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BUREAU OF ENGINEERING

FR-1391

Report on

Use of Infra-red Absorption Data for Showing Presence of Unsaturates and Aromatic Components in Aviation Gasoline.

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- BuC&R. (2)

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ABSTRACT

It has been found that by examination of the near infra-red absorption spectrum of a gasoline information can be obtained regarding the atomic groups present. In particular, the presence of unsaturates and aromatics can be ascertained, although the sensitivity of the test in detecting very small concentrations of di-iso-butylene in iso-octane is not great. This limitation of the method is offset by the fact that it is capable of determining the presence of additions such as aromatics which would defeat the purpose of present chemical tests. The method is proposed as a supplement to chemical investigations of the molecular structure and stability of gasoline.

I. INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Aeronautics letter Aer-E-46-MN JJ7G1 of 30 September 1936.

(b) Statement of Problem

2. Part of the problem as stated in the letter of authorization is to study the stability of aviation fuel blends. NRL Report No. P-1360 discusses the "acid heat" of aviation gasolines. In the report P1360, it is shown that the presence of aromatic hydrocarbons tend to neutralize the effect due to the presence of unsaturated hydrocarbons.

(c) Known Facts Bearing on the Problem

3. The application of infra-red and Raman spectroscopy to investigations of molecular structure is well established (1). A recent compendium of Raman frequencies of organic compounds has been made by Hibben (2), and Barnes (3) has given a survey of the emperical rules underlying the application of infra-red spectroscopy to the determination of structure of complex organic molecules. The infra-red spectra of the principal types of compounds present in gasoline have been measured by Kettering and Sleator (4) who worked with pure compounds in the vapor phase.

4. The present investigation was proposed to supplement chemical data dealing with stability and gum forming properties of gasolines. Accordingly, its general purpose was the detection and identification of unsaturates in the gasoline.

II. SUMMARY OF RESULTS

5. It has been found possible to identify linkages of the type X = X and to distinguish between C = C and C = O linkages by inspection of the infra-red absorption spectrum of a compound.

6. A limitation of the method is in the quantitative investigation of the concentration of unsaturates. It has been found that 1% di-iso-butylene in iso-octane can just be detected by its effect upon the infra-red absorption, while this concentration gives a very positive reaction in chemical tests. On the other hand, addition of aromatics, which vitiates the chemical tests, produces a pronounced effect upon the infra-red absorption spectrum.

7. The method, therefore, offers definite value as a research tool for the determination of molecular structure types, which may be difficult chemically, and as a supplement to the current chemical specification test for the presence of unsaturates.

III. EXPERIMENTAL METHOD

8. The compounds have been investigated in the liquid state in order that the effect of gums and other non-volatile components might not be overlooked. Organic liquids absorb very strongly so that thin cells (0.01 cm - 0.03 cm) were required. It has been found that the type of cell described by

Barnes (5) fitted with rock salt windows is entirely satisfactory. The spectrometer was equipped with a rock salt prism and a Pfund type vacuum thermo-couple. Slit widths were kept as narrow as permitted good galvanometer deflections and ranged from a maximum effective width of about 250 cm^{-1} at 1.5 μ to about 9 cm^{-1} at 10μ, depending upon the dispersion of the rock salt prism.

9. The usual procedure was followed in obtaining transmission curves. The galvanometer deflection with the cell in the path of the radiation from the Nernst lamp was compared at each wave-length to the deflection with the cell removed. The ratio was plotted as percent transmission against wave-length.

10. Readings were made at intervals of 0.1μ, the positions of maxima of absorption being rechecked to 0.05μ.

IV. CHARACTERISTIC SPECTRA OF HYDROCARBONS

11. Plate 1 shows the infra-red absorption spectra of cyclo-hexene and normal heptane and is introduced to show the remarkable similarity in the absorption spectra of compounds having similar groups of atoms. Where the origin of a given band is clear it has been designated on the Plate. The band at 3.45μ, for example, arises from vibration of a carbon relative to a hydrogen atom. Normal heptane, containing no double bonds, does not show an absorption band in the 6μ region, whereas cyclo-hexene shows two, one at 5.3μ and a stronger band at 6.1μ. These may both be due to the C=C bond, the double frequency arising from the equality of the masses attached to the two carbon atoms involved in the vibration.

12. In the 7μ region cyclo-hexene shows a single band arising from deformation of the CH_2 group, while heptane, having both CH_2 and CH_3 groups, gives two bands, at 6.8μ and 7.2μ.

13. The remainder of the spectral interval from 8 to 10μ is occupied by bands resulting from X-X bonds. These may all be caused by C-C bands, or some of the weak bands may well be overtones of strong bands at longer wave-lengths. This region of the spectrum is consequently more difficult of interpretation than that lying at shorter wave-lengths, but fortunately for the purpose at hand, the double and triple bond vibrations lie between 4μ and 6.5μ and can usually be readily identified.

V. QUANTITATIVE DETERMINATION OF UNSATURATES

14. The importance of test methods for the detection of unsaturates in gasoline and the limitations of the present "acid heat" method have been discussed in Naval Research Laboratory Report No. P-1360 (7). In that report it is pointed out that unsatisfactory gasolines may pass the present test and that the addition of aromatics to an unsaturated gasoline may vitiate the acid heat test by masking the temperature rise which normally takes place when acid is added to an unsaturated gasoline.

15. It was anticipated, therefore, that the method of infra-red spectroscopy might prove of some practical use as a supplement to the acid heat test because it possesses the advantage that whatever information it is capable of giving cannot be negated by the addition of aromatics.

On the contrary, the method affords a good test for the presence of aromatics since these compounds have absorption spectra readily distinguishable from the absorption spectra of aliphatic hydrocarbons. The success of the infra-red method as a complete substitute for the acid heat test depends accordingly upon its ability to detect concentrations of unsaturates comparable with those which given measurable reactions in the acid heat test.

16. Iso-octane and di-iso-butylene may be considered as typical saturated and unsaturated components of gasoline. The infra-red absorption spectra of these compounds over the wave length interval 1μ to 10μ are shown in Plate 2. The general similarity of the two curves is characteristic of the near infra-red spectra of similar organic compounds containing similar groups of atoms.

17. The most interesting part of the spectrum is the 6μ region in which more explicit identification of the bands is possible than at longer wave-lengths. It is observed that iso-octane has a shallow absorption band at 6μ. A shallow band at this location seems to be characteristic of saturated branch chain compounds, although it falls in the spectral region usually occupied by bands due to X = X bonding. This shallow band is readily distinguishable from the sharp absorption band at 6.2μ in di-iso-butylene which is definitely due to vibration of the C = C group. It is probable that the weaker band at 5.6μ is also due to the C = C bond, although it is more probably an overtone of a strong band at longer wave-length.

18. In order to determine the smallest concentration of unsaturates in iso-octane detectable by observations on the C = C absorption at 6.2μ, absorption coefficients of 1%, 10% and 20% di-iso-butylene in iso-octane were measured in the 6μ region. These were obtained by the usual method of comparing the intensities of light transmitted by two absorption cells of different thickness. The absorption coefficient, α , is then given by the relation

$$\frac{I_2}{I_1} = e^{\alpha(t_1 - t_2)}$$

where I_2, I_1, and t_2, t_1, are the intensities of transmitted light and thickness of cell, respectively, for cells 1 and 2.

19. The results are shown in Plate 3 in which not the actual absorption coefficient but $\log \frac{I_2}{I_1}$ is plotted against wave-length.

20. It is clear that 1% di-iso-butylene in iso-octane produces a measurable increase in absorption over pure iso-octane, but it is also obvious that given a gasoline of unknown constituency it would be difficult to determine what part of the absorption in the 6μ region was due to undesirable unsaturates and what part due to pure iso-octane or other saturated branch chain compounds because of the general similarity in shape of the absorption bands representing different concentrations of unsaturates and that due to pure iso-octane.

21. It has been established that the acid heat test is highly sensitive to concentrations of 1% di-iso-butylene in iso-octane, but that addition of 15% aromatics to a gasoline containing unsaturates may conceal the presence of

the unsaturates because of the temperature rise resulting from the reaction of the acid used in the test with the aromatics.

22. The infra-red absorption spectrum of such a mixture, however, is radically different in the 6μ region from that of a gasoline containing no unsaturates. Plate 4 shows the absorption spectra in the 6μ region of pure iso-octane (curve a) and 1% di-iso-butylene in iso-octane (curve b). Curve c is the absorption spectrum from 1μ to 10μ of a mixture containing 1% di-iso-butylene, 15% mixed aromatics, and 84% iso-octane. Each curve is drawn to a different set of ordinates in order to avoid over-lapping. It is clear that there is little difference between curves (a) and (b). The bands at 5.2μ, 5.6μ, and 6.2μ in curve (c) are due to the presence of aromatics, the last arising from vibration of C=C bonds. The band at 6μ in curves (a) and (b) is somewhat sharper than the iso-octane absorption band in the 6μ region of Plate 1. This difference is probably experimental in nature.

23. Inspection of such absorption spectra as those shown in Plate 4 is perhaps the most convenient method of determining whether a gasoline having a high acid heat value contains double bonds in its aliphatic components or in aromatic components which have been added for the purpose of concealing the presence of unstable double bonds.

VI. CONCLUSIONS AND RECOMMENDATIONS

24. The work reported here has been exploratory. It has established possibilities which warrant further investigation with the purpose of establishing more definitely the limitations which must be placed on quantitative measurements. To this end, it is proposed to determine the smallest concentrations of various oxidation products which can be detected and to compare the sensitivity of the method with that of chemical tests.

25. The anticipated addition of a KCL prism to the spectroscopic equipment will extend the range of measurements to 22μ, thus including the entire spectral range in which molecular vibration frequencies occur. This will facilitate the identification of structure in the molecule because the remarkable similarity of the spectra of different compounds which is observed at wave lengths less than 10μ does not obtain at longer wave lengths.

References

(1) See, for example, Schaeffer and Matossi, Das Ultrarote Spektrum, Lecompte, Le Spectre Infrarouge; Rawlins and Taylor, The Infra Red Spectrum;

(2) James H. Hibben, Chemical Reviews, 18, 1. (1936);

(3) R. Bowling Barnes, Rev. Sci. Inst. 7, 265 (1936);

(4) Kettering and Sleator, Physics, 4, 39, (1935); this research was instigated by General Motors;

(5) Barnes, Phys. Rev. 35, 1524 (1930);

(6) Schaeffer and Matossi, Op Cit. p. 268;

(7) Borgstrom & Rehbein, Acid Heat of Aviation Gasoline, NRL Report No. P-1360.

INFRA-RED ABSORPTION SPECTRA OF CYCLO-HEXENE AND N HEPTANE

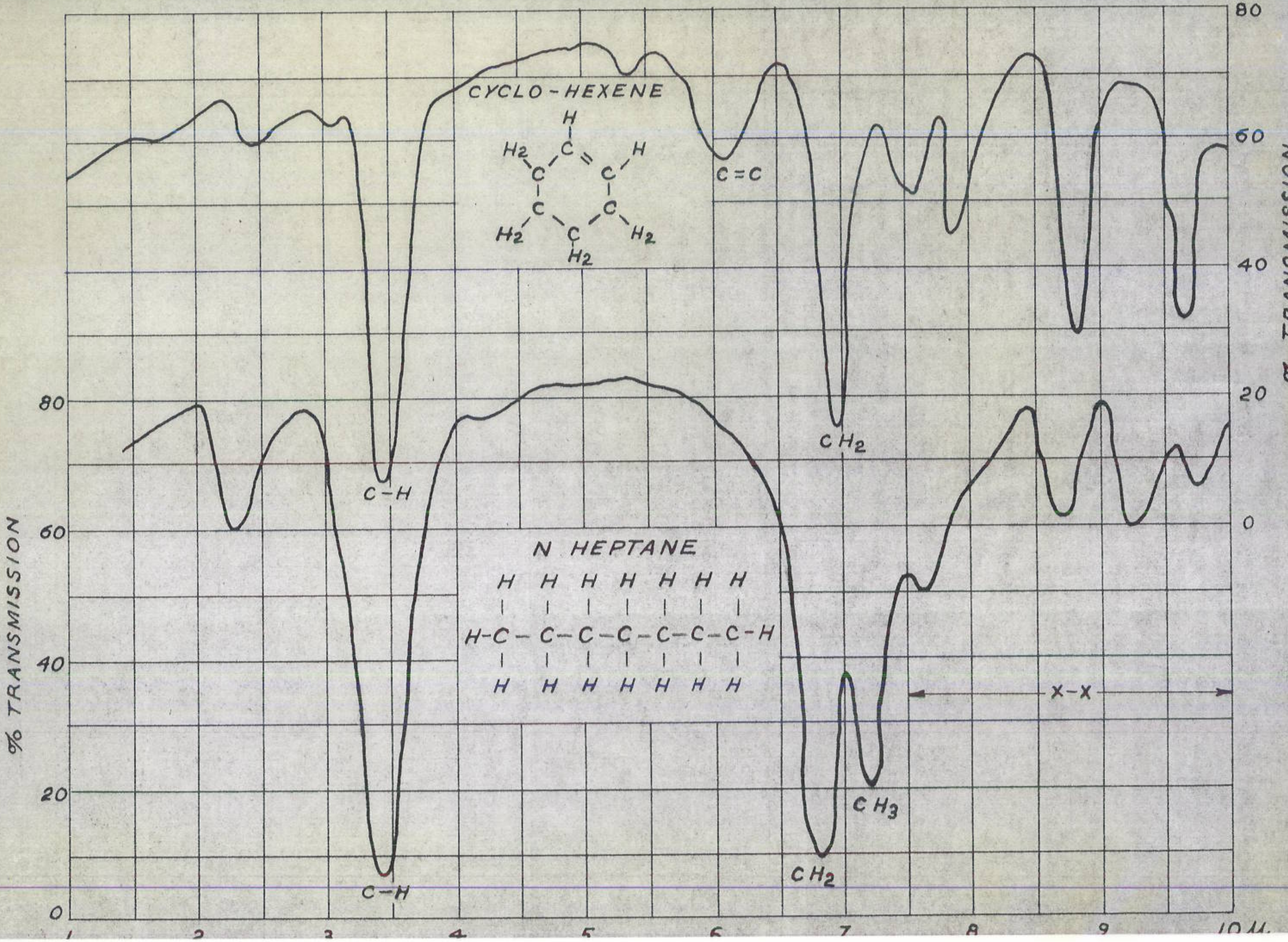

PLATE I

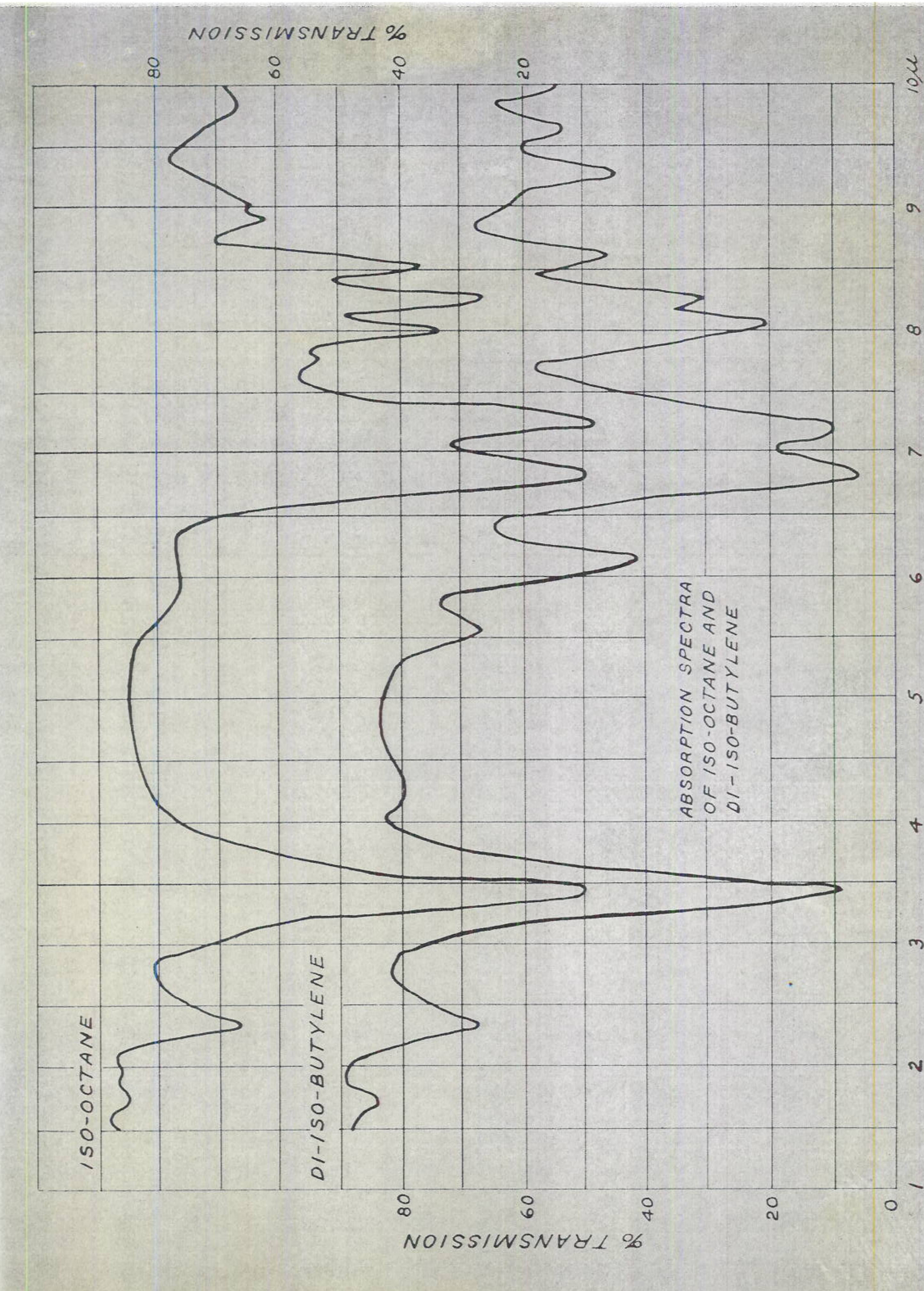
ISO-OCTANE
DI-ISO-BUTYLENE
ABSORPTION SPECTRA
OF ISO-OCTANE AND
DI-ISO-BUTYLENE
% TRANSMISSION
% TRANSMISSION
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10μ

PLATE 2

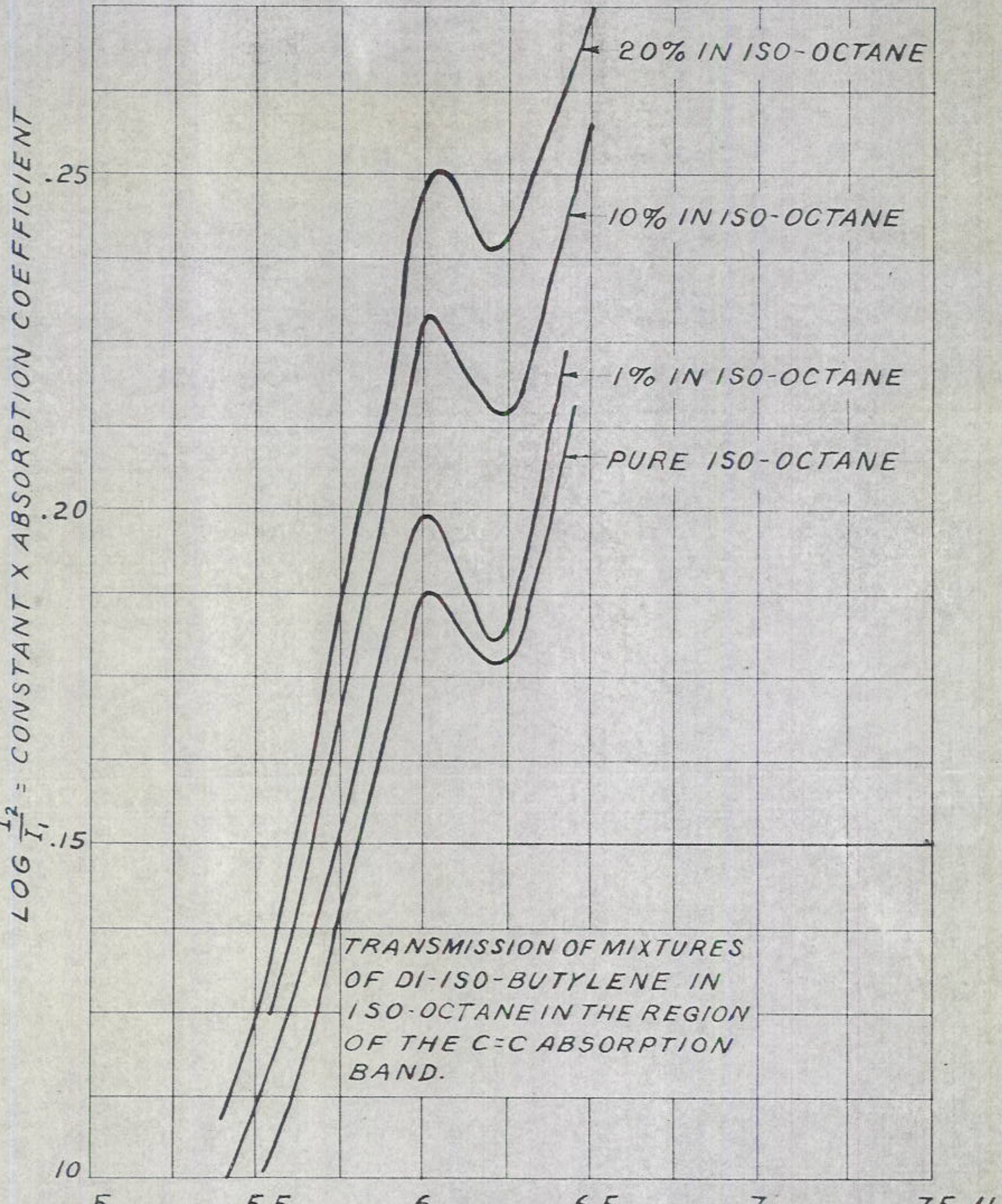
20% IN ISO-OCTANE
10% IN ISO-OCTANE
1% IN ISO-OCTANE
PURE ISO-OCTANE
TRANSMISSION OF MIXTURES OF DI-ISO-BUTYLENE IN ISO-OCTANE IN THE REGION OF THE C=C ABSORPTION BAND.
LOG $\frac{I_2}{I_1}$ = CONSTANT X ABSORPTION COEFFICIENT
.25
.20
.15
10
5
5.5
6
6.5
7
7.5 μ

PLATE 3

ABSORPTION BY SOLUTIONS OF DI-ISO-BUTYLENE AND AROMATICS IN ISO-OCTANE

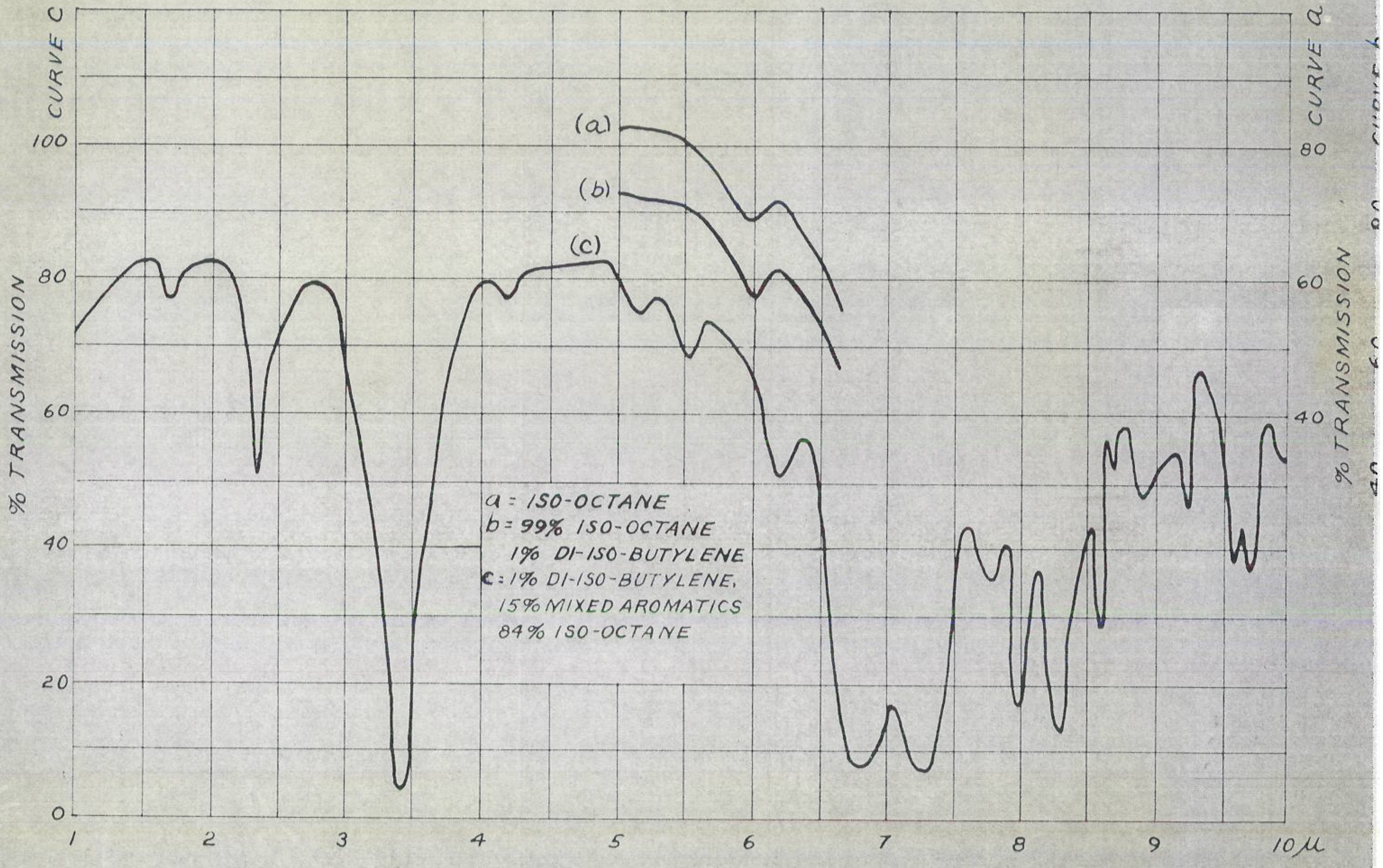

PLATE 4