ENCLOSURE (B) 38

STUDIES OF SLOW OXIDATION OF HYDROCARBONS BY ABSORPTION SPECTRA

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

It is well known that the antiknock property of iso-octane is very good while that of normal heptane is very poor. To clarify the cause of this difference the slow oxidation method was adopted. The mixtures of these fuels and air were heated in a quartz tube, and their activities were examined by absorption spectra. Normal heptane reacted with oxygen at lower temperature and gave peculiar continuous absorption band, while isooctane was inactive with oxygen up to higher temperature.

I. INTRODUCTION

A. History of Project

Excellent reports were written by Withrow and Rassweiler on the subject of the mechanism of engine detonation. Nakata also constructed in 1938 an engine which had two quartz windows on both sides of the engine and a stroboscopic plate which enabled the flame to be observed at any phase of revolution. The object of this work was to study the mechanism of engine combustion by observing emission or absorption spectra of engine flame. As the engine was constructed unsatisfactorily, he began the work of slow oxydation in a quartz tube as Ubbelohde and Egerton had performed. This work was done from 1939 to 1944 when he came to the First Naval Fuel Depot at OFUNA.

B. Key Research Personnel Working on Project

Eng. Comdr. K. Nakata.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus and Test Procedure

Schematic figure of the test apparatus is shown in Figure 1(B)38. Reaction vessel is a quartz tube with flat windows at both ends. The internal diameter and the length of the tube are 15mm and 800mm respectively. It has two side tubes with a stop cock near both ends and serve as mixture inlet and exhaust. Inside of them are two more small tubes inside of which are thermojunctions to measure the temperature of the reaction vessel. This vessel is surrounded by an electric furnace and the temperature of the quartz tube is to be raised up to 1,000°C. The distribution of the temperature inside of the reaction tube was measured by moving a thermojunction throughout the tube and was found to be almost constant. The maximum deviation was only 2°C.

Hydrocarbon air mixture was made by passing air bubble through the liquid hydrocarbon contained in a glass bottle which was kept in a thermostat. Misture strength was controlled by the temperature of the thermostat and examined by "Doi" type refractometer and was kept constant to be 13:1.

In the case of the flow method 60cc of the mixture was passed through the reaction tube per minute. In the case of the stagnant method, the temperature of the reaction tube was kept constant at the desired temperature, the tube was evacuated by a vacuum pump, and the tube was filled with the mixture at atmospheric pressure.

Adam Hilger's hydrogen discharge tube was used as the source of continu-

ous ultraviolet rays. Shimadu's small quartz spectrograph was used to take absorption spectra.

3. Experimental Results

1. Relationship between reaction temperature and octane number

a. Flow Method: Each of Isooctane, normal heptane and cyclohexane were each mixed with air, the mixture strength being 1:13, and the mixture was flown through the reaction tube. The temperature of the tube was raised slowly from room temperature, and the absorption spectrum was taken at every 10°C rise of temperature. These are shown in Figures 2(B)38 and 4(B)38.

(1) Isooctane Figure 2(B)38: No absorption nor any reaction examined by gas analysis was recognized till 450°C. At 460°C, the edge of the shortest wave length was absorbed faintly. If the temperature was higher than 460°C, the region of absorption became larger and the mixture was burnt with a blue flame.

(2) Normal heptane Figure 3(B)38: No absorption and no reaction till 200°C. At 210°C, reaction occurred and a peculiar continuous absorption band, the center of which being 2,600 Å, appeared. This has no structure in it. The nature of this band is not yet known and is called U-band for the present. The absorption area was broadened with a rise of temperature. A wave length shorter than the band remained till 230°C. At 240°C all under 3000 Å was absorbed and faint formaldehyde bands appeared at the edge of the spectrum. Formaldehyde bands became clear with the rise of temperature but they began to disappear above 470°C and a combustion took place with a blue flame.

(3) Cyclohexane Figure 4(B)38: No reaction took place till 300°C. At 310°C, the edge of the shortest wave length was absorbed like isooctane. At 320°C, the region of shorter wave length than 3,000 Å was absorbed and formaldehyde bands appeared near the end of the spectrum. This state continued till 370°C and then above this temperature the spectrum began to become longer. Above 450°C, the absorption reappeared but no formaldehyde band was observed. At 520°C the mixture began to burn with a blue flame and the spectrum became longer again.

From these results, it may be concluded that isooctane is stable with the temperature but low octane fuel such as normal heptane is active with oxygen at relatively low temperature. The absorption of cyclohexane at 310°C may take place in the form of a ring, but the absorption above 450°C may be due to a chain compound like isooctane resulting from the bond breaking. In the region between 380°C and 440°C no reaction was recognized both by spectrum and gas analysis. Oxygen which coupled loosely to the cyclohexane molecule below 370°C may be supposed to detach the molecule in the region of temperature between 380°C to 440°C.

b. Stagnant Method: To determine the accurate temperature at which reaction takes place, experiments were performed by the stagnat method. The reaction tube was heated at fixed temperature and evacuated, then the mixture was sent in and the cock was closed at the atmospheric pressure.

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At every 5 minutes, absorption spectrum was taken, and for 2 hours kept constant at the same temperature. Internal pressure of the reaction tube was measured by the mercury manometer simultaneously. Gas analysis was also conducted after 2 hours' exposure if necessary. The same experiments were repeated by changing the temperature. At first normal heptane was mainly used as its reaction temperature was relatively low. Air-fuel ratio was kept constant to 13:1. Experimental results are shown in Figures 5(B)38 to 14(B)38. In these figures, pressure changes in the reaction tube measured at every 10 minutes are shown on the right hand side of the photographs. The explanation of these figures is as follow:

(1) Figure 5(B)38: Below 120°C, no absorption and no pressure change were observed.

(2) Figure 6(B)38: At 130°C, after heating 80 minutes a faint U-absorption band appeared and became darker as time elapsed. No pressure change was observed.

(3) Figure 7(B)38: At 150°C, after heating 25 minutes U-band began to appear and became evident as time went on. A slight depression in pressure was observed.

(4) Figure 8(B)38: At 160°C, after heating 15 minutes U-band began to appear and was clearer than that which was shown in Figure 7(B)38. The short wave portion below 2,400 Å still remained. Pressure change was still a depression.

(5) Figure 9(B)38: At 180°C, U-band appeared after heating 10 minutes. After 25 minutes all the spectrum below 2,900 Å disappeared. At this stage, faint formaldehyde bands could be detected near the edge of the spectrum (3,000 Å). These were scarcely recognized on the negative plate. At first the pressure decreased but after 30 minutes it increased.

(6) Figure 10(B)38: At 190°C, the portion of the spectrum below 2,900 Å was absorbed after heating it 5 minutes, without the appearance of the U-band. Formaldehyde bands were recognized faintly. Pressure in the reaction tube increased without initial depression.

(7) Figure 11(B)38: At 200°C, the spectrum was the same as in Figure 10(B)38 but the pressure increase was remarkable.

(8) Figure 12(B)38: At 230°C, reaction took place immediately after the mixture had been introduced into the reaction tube. After 5 minutes, all below 2,900 Å disappeared. Formaldehyde bands were clearly observed even on the positive print. But as time elapsed spectrum became longer and showed the disappearance of such substances which absorbed these portions of the spectrum. Pressure increased remarkably but it was interesting to observe its depression after 100 minutes.

(9) Figure 13(B)38: At 250°C, the reaction took place vigorously, immediately after the mixture had been introduced into the tube and below 2,900 Å was entirely absorbed. As time elapsed, spectrum became longer and formaldehyde absorption bands appeared clearly. Pressure increased for 30 minutes and remained constant for about 30 minutes: then

it began to decrease. The maximum and the last pressures were lower than in the case shown in Figure 12(B)38

(10) Figure 14(B)38: At 280°C, the reaction very abruptly occurred, but the recovery of the spectrum was remarkable and after 100 minutes the mixture was almost transparent down to 2,300 Å. The pressure of the mixture rose initially but decreased after 60 minutes and the last pressure was slightly higher than the atmospheric pressure.

From the above results the following conclusions may be drawn:

(1) The appearance of U-band is accompanied by the depression of the pressure.

(2) When formaldehyde bands appear, the portion of the spectrum below 2,900 Å is also absorbed and the pressure increases. With the rise of temperature, the pressure increases more and more, perhaps according to the decomposition of the substances which absorb light.

(3) At higher temperatures, these substances oxidized and polymerized, so the pressure decreases and the absorption disappears.

It is natural that in the stagnant method reaction occurs at lower temperature compared with the flow method.

Next, 6 samples of fuel whose octane values are 0, 20, 40, 60, 80, 100 respectively were obtained by mixing isooctane and normal heptane. The reaction temperatures of these samples were observed by the stagnant method. When they are plotted taking octane value as abscissae, a curve is obtained as shown in Figure 15(B)38. The reaction temperatures of hexane, isopentane, cyclohexane, benzene and isopropyl ether as representatives of normal paraffins, isoparaffins, naphthenics, aromatics and fuels which have oxygen in their molecules were measured by the same method. They are shown in the second column of the following table.

Table I(B)38

Reaction Temperatures and Octane Numbers

	Reaction Temp.	Octane No. from Reaction Temp.	C.F.R. Octane Number
Hexane	230°C	60	59
Isopentane	270°C	86	86
Cyclohexane	260°C	80	79
Benzene			130(?)
Isopropyl ether	210°C	48	98

Octane numbers obtained by the curve in Figure 15(B)38 are shown in the third column. In the fourth column, octane values obtained by C.F.R. motor method are shown as comparison. Except for isopropyl ether, octane numbers obtained by reaction temperatures agree well with those obtained by the C.F.R. motor method. Benzene itself has selective absorption in the region of 2,600 Å, so the reaction temperature can not be determined. The C.F.R. octane value of isopropyl ether is very high but that obtained by the reac-

tion temperature is very low. This must be due to the difference of combustion mechanisms, and be thought as the means of studying combustion mechanism.

2. Gas analysis

To investigate the substance which gives U-band i.e., the substance which gives continuous absorption band, its center being at 2,600 Å, the mixture of normal heptane and air was taken out of the reaction vessel after two hours' exposure at the temperature between 130° and 150°C and the consumptions of O_2, C_7H_{16} and production of CO_2 etc. were measured by gas analysis. CO_2 was not generated and the same number of mols of O_2 and C_7H_{16} was found to be consumed. Judging from the fact that when U-absorption band occurs, the pressure of the mixture decreases, the substance which gives U-band may be a peroxide of some sort composed of one molecule of normal heptane which is coupled with one molecule of O_2 loosely. The examination of the existence of peroxide by acidic solution of potassium iodide and starch revealed to be positive. 170°C is the temperature at which the portion below 2,900 Å is absorbed, the formaldehyde bands appear faintly and pressure of the mixture rises slightly. The result of the test for the existence of formaldehyde at this temperature was positive.

These relations are shown in Figure 16(B)38.

The supposed mechanism of slow oxidation of normal heptane at the initial stage may be as follows.

$$C_7H_{16} + O_2 \rightarrow C_7H_{16}.O_2 \rightarrow \overset{H}{H}>C=O + H_2 + C_5H_{11}\overset{H}{>}C=O.$$

U-band — Formaldehyde band — Absorbs below 2,900 Å

3. Effect of tetra ethyl lead

Three samples of normal heptane and air mixture, one of which being normal heptane only and the others containing tetra ethyl lead 0.1% and 0.2% respectively, were experimented in the same way as is shown in (1). The temperature at which the U-absorption band appears was the same with or without tetra ethyl lead. The remarkable difference was that at higher temperatures absorbed spectrum became transparent as time elapsed when normal heptane alone is used as shown in Figures 13(B)38 and 14(B)38, but when a small quantity of tetra ethyl lead was contained in normal heptane, absorption continued up to higher temperatures.

4. Engine test of fuel which contains small quantity of substance which gives U-band

A small quantity of the substance which gives the U-absorption band was taken out of the reaction vessel by cooling the exhaust gas with ice. This was mixed with a gasoline and a test was conducted so as to see whether it was easy to detonate by the C.F.R. engine and it was found that this was true.

III. CONCLUSION

A. If a fuel of low octane value such as normal heptane is mixed with air and heated to commence slow oxidation in a quartz tube, reaction takes place at a very low temperature, say 130°C, and some substance is generated which gives a continuous absorption band in the region of wave length 2,600 Å

As the temperature rises the portion of the spectrum below 2,900 Å is absorbed and formaldehyde bands appear in the region of 3,000 Å.

B. High octane fuels such as isooctane do not give such absorption, and at relatively higher temperature, say 300°C, absorption occurs at the shortest wave length region and gives formaldehyde bands.

C. At still higher temperatures, formaldehyde bands begin to disappear and by and by the spectrum recovers its length.

D. The first absorption of cyclonexane-air mixture begins at a temperature between that of normal heptane and isooctane and the form of absorption differs from both. If the temperature is increased above this, absorption disappears but at higher temperatures absorption occurs again and this resembles the absorption of isooctane.

E. Octane numbers of hydrocarbons except aromatics can be determined by the reaction temperature thus determined.

F. In the case of normal heptane, the appearance of the peculiar absorption band accompanies the depression of the pressure of the mixture and this is due to the formation of a peroxide which is composed of one molecule of normal heptane and oxygen.

G. At the stage when formaldehyde bands appear, all the shorter wave length portions are absorbed and the pressure in the reaction vessel increases.

H. At higher temperatures, these absorptions disappear by and by and the pressure in the reaction vessel which have been increased by the appearance of formaldehyde bands begins to decrease.

I. There is an indication of peroxide when the U-band appears in the spectrum and of formaldehyde when its bands are recognized. The slow oxidation of normal heptane is supposed to be as follows.

$$C_7H_{16} + O_2 \rightarrow C_7H_{16}.O_2 \rightarrow \overset{H}{H} > C = O + H_2 + C_5\overset{H}{H}11 > C = O.$$

J. The existence of tetra ethyl lead in normal heptane does not suppress the formation of the substance which gives the U-band, but it has some effect on the recovery of spectrum (i.e., decomposition of polymerization of absorbing substances) at higher temperature.

ENCLOSURE (B)38

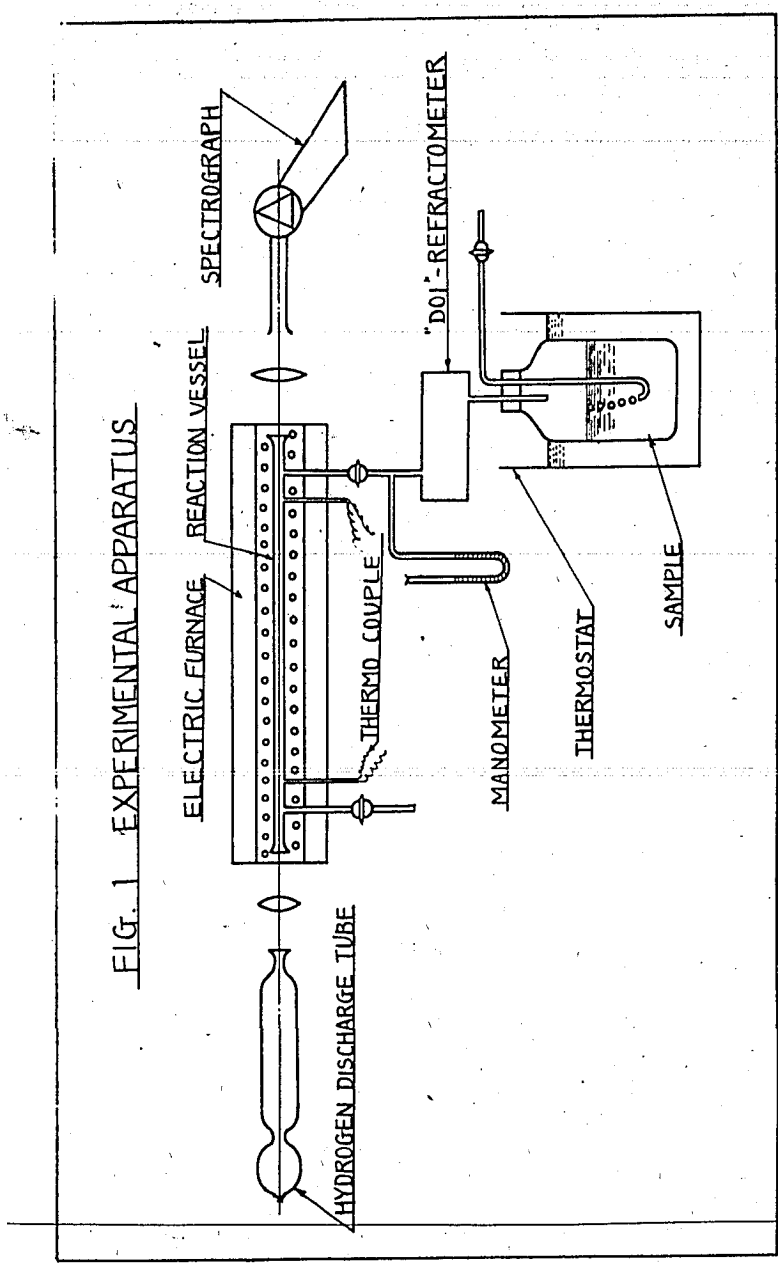


Figure 1(B)38
EXPERIMENTAL APPARATUS

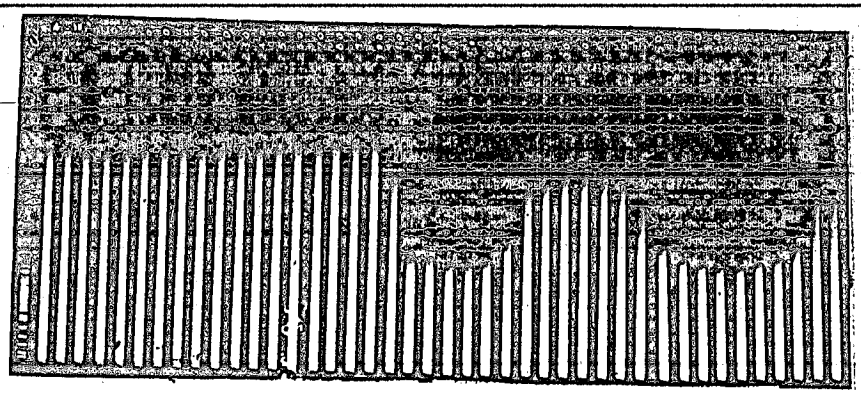


Figure 4(B)38
ABSORPTION SPECTRA OF CYCLOHEXANE

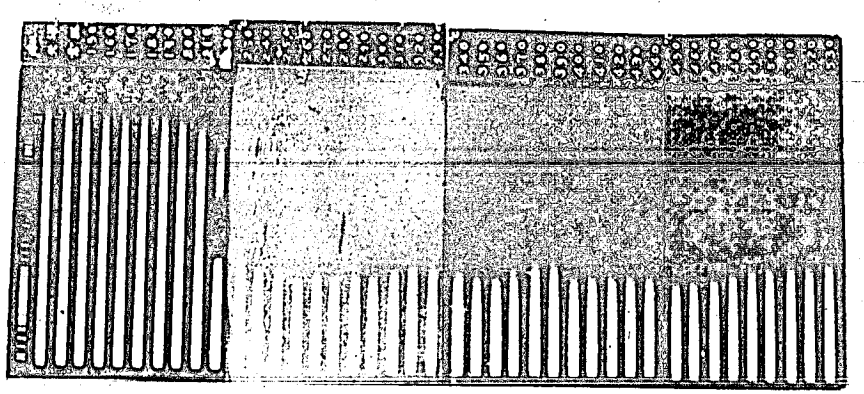


Figure 3(B)38
ABSORPTION SPECTRA OF NORMAL HEPTANE

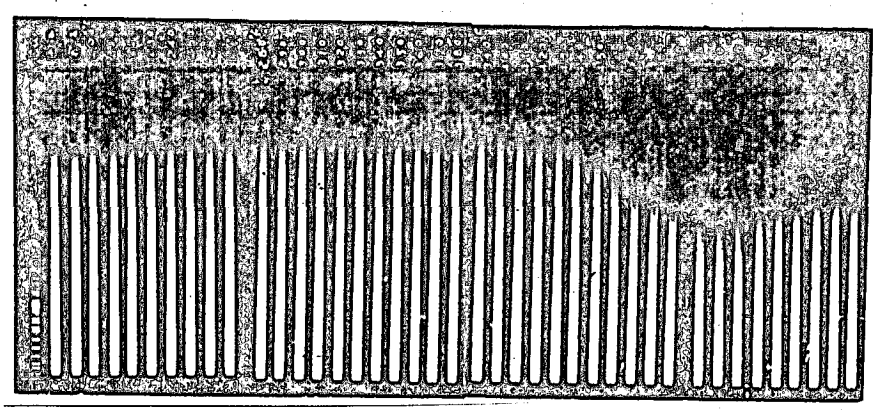


Figure 2(B)38
ABSORPTION SPECTRA OF ISO-OCTANE

ENCLOSURE (B)38

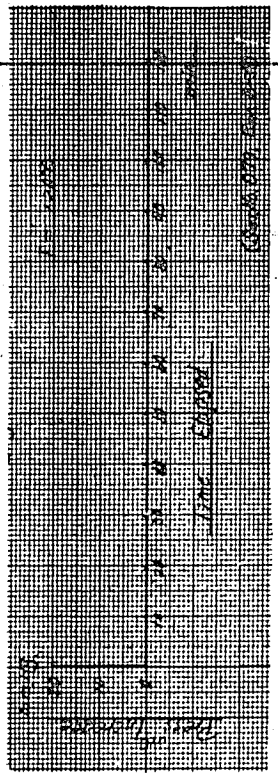


Figure 5(B)38
n-HEPTANE, REACTION TEMP. = 120°C

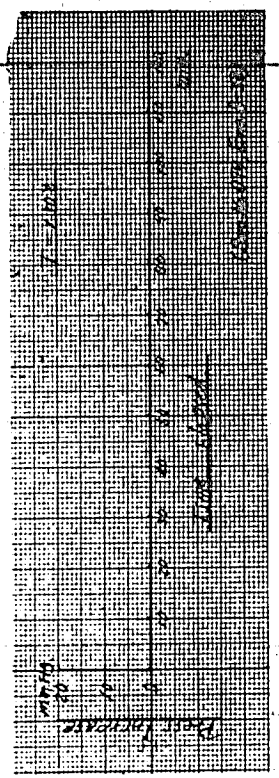
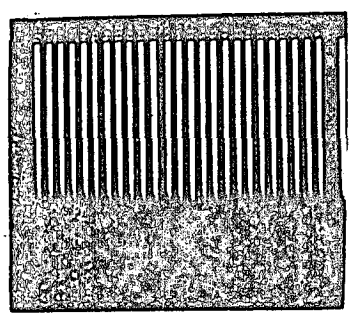
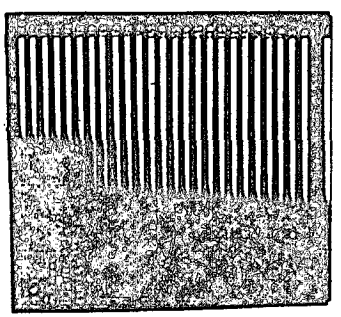


Figure 6(B)38
n-HEPTANE, REACTION TEMP. = 134°C





ENCLOSURE (B)38

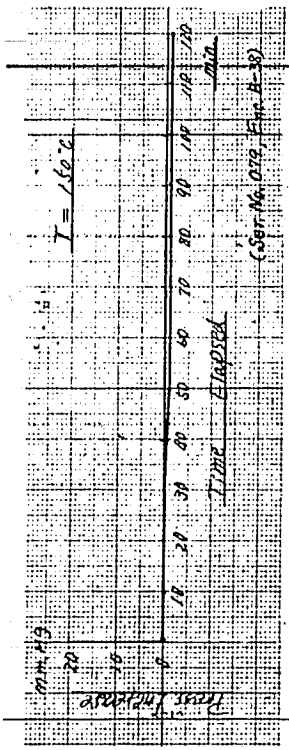


Figure 7(B)38
n-HEPTANE, REACTION TEMP. = 150°C

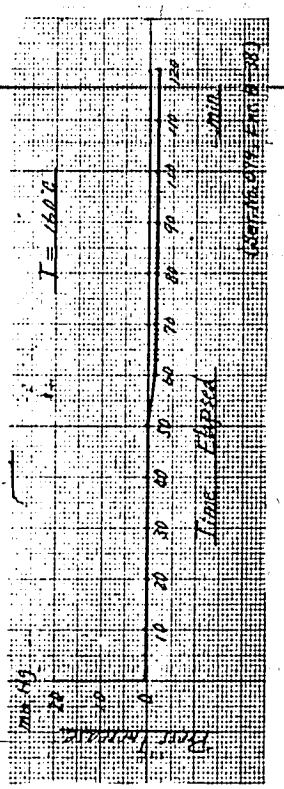
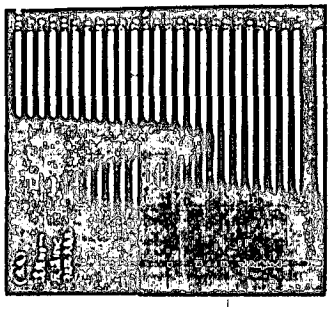
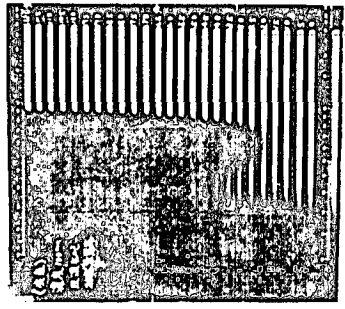


Figure 8(B)38
n-HEPTANE, REACTION TEMP. = 160°C





ENCLOSURE (B)38

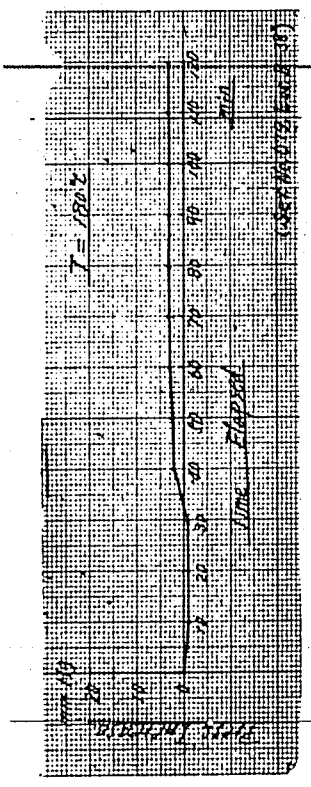


Figure 9(B)38
n-HEPTANE, REACTION TEMP. = 180°C

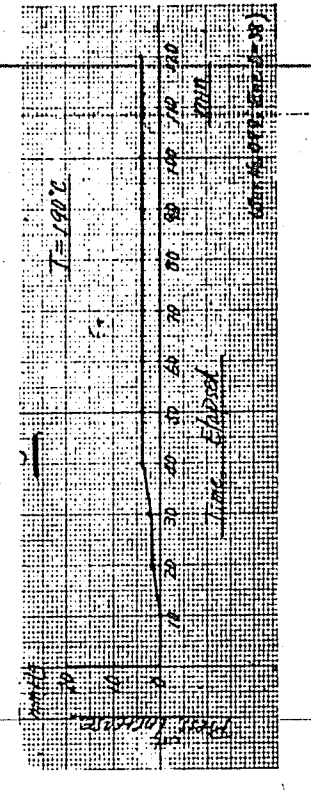
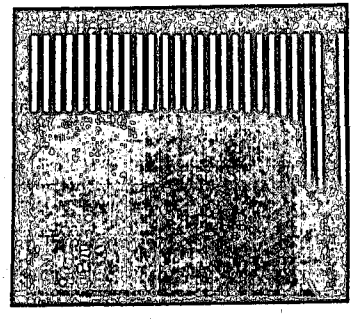
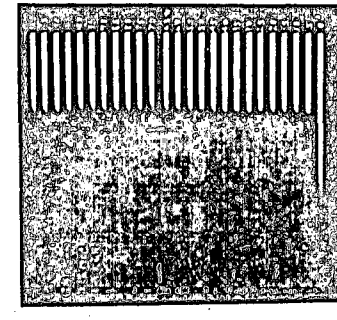


Figure 10(B)38
n-HEPTANE, REACTION TEMP. = 190°C





ENCLOSURE (B)38

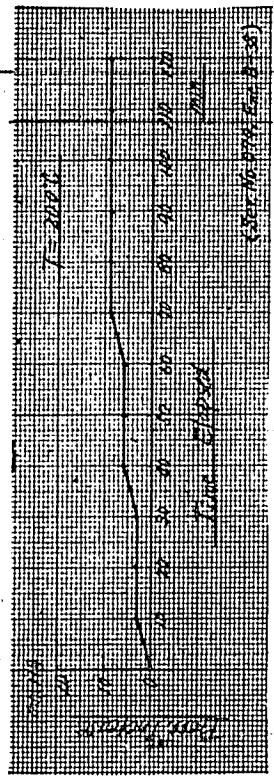


Figure 11(B)38
n-HEPTANE, REACTION TEMP. = 200°C

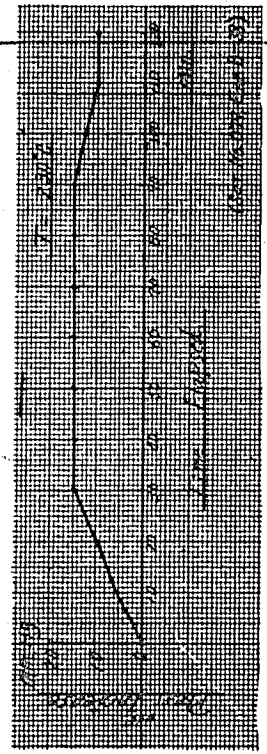
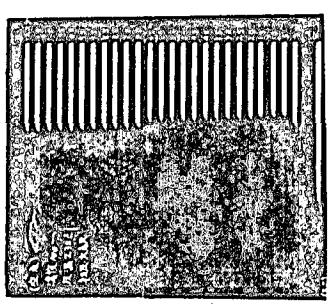
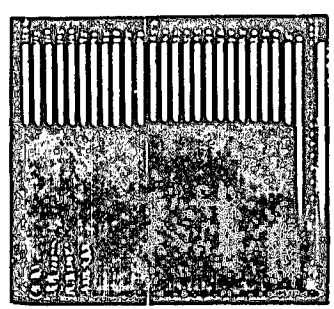


Figure 12(B)38
n-HEPTANE, REACTION TEMP. = 230°C





ENCLOSURE (B)38

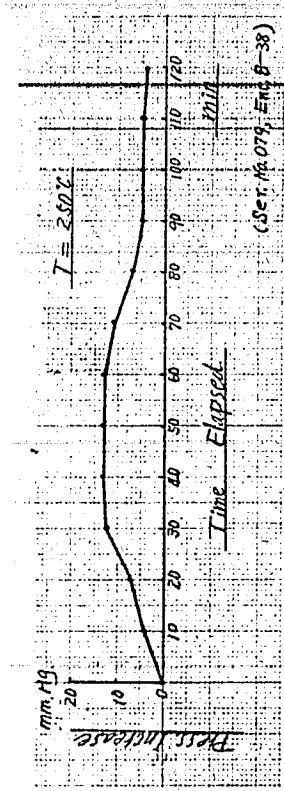


Figure 13(B)38
n-HEPTANE, REACTION TEMP. = 250°C

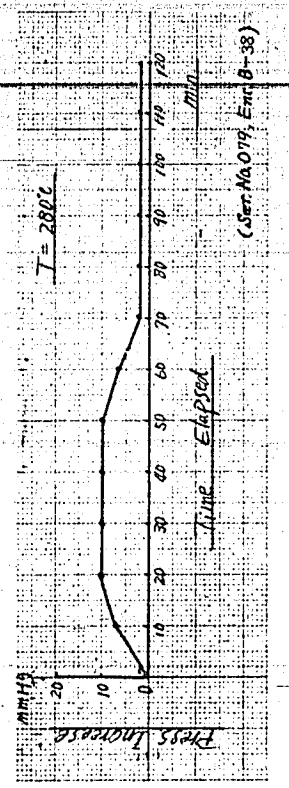
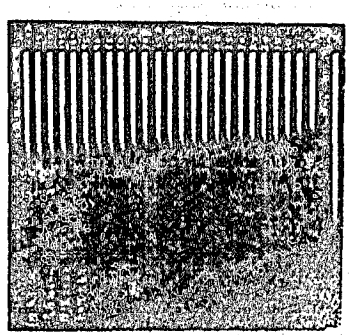
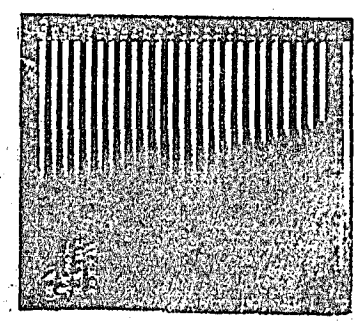


Figure 14(B)38
n-HEPTANE, REACTION TEMP. = 280°C





ENCLOSURE (B)38

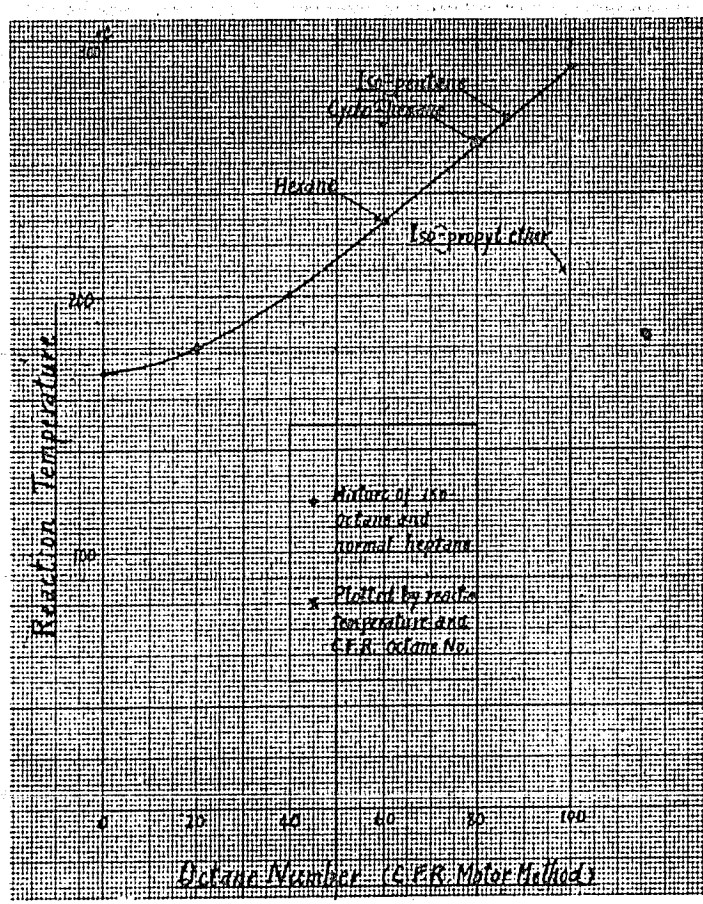


Figure 15(B)38

RELATION BETWEEN REACTION TEMP. AND OCTANE NO.

ENCLOSURE (B)38

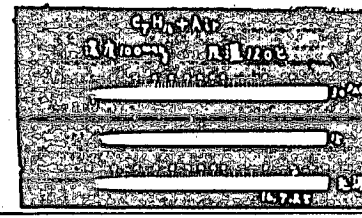
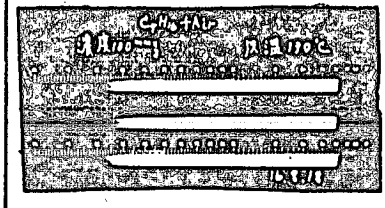
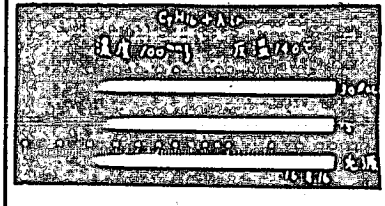
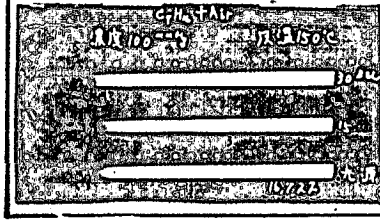
ABSORPTION SPECTRUM OF C_7H_{16}+AIR MIXTURE UPPER 30 SEC. EXPOSURE MIDDLE 15 " " LOWER LIGHT SOURCE	TEMP.	PEROXIDE
	120°C	NONE
	130 °C	TRACE
	140 °C	PRESENT
	150°C	"

Figure 16(B)38

ENCLOSURE (B)38

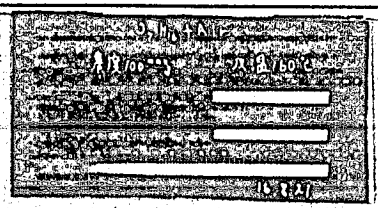
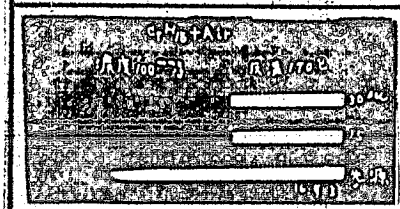
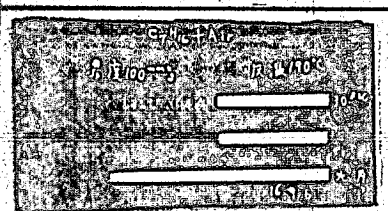
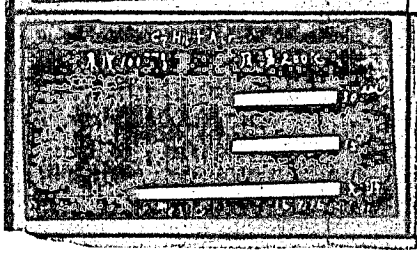
ABSORPTION SPECTRUM OF C_7H_8+AIR MIXTURE UPPER 30 SEC. EXPOSURE MIDDLE 15 " " LOWER LIGHT SOURCE	TEMP.	PEROXIDE
	160°C	PRESENT
	170°C	"
	180°C	"
	200°C	"

Figure 17(B)38