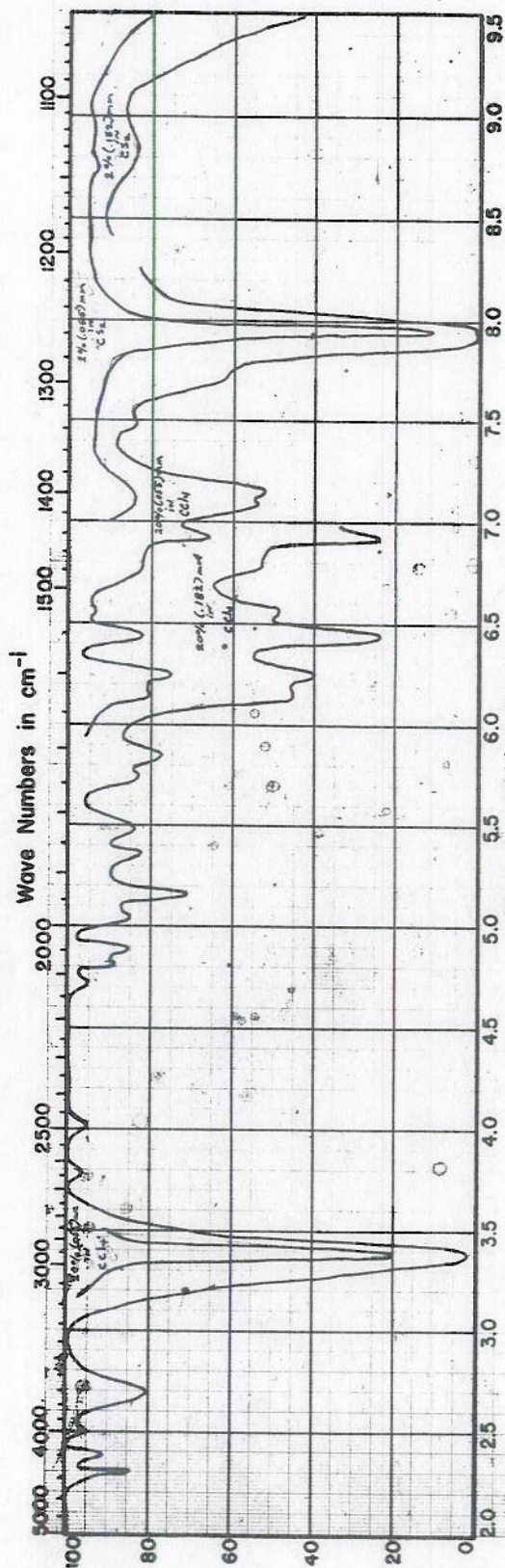
187

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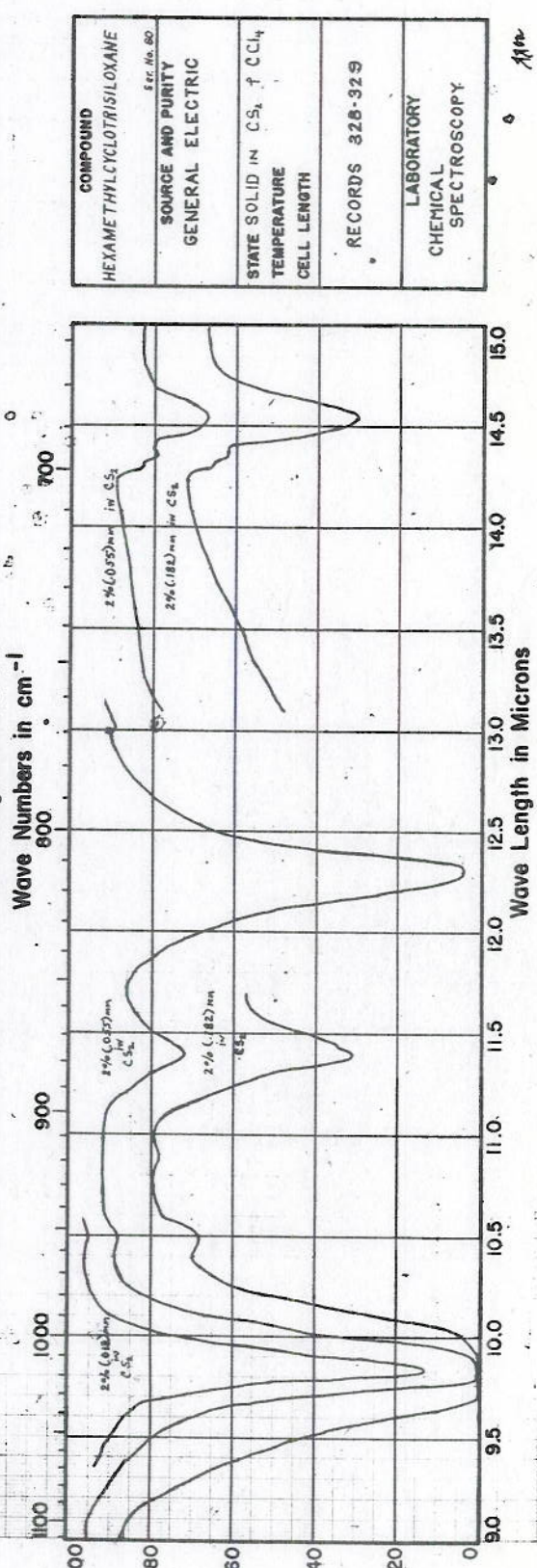
PLATE 8

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Wave Numbers in cm^{-1}

Wave Length in Microns



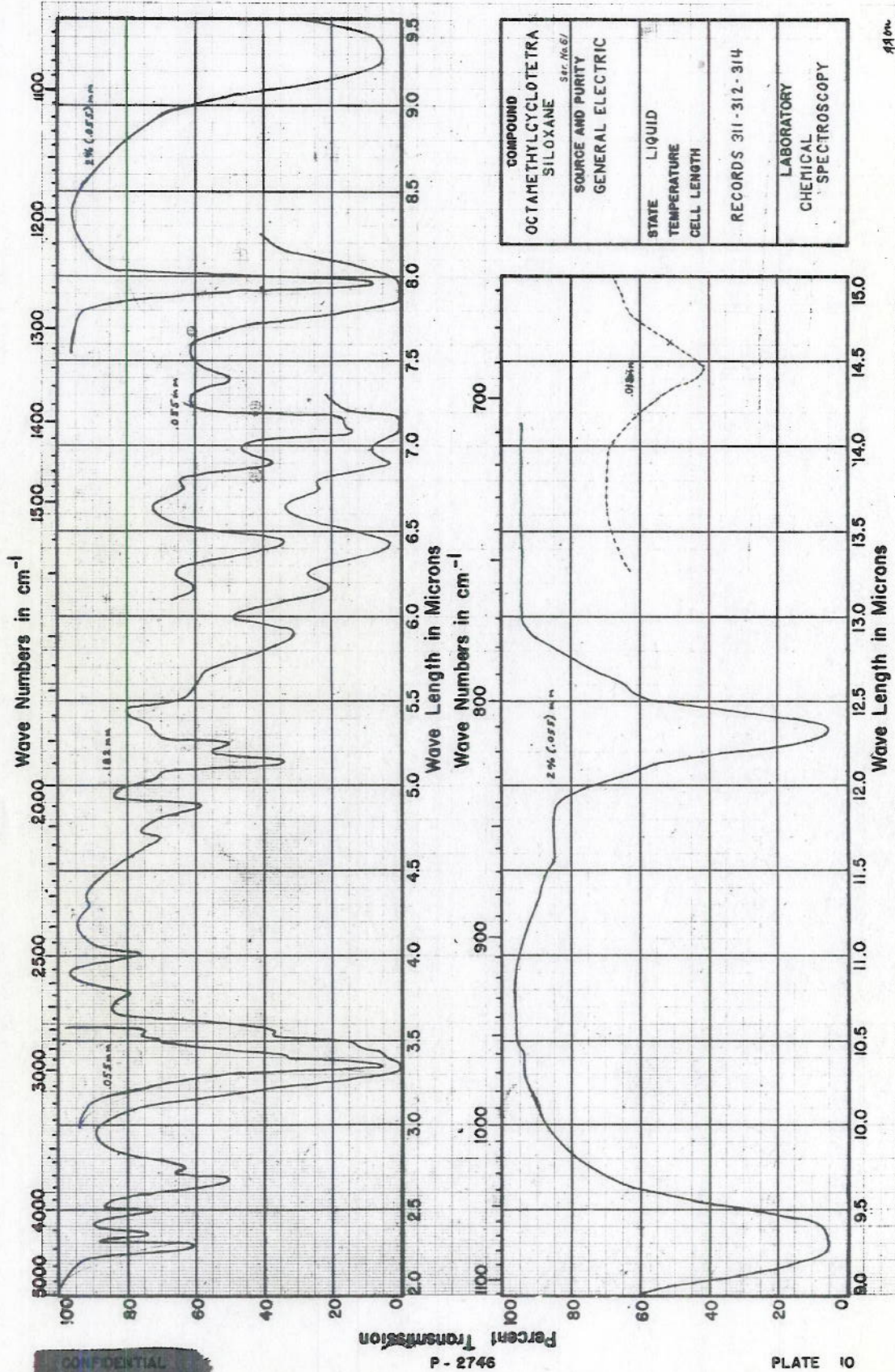
COMPOUND	HEXAMETHYLCYCLOTRISILOXANE
SOURCE AND PURITY	GENERAL ELECTRIC
STATE SOLID IN	CS_2 & CCl_4
TEMPERATURE	
CELL LENGTH	
RECORDS	328-329
LABORATORY	CHEMICAL SPECTROSCOPY

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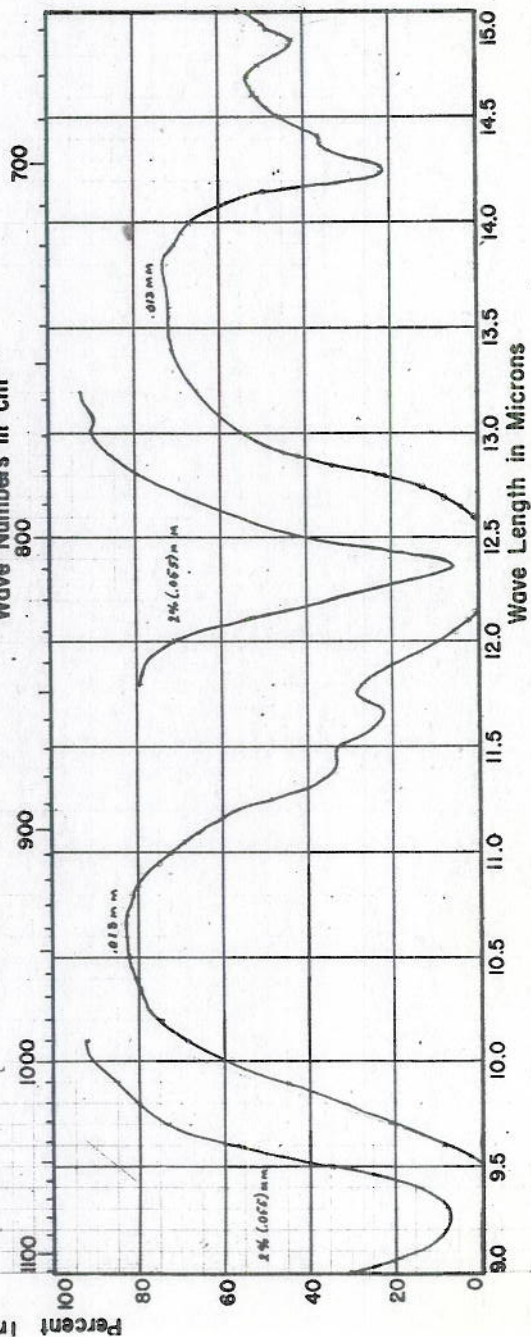
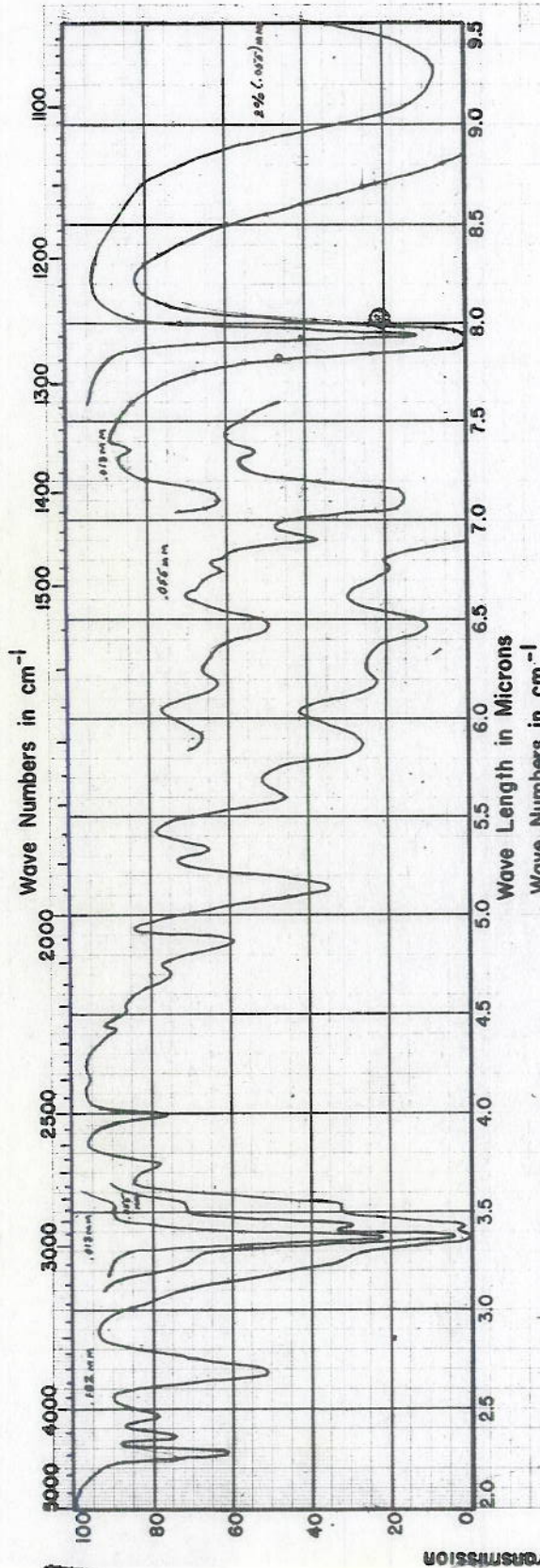
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PLATE 9

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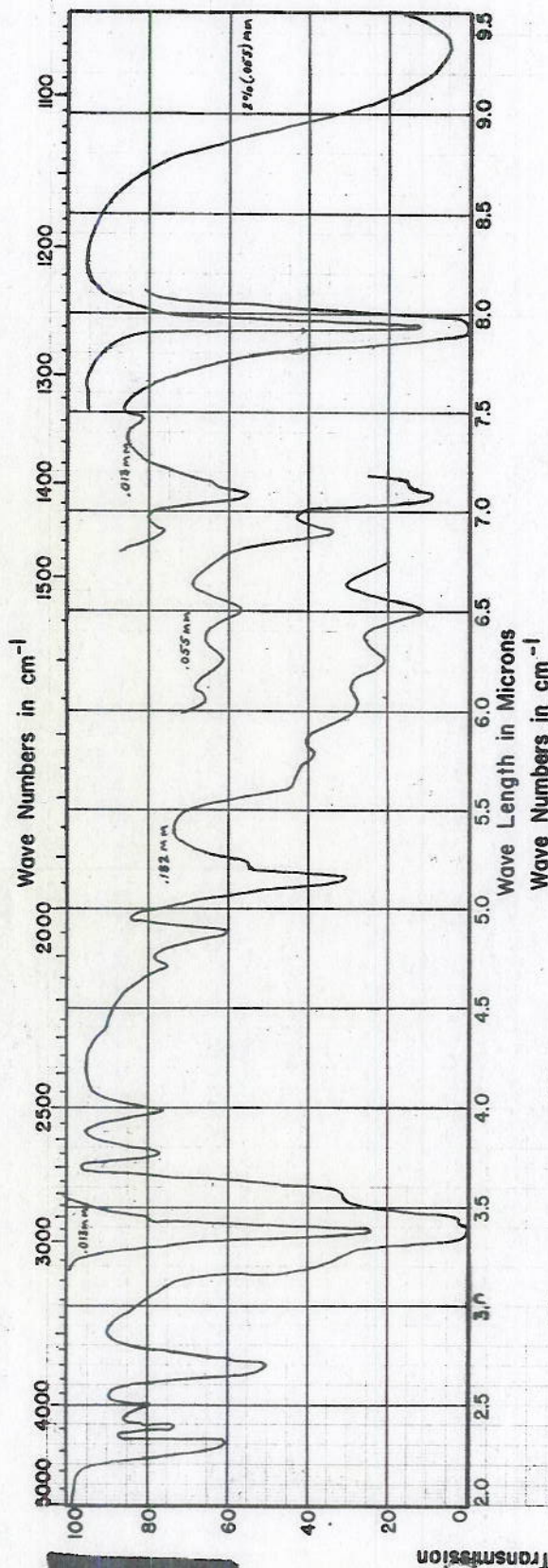
COMPOUND	DECAMETHYLCYCLOPENTASILOXANE
SOURCE AND PURITY	Gen. No. 62
GENERAL ELECTRIC	
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	322-323
LABORATORY	CHEMICAL SPECTROSCOPY

88 m

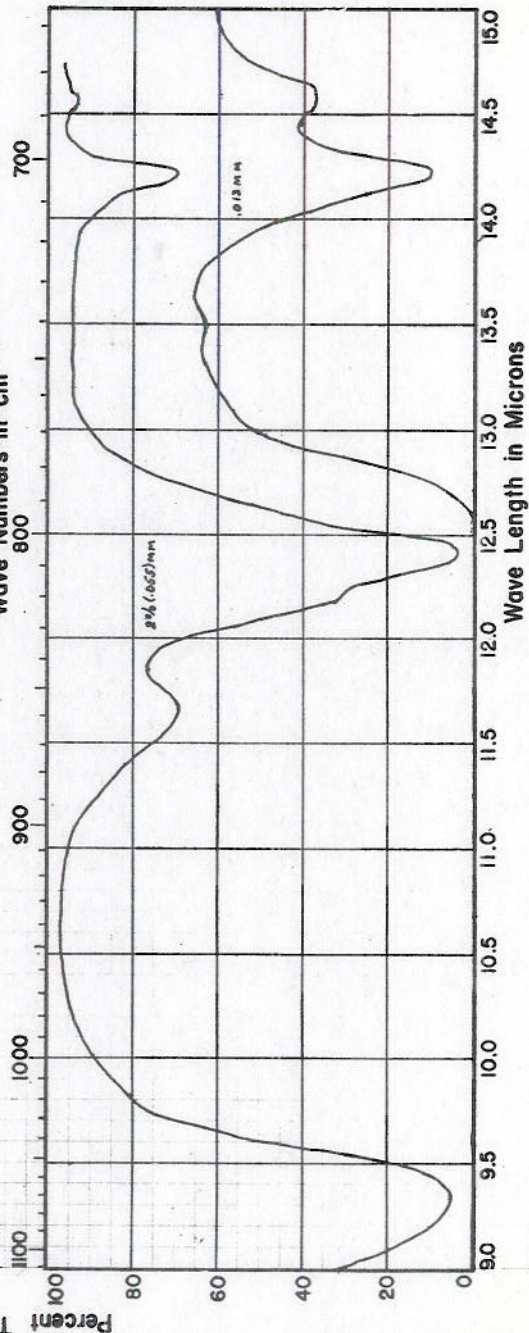
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PLATE II

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COMPOUND	DODECAMETHYLCYCLOHEXASILOXANE
SOURCE AND PURITY	Ser. No. 63
GENERAL ELECTRIC	
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORD	324
LABORATORY	CHEMICAL SPECTROSCOPY

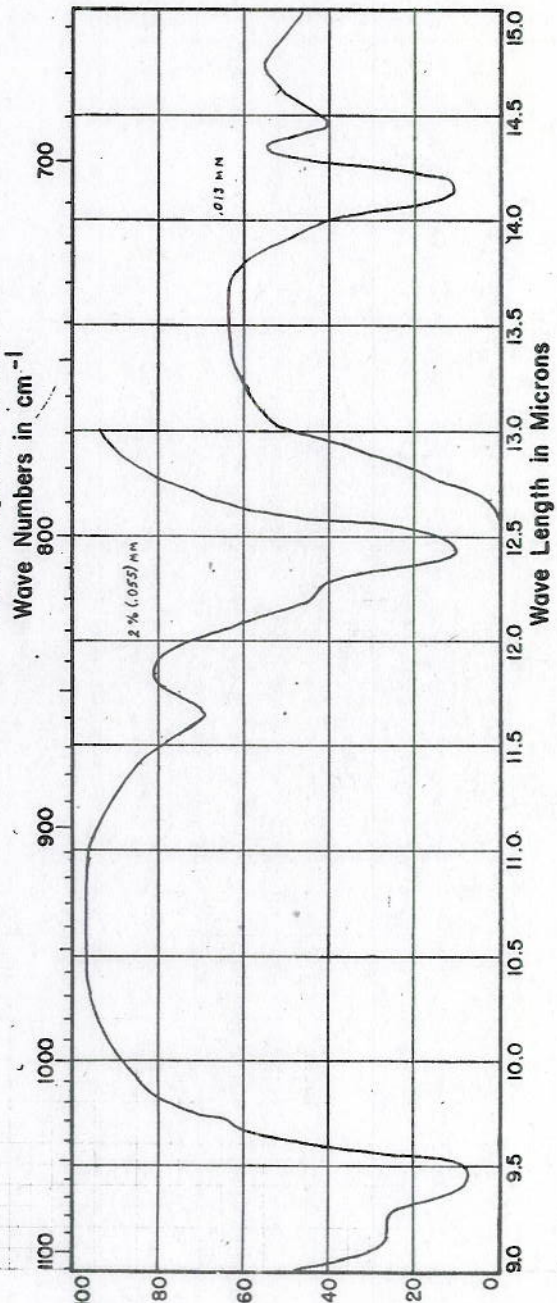
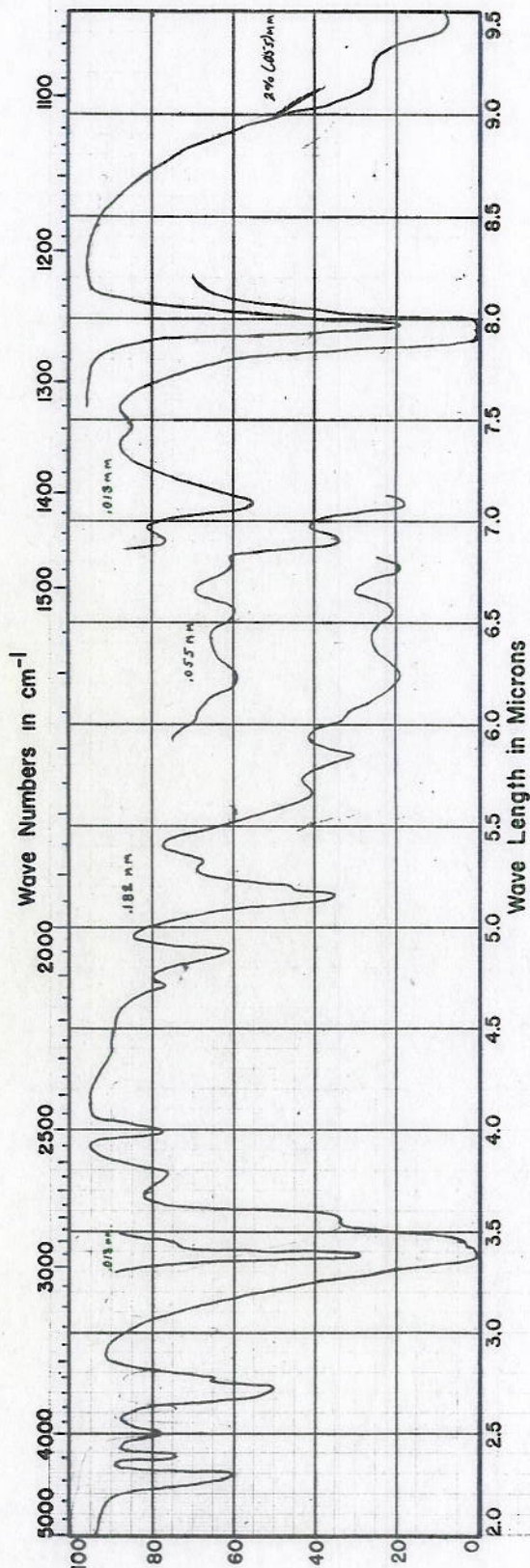


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PLATE 19



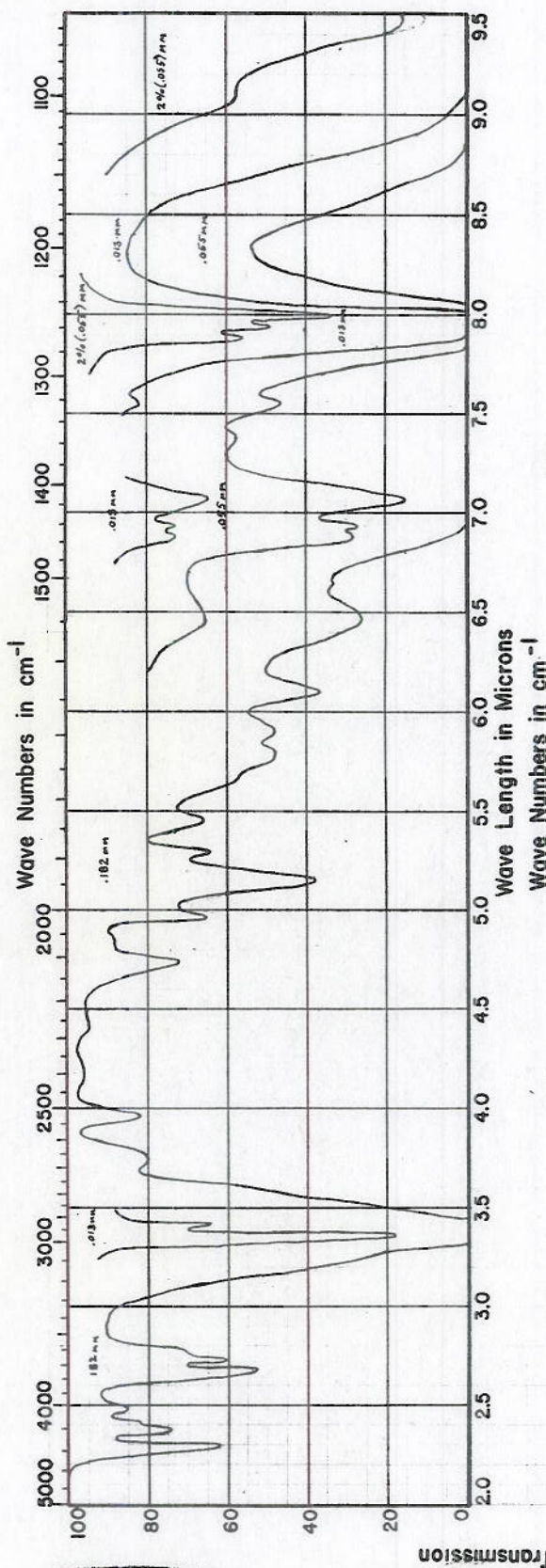
COMPOUND	TETRADECAMETHYLCYCLO HEPTASILOXANE Ser. No. 64
SOURCE AND PURITY	GENERAL ELECTRIC
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	325-326
LABORATORY	CHEMICAL
SPECTROSCOPY	

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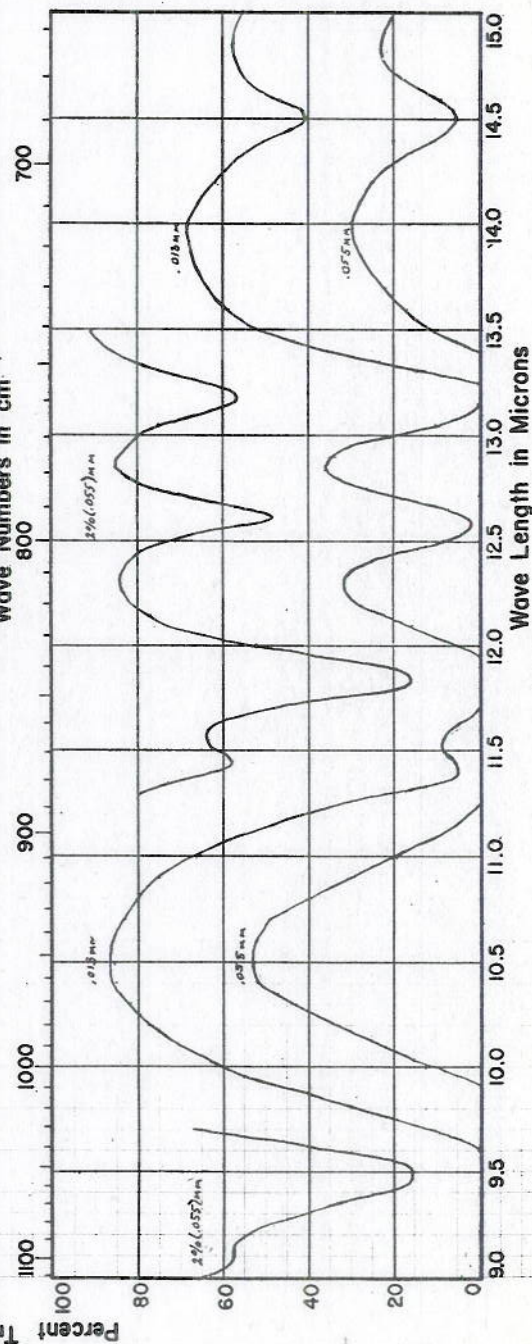
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PLATE 13

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COMPOUND	DECAMETHYLISOTETRA-SILOXANE
SOURCE AND PURITY	85% #155 ECON CORNING
STATE	LIQUID
TEMPERATURE	-25°C
CELL LENGTH	
RECORDS	578,580,1582
LABORATORY	NAVAL RESEARCH LABORATORY

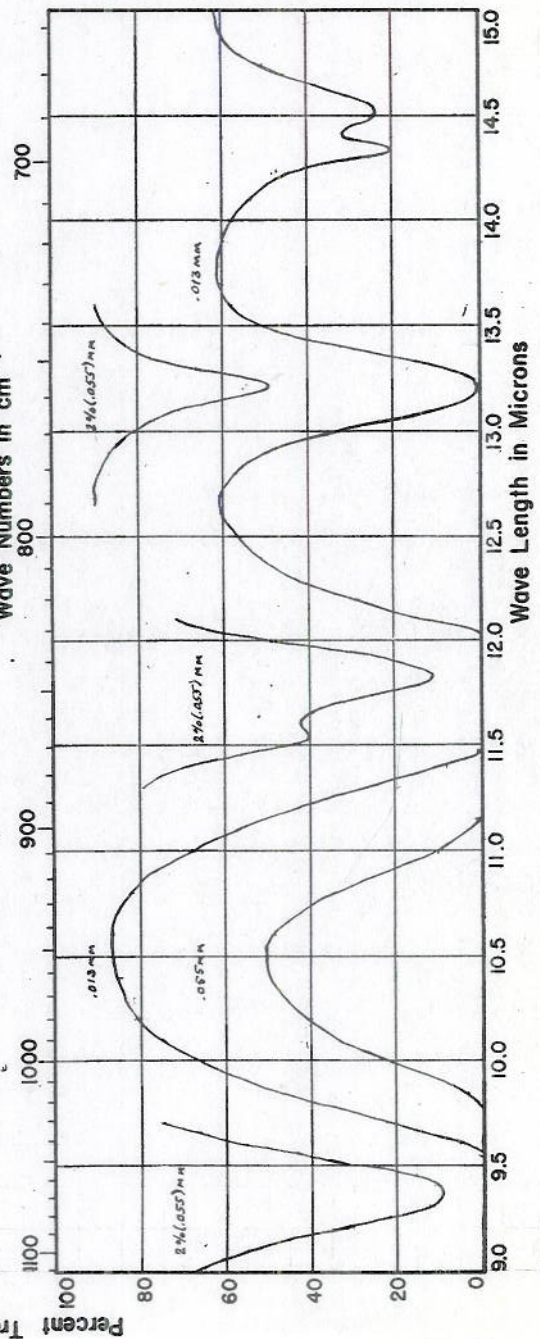
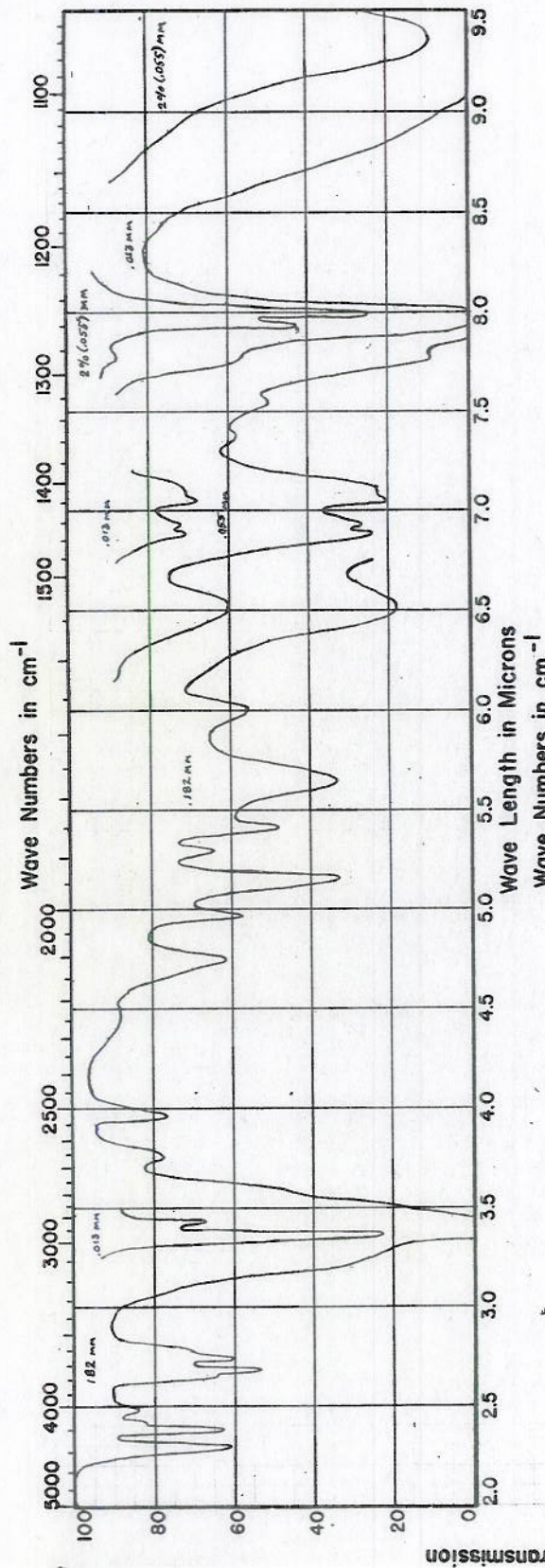


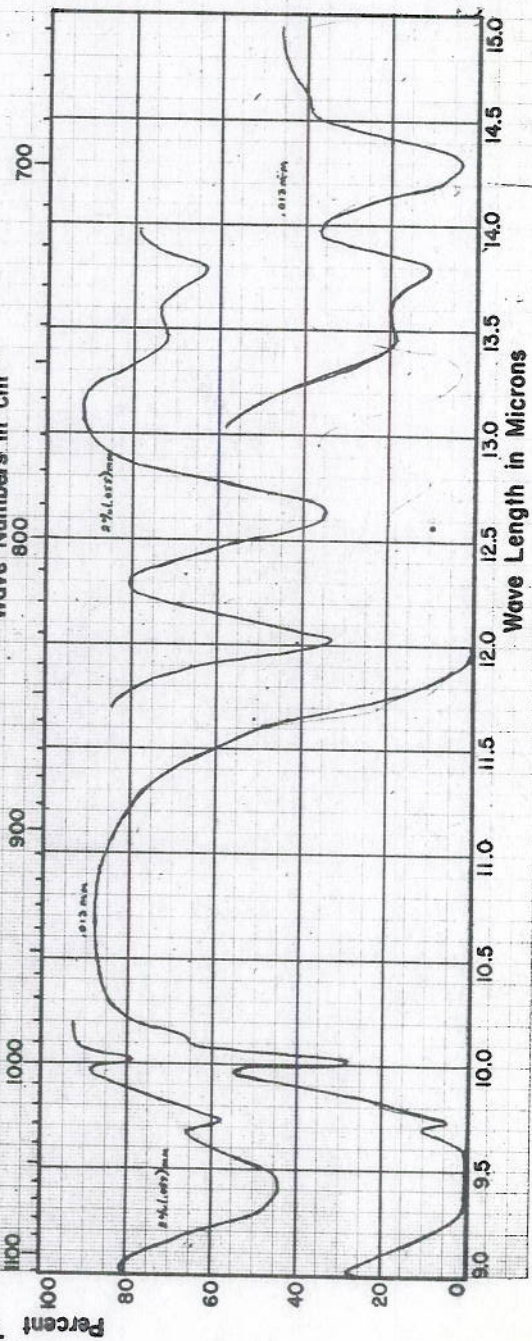
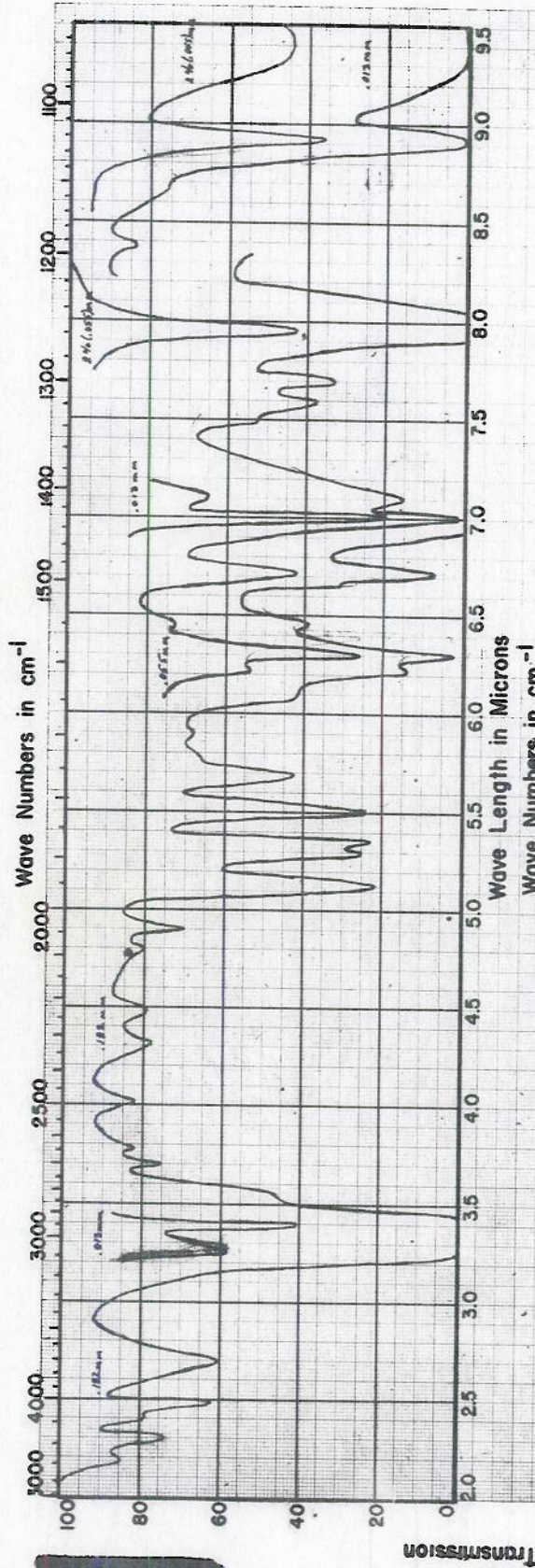
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PLATE 14

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COMPOUND	D.C. 700
HS 15	416-III-292
SOURCE AND PURITY	3.5 G.S.
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	468, 493
LABORATORY	
CHEMICAL	
SPECTROSCOPY	
NAVAL RESEARCH	

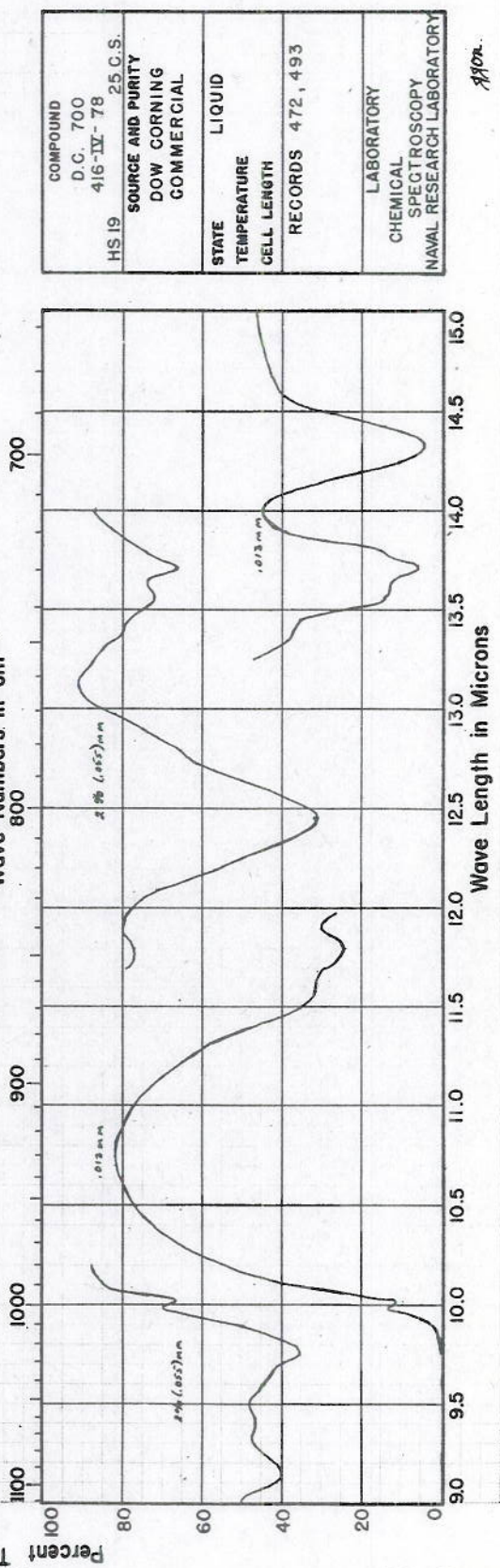
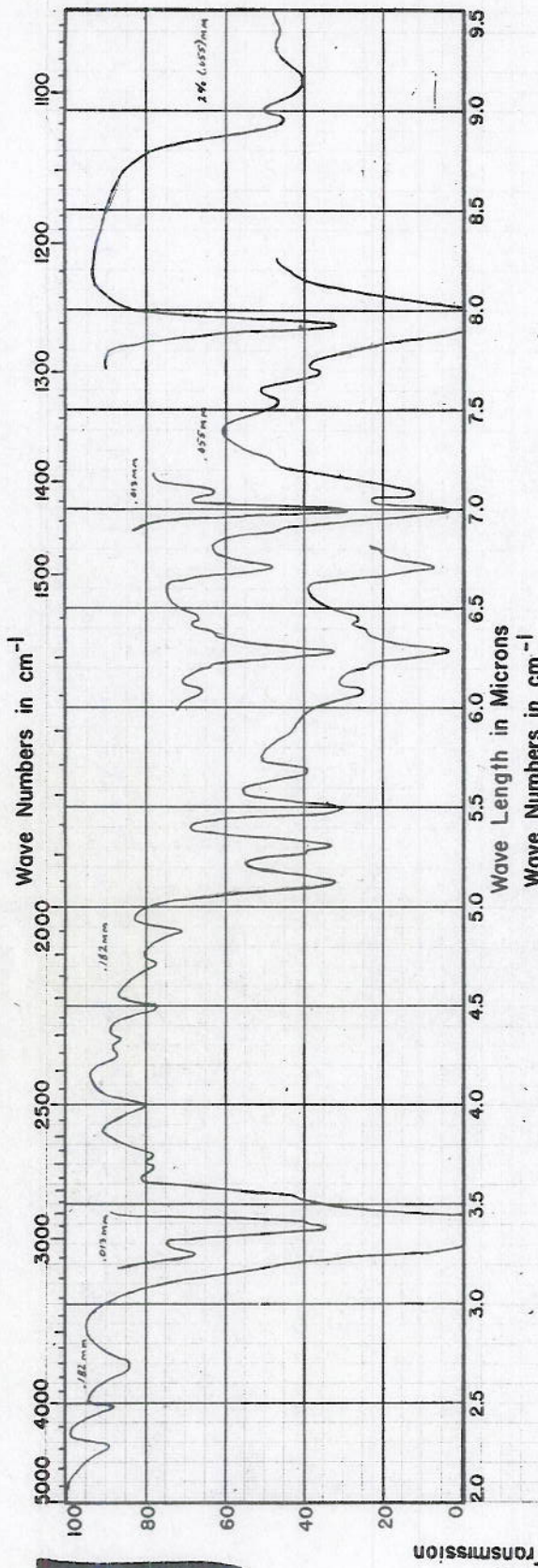
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PLATE 16

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COMPOUND	LIQUID
D.C. 700	TEMPERATURE
416-IV-78	CELL LENGTH
HS 19	RECORDS 472, 493
SOURCE AND PURITY	
DOW CORNING	
COMMERCIAL	
	LABORATORY
	CHEMICAL
	SPECTROSCOPY
	NAVAL RESEARCH LABORATORY

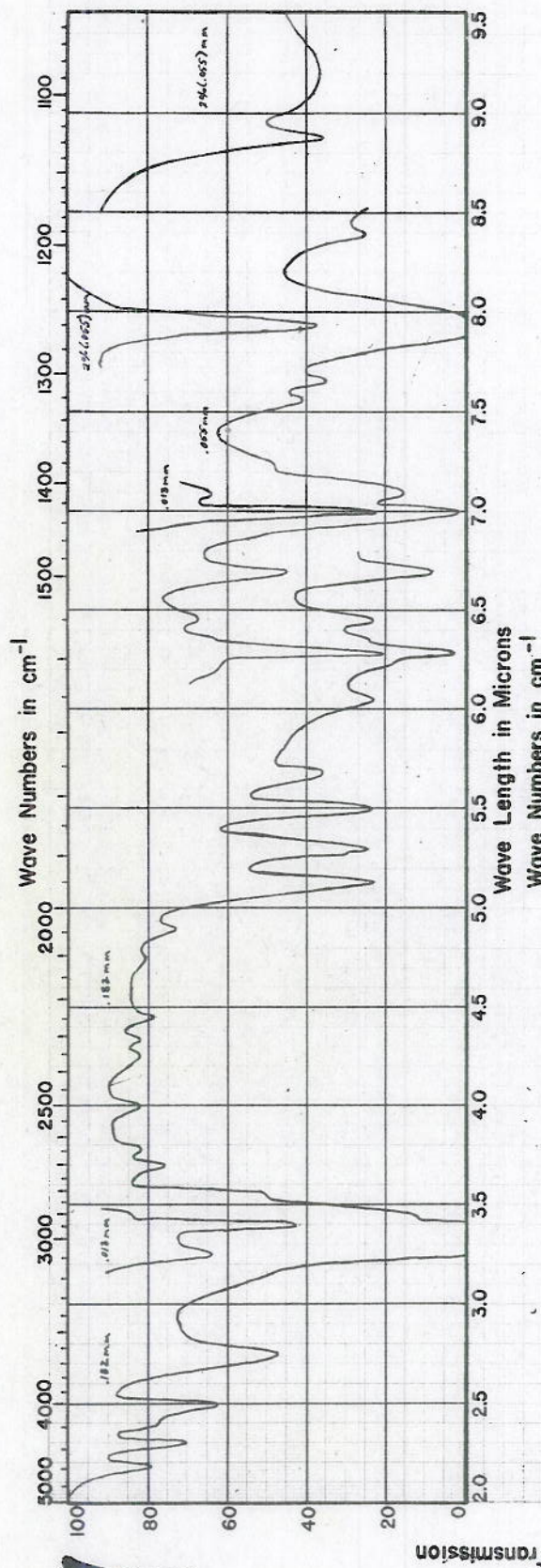
8102

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PLATE 17

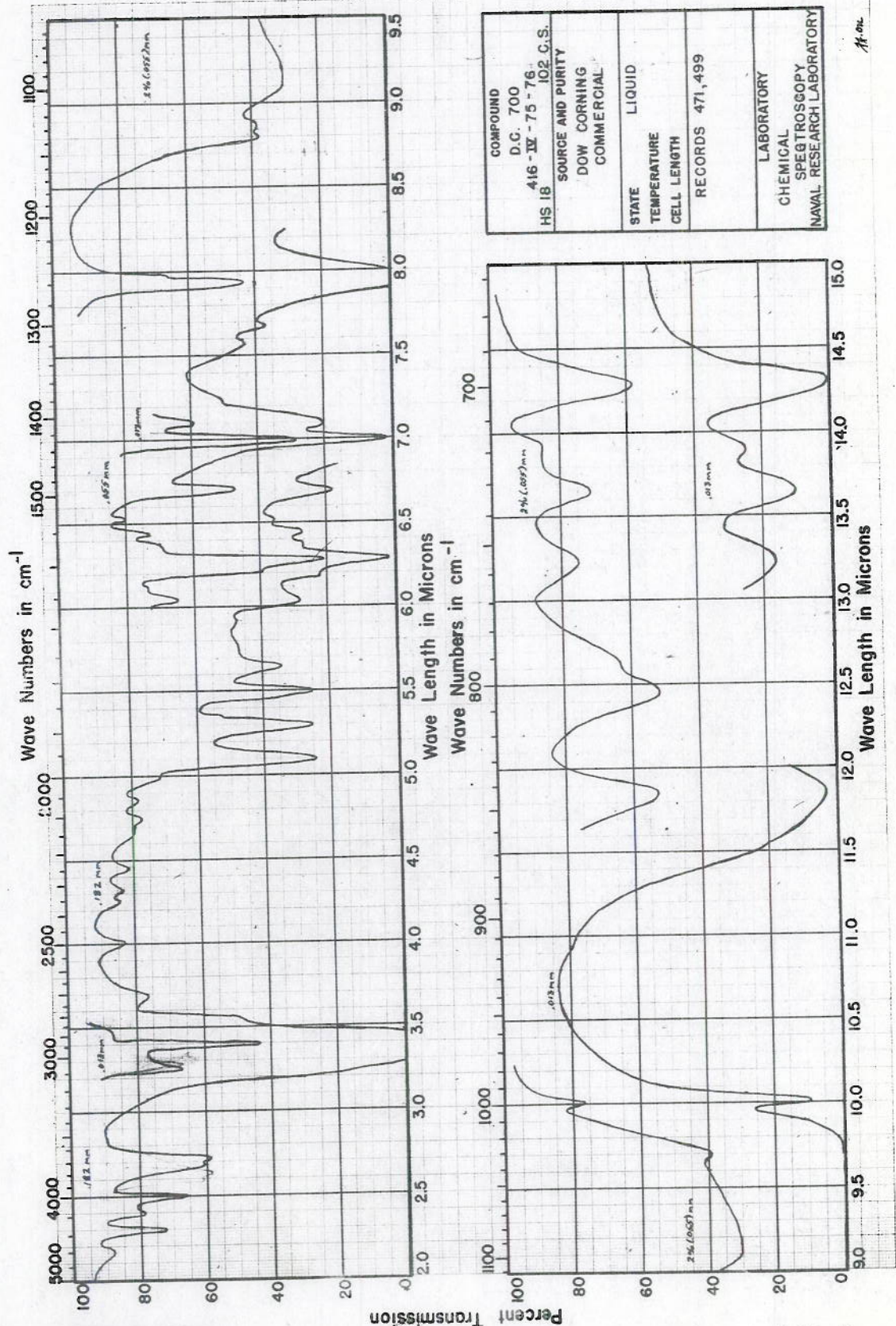
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PLATE 18

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COMPOUND	D.C. 700
HS 18	416 - IV - 75 - 76
	102 C.S.
SOURCE AND PURITY	DOW CORNING COMMERCIAL
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	471,499
LABORATORY	CHEMICAL SPECTROSCOPY NAVAL RESEARCH LABORATORY

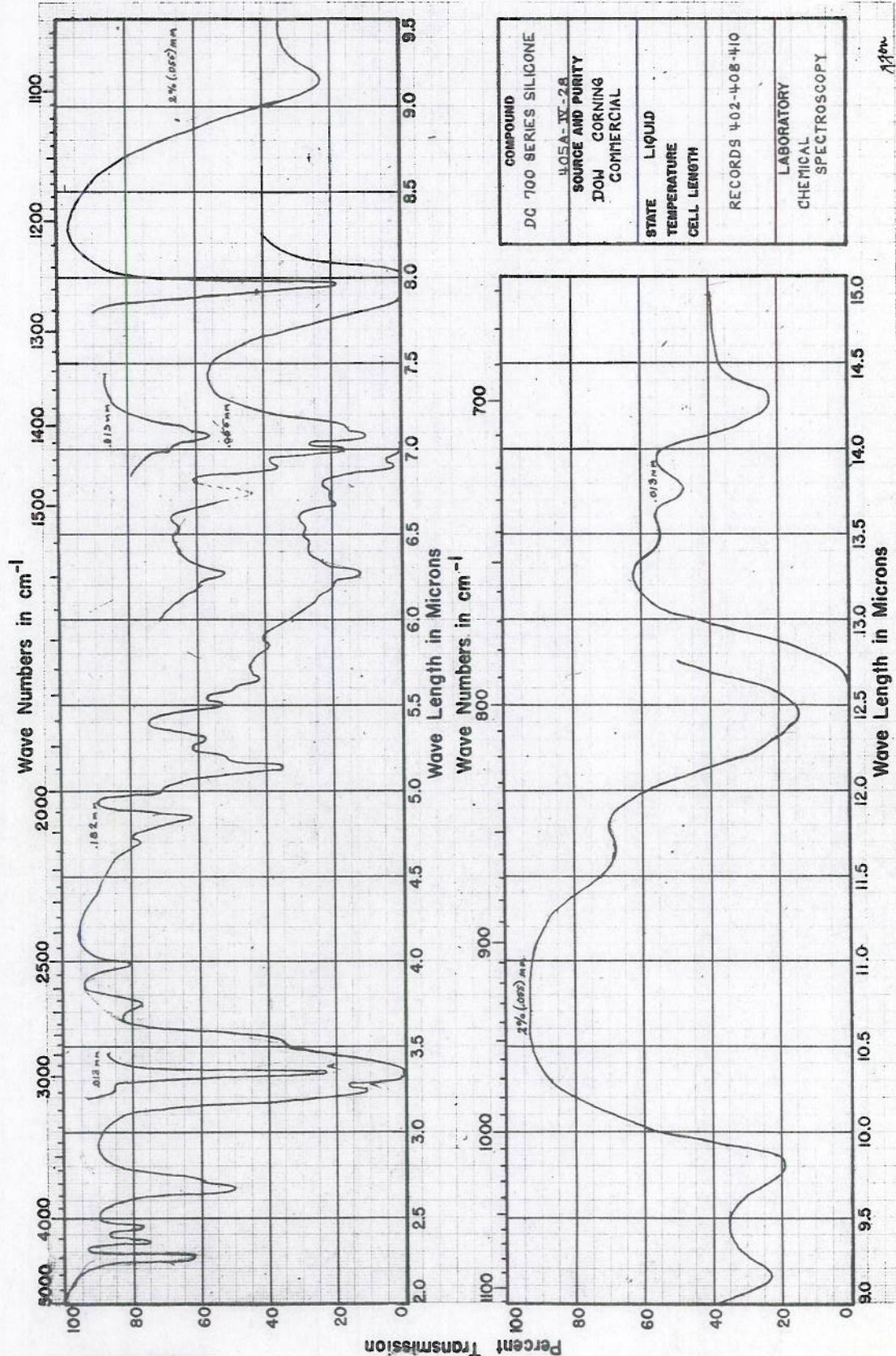
11-01

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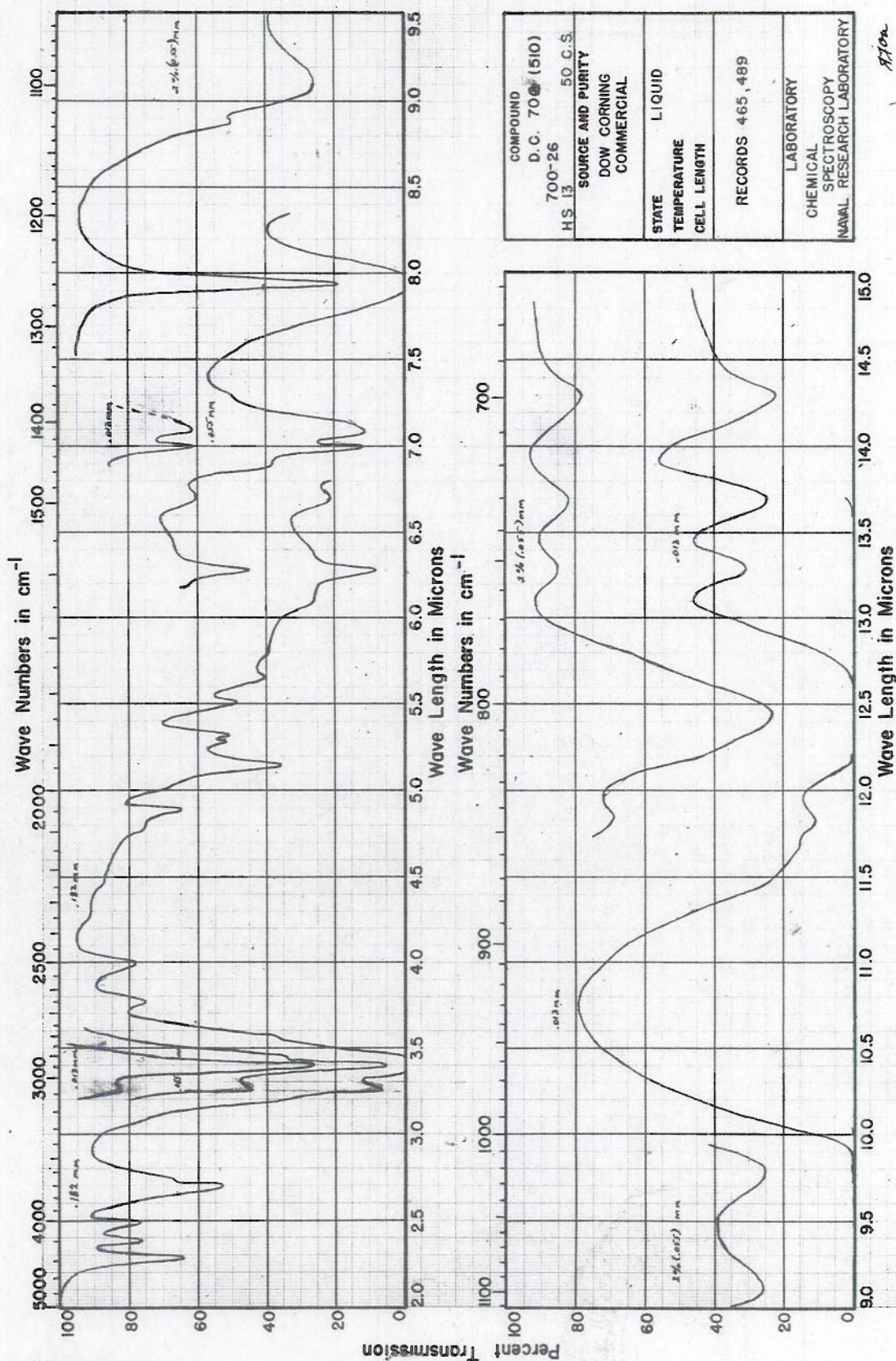
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PLATE 19

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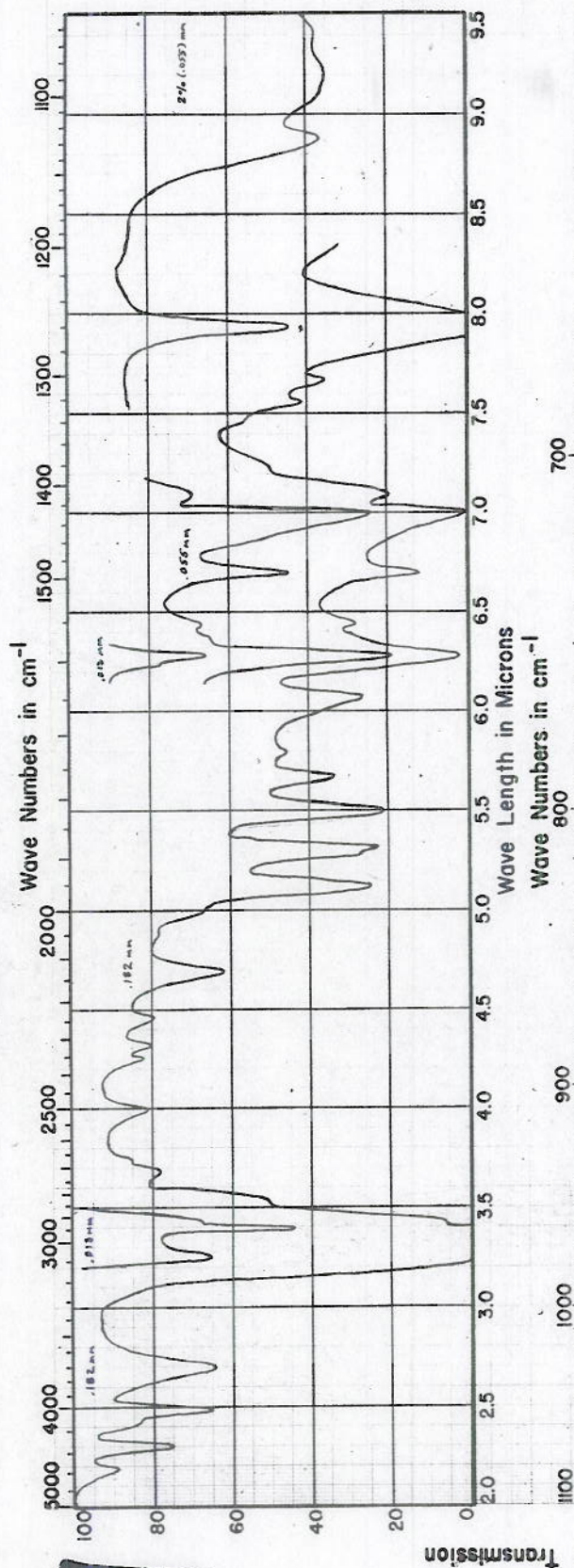
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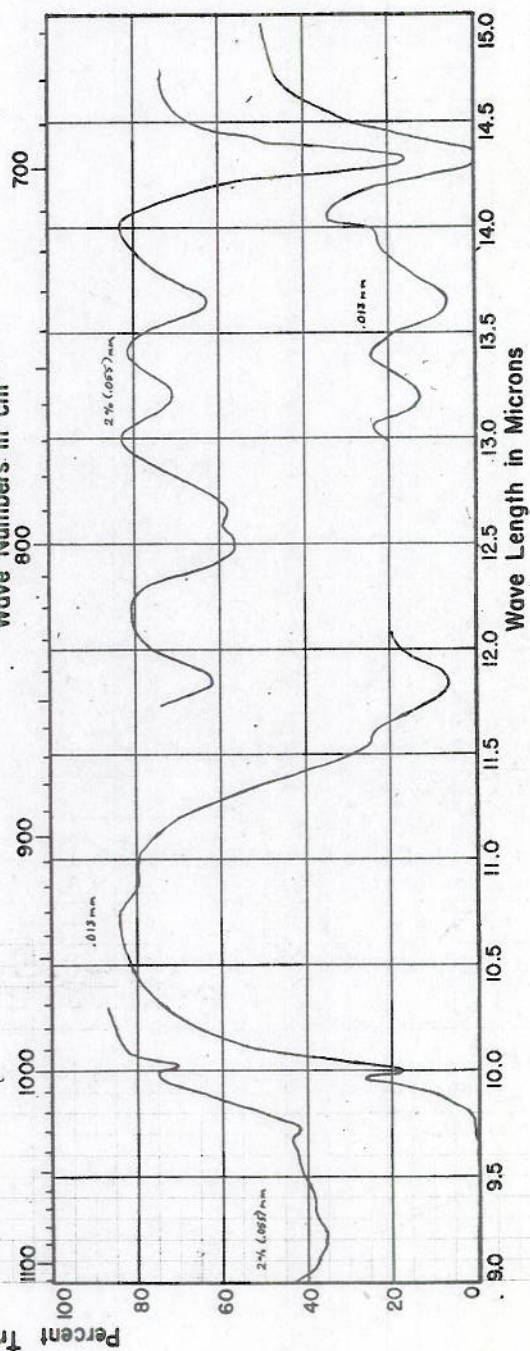
COMPOUND	D.C. 700 (510)
700-26	HS 13
SOURCE AND PURITY	DOW CORNING COMMERCIAL
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	465,489
LABORATORY	CHEMICAL SPECTROSCOPY NAVAL RESEARCH LABORATORY

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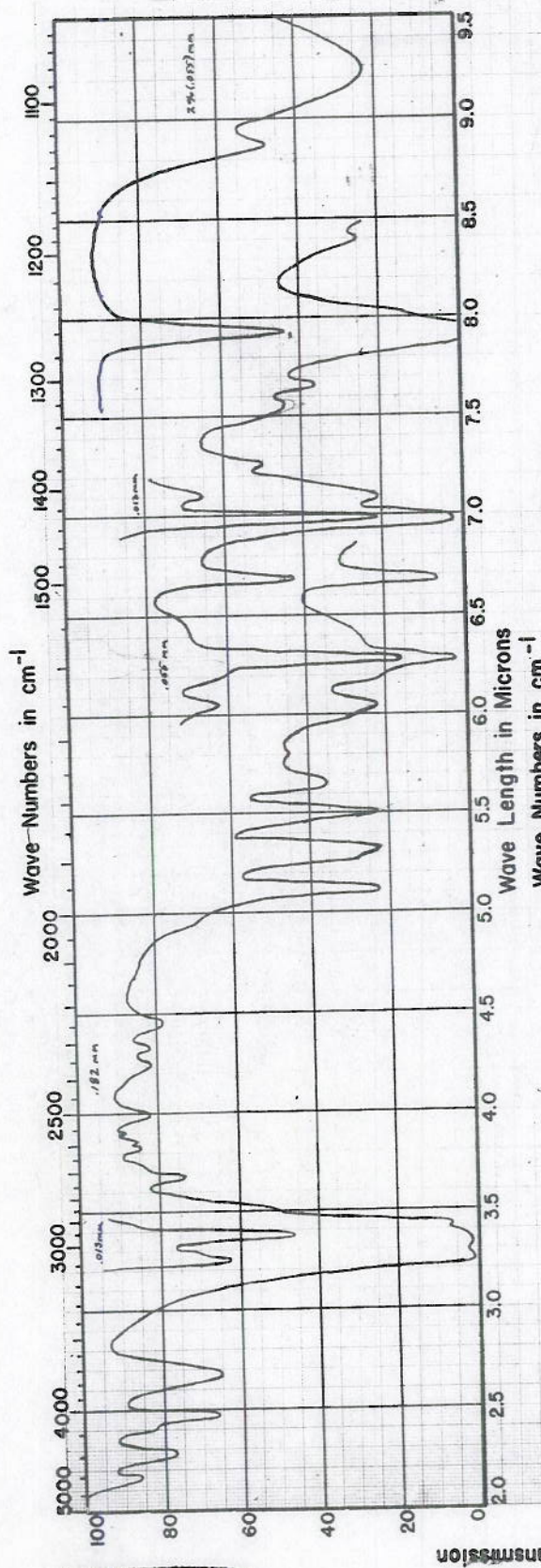
COMPOUND	D.C. 700 (550)
HSIS	405A-IV-30
SOURCE AND PURITY	100 C.S.
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	RECORDS 469, 486,
LABORATORY	
CHEMICAL SPECTROSCOPY	
NAVAL RESEARCH LABORATORY	



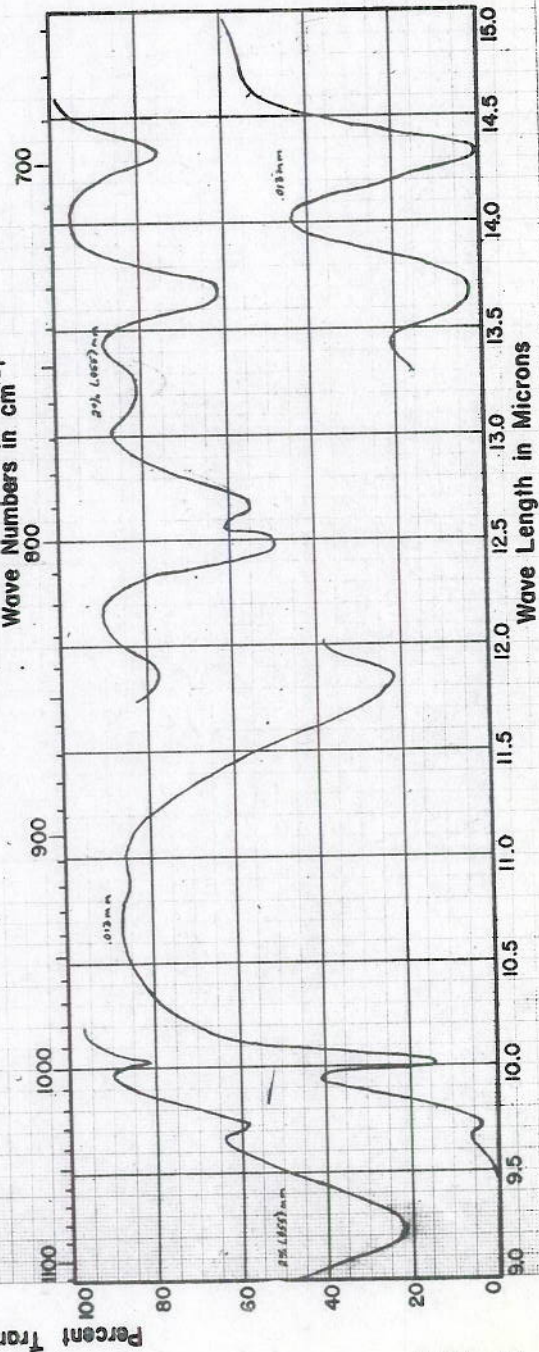
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PLATE 22

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COMPOUND D.C. 702 408A-III-33	SOURCE AND PURITY DOW CORNING COMMERCIAL	STATE LIQUID	TEMPERATURE CELL LENGTH RECORDS 463, 486	LABORATORY CHEMICAL SPECTROSCOPY NAVAL RESEARCH LABORATORY
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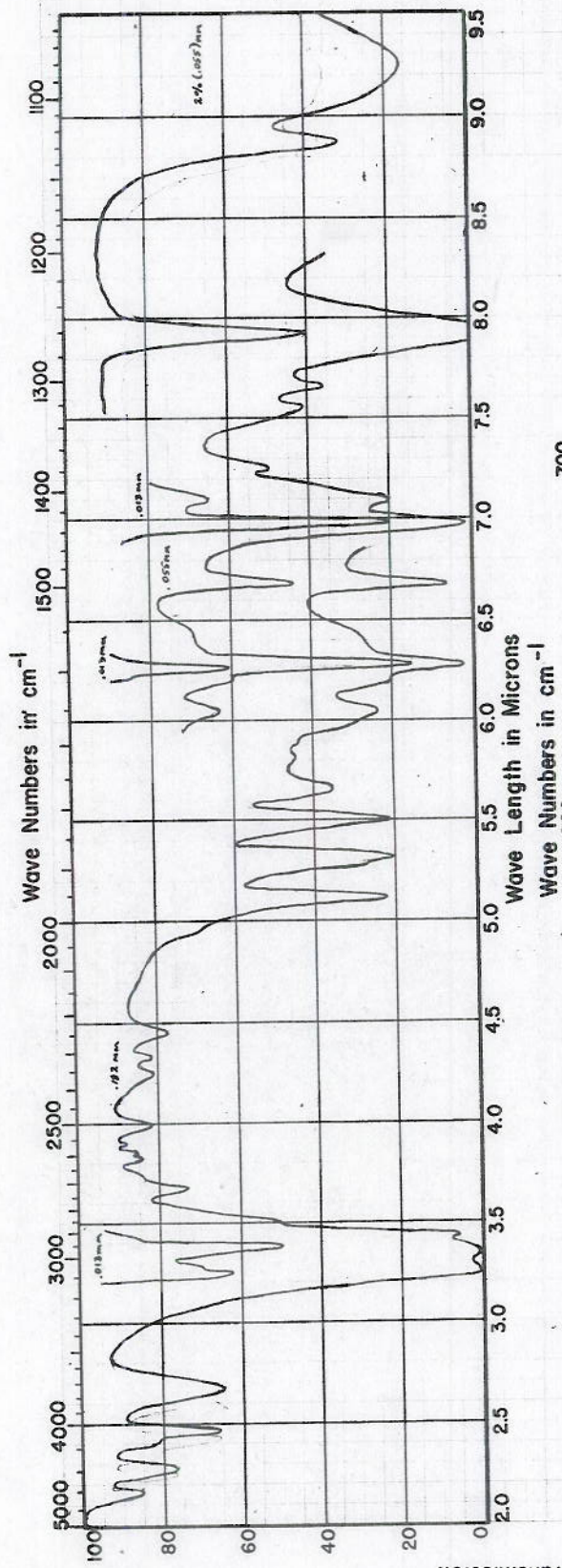


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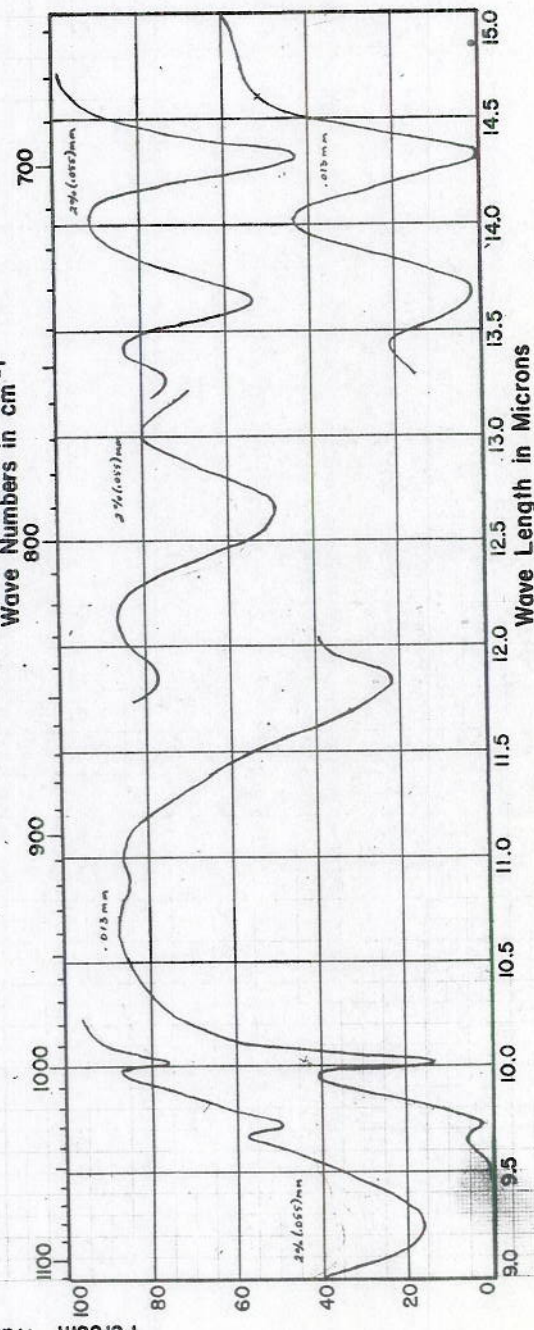
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PLATE 23

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COMPOUND	D.C. 703
HS 12	408A-III-44
SOURCE AND PURITY	DOW CORNING COMMERCIAL
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	RECORDS 464, 486
LABORATORY	CHEMICAL SPECTROSCOPY NAVAL RESEARCH LABORATORY

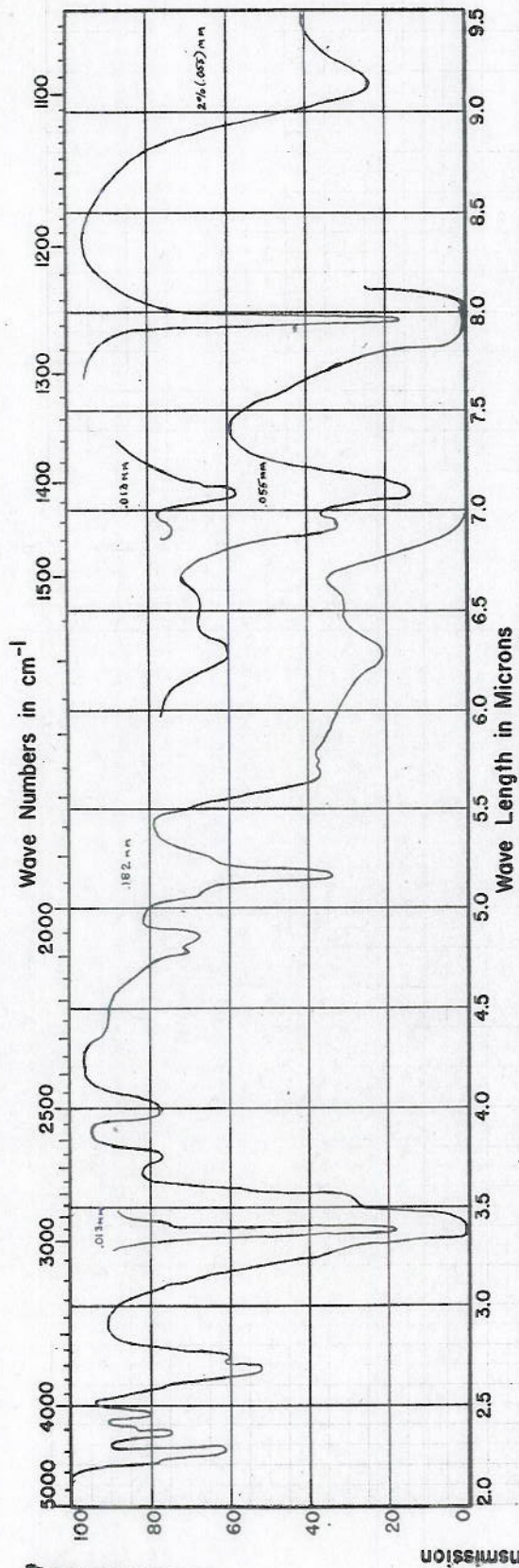


2902

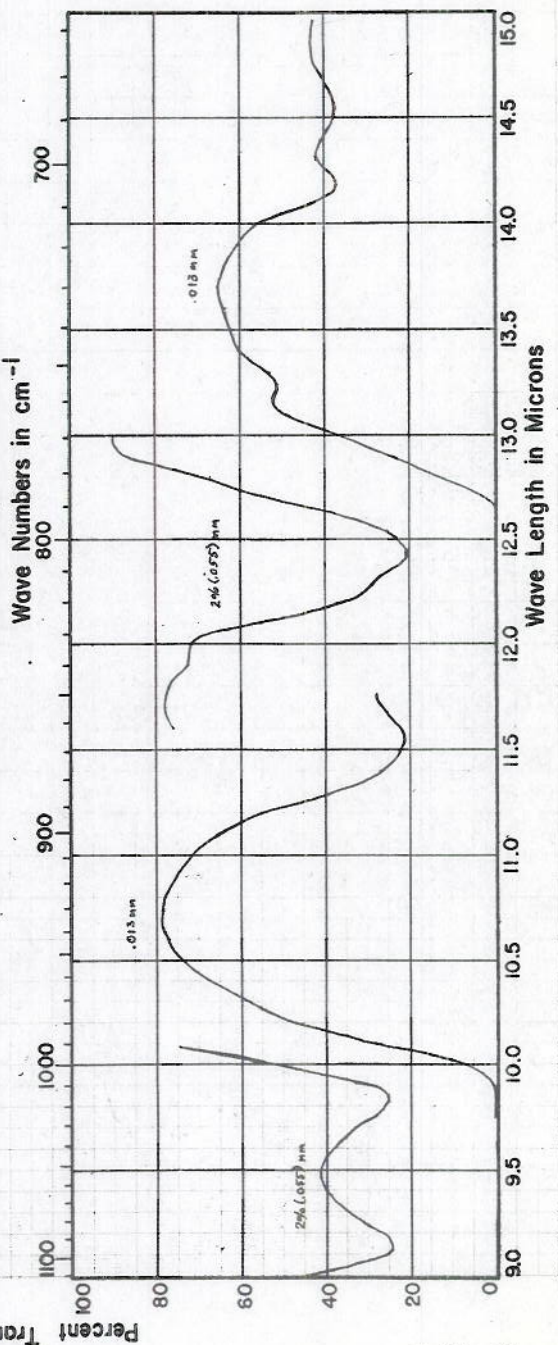
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PLATE 24

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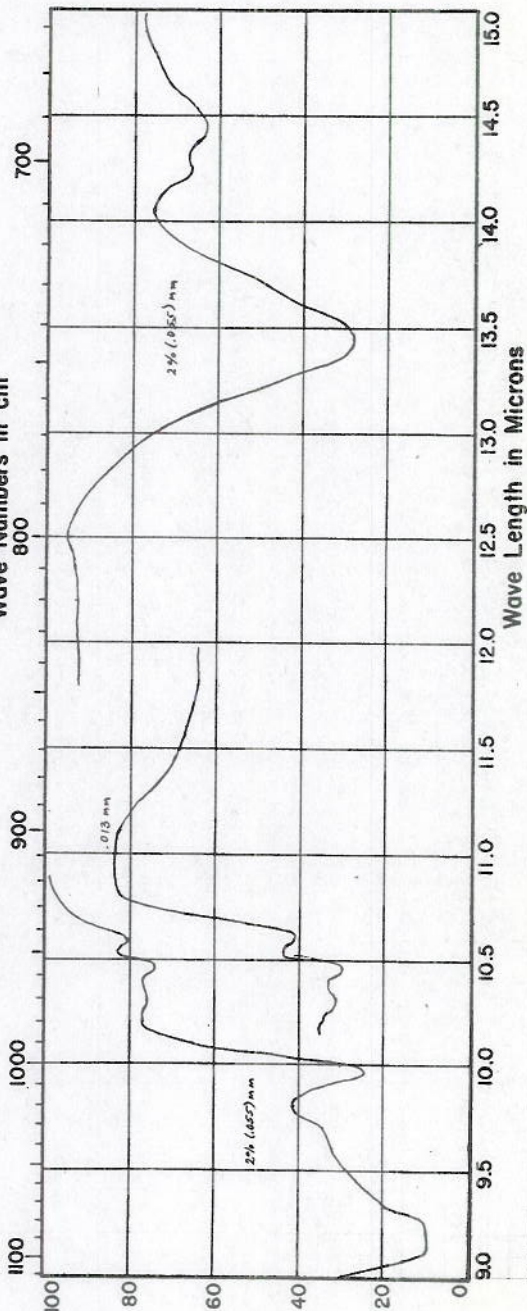
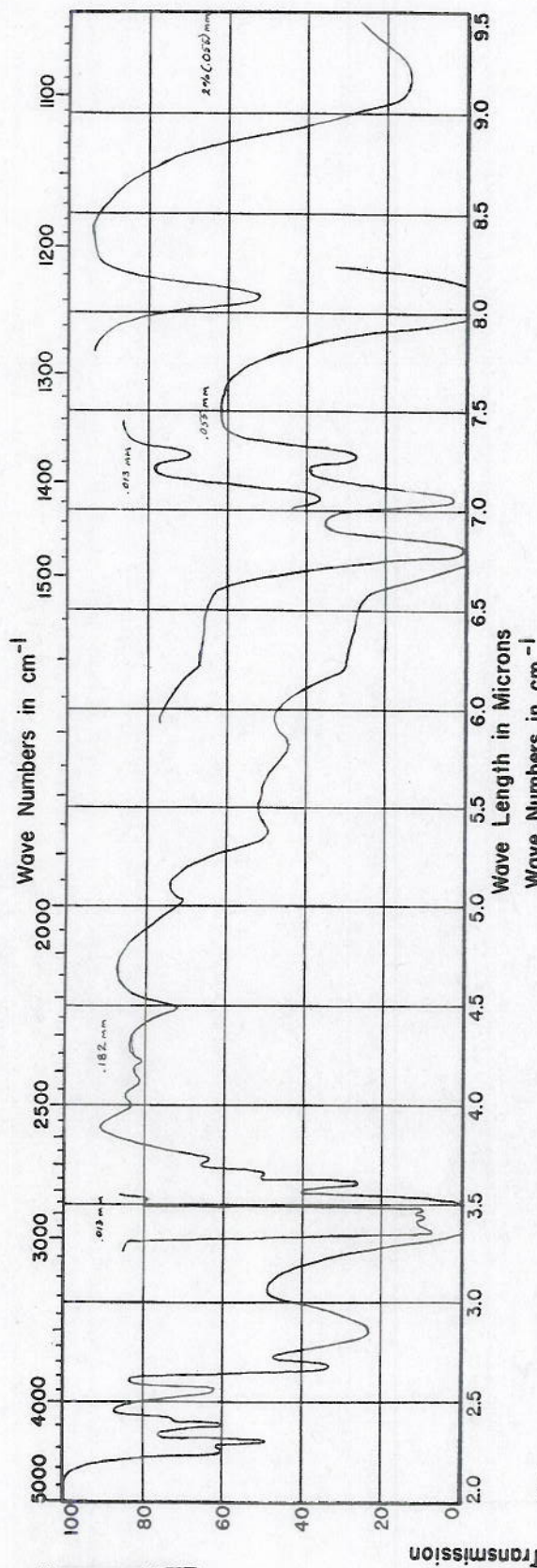
COMPOUND	DC 500 SERIES SILICONE
SOURCE AND PURITY	36.8-62-63
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	393 & 398
LABORATORY	
CHEMICAL SPECTROSCOPY	



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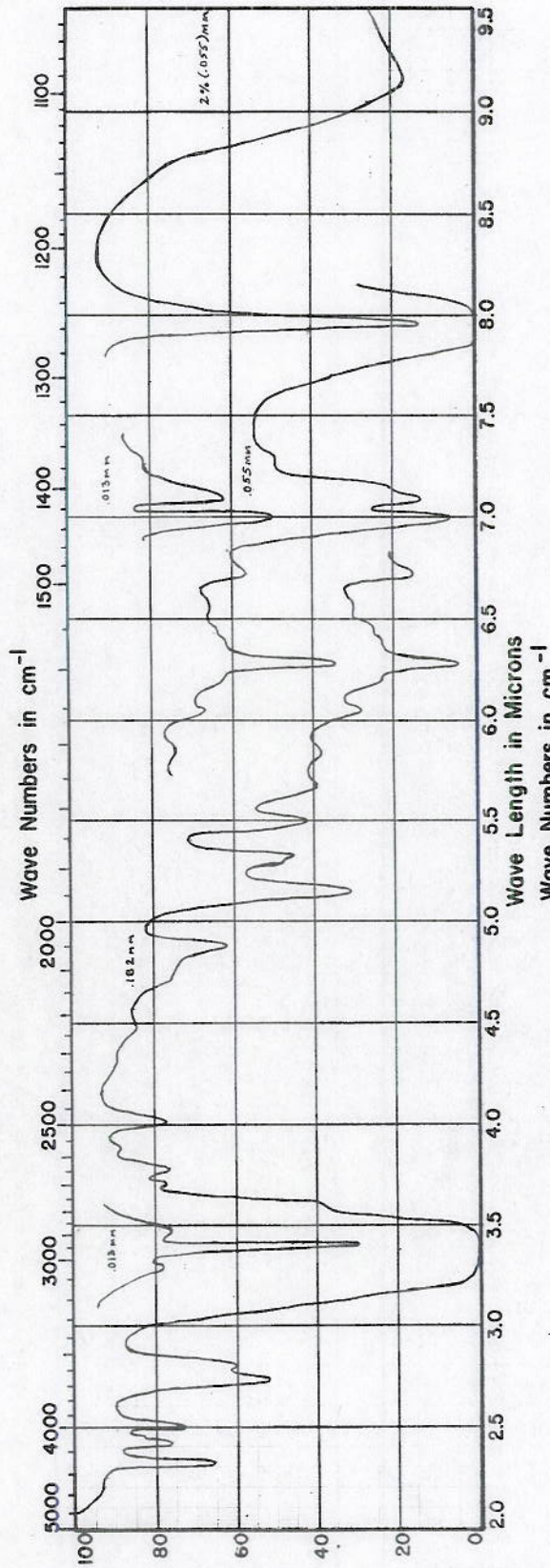
PLATE 25

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COMPOUND	DC 400 SERIES SILICONE
SOURCE AND PURITY	405A-2-54
STATE	LIQUID
TEMPERATURE	DOW CORNING
CELL LENGTH	COMMERCIAL
RECORDS	409-410
LABORATORY	
CHEMICAL SPECTROSCOPY	

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COMPOUND	G.E. A-249 SILICONE FLUID
SOURCE AND PURITY	GENERAL ELECTRIC COMMERCIAL
STATE	LIQUID
TEMPERATURE	
CELL LENGTH	
RECORDS	401-407-410
LABORATORY	CHEMICAL SPECTROSCOPY

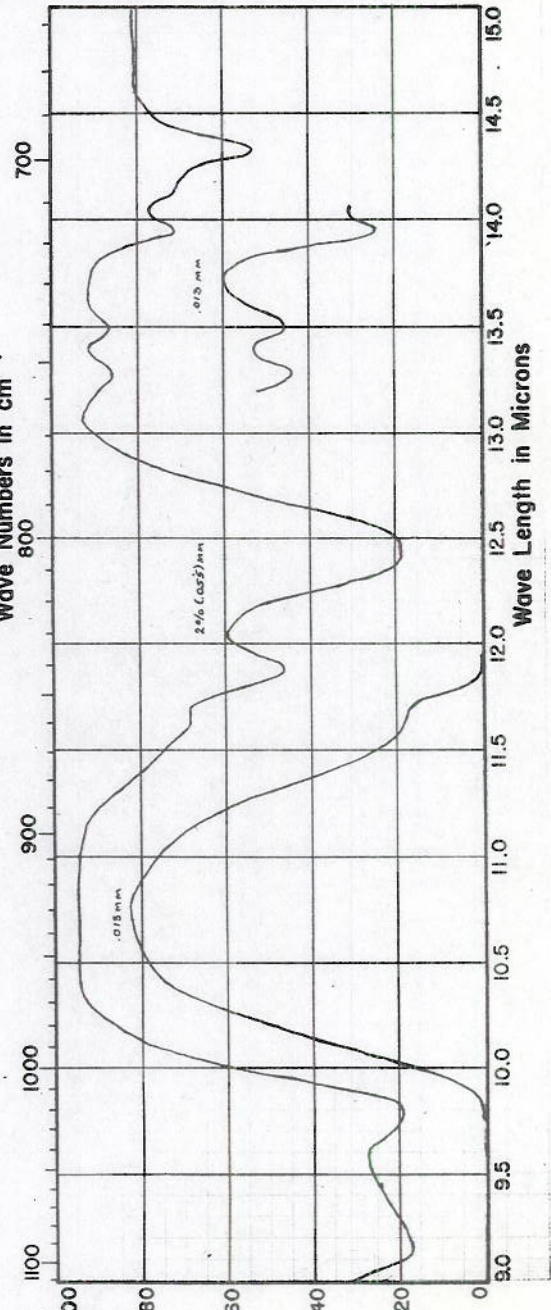


PLATE 27

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