THE INFLUENCE ON COMBUSTION OF COMPOUNDS
CONTAINING A DIRECT CHROMIUM-CARBON LINKAGE.

A thesis submitted by

James A. Horn, B.Sc., A.R.T.C., A.R.I.C.,

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Technical Chemistry Dept.,
Royal Technical College,
Glasgow.

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SUMMARY.

The thesis opens with an introduction in which the phenomenon of "knock" in internal combustion engines is reviewed. The use of metallic anti-knock compounds is discussed and the previous work on chromium compounds for this purpose is described. There is some disagreement in the literature regarding the efficacy of chromium compounds as anti-knock agents. Chromium hexacarbonyl appears to be the most suitable chromium compound for testing as a fuel additive. The various methods of preparing the hexacarbonyl are reviewed.

The remainder of the thesis is divided into five sections and two appendices.

Section 1 describes attempts to prepare chromium hexacarbonyl by three different methods, various modifications of the methods being tried in order to improve the yields. Chromium hexacarbonyl is prepared by the method of Hieber & Romberg, the maximum yield being 9.5% (Claimed by Hieber & Romberg : 14%). The method involves the absorption of carbon monoxide by a violently agitated suspension of anhydrous chromic chloride in presence of a Grignard reagent. The reaction is conducted at 0 - 5°C. None of the modifications made in this method improve the yield. Chromium hexacarbonyl is also prepared by the "Low Pressure Method" of Owen, English, Cassidy and Dundon, the maximum yield obtained being 3.4% (Claimed by Owen et. al. : 24%). The method differs from that of Hieber & Romberg in that the reaction is partly conducted at - 70°C. Otherwise the two methods are similar in principle although the procedural details

vary considerably.   This method is modified by omitting the low temperature (- 70°C), stage of the preparation and by excluding air from the reaction flask.   Under these conditions a yield of 10.6% is obtained. Continuous fast stirring, rigid temperature control (0-5°C.), and the use of a finely powdered, apparently amorphous form of anhydrous chromic chloride, are found to contribute to optimum yield in both the above methods of preparation.   An attempt to prepare chromium hexacarbonyl by the method used by Kocheshkov, Nesmeyanov, Rossinskaya & Borissova for preparing molybdenum and tungsten hexacarbonyls was unsuccessful.   An attempt has been made to propound a reaction mechanism for the formation of chromium hexacarbonyl based on the work of all the workers on the subject, including the author.   This assumes the formation of an unstable phenyl chromium chloride $(PhCrCl_2)$.   The reaction mechanism has not been proved but is believed to be the only one in accord with all the known facts.

Section 11 deals with the stability of chromium hexacarbonyl.   Although chromium hexacarbonyl is very stable chemically its solutions tend to decompose on standing, depositing a gelatinous precipitate.   Tests show that the presence of light and oxygen is necessary for decomposition. Attempts to find a suitable inhibitor of the decomposition are described.   Long chain monocarboxylic acids containing 14 or more carbon atoms inhibit the formation of the insoluble gelatinous precipitate when present in a higher molar concentration than the hexacarbonyl but U.V. Absorption Spectra tests

show that decomposition of the chromium hexacarbonyl is not inhibited. If mixed solutions of chromium hexacarbonyl and stearic acid are exposed to light the chromium is retained in solution in an active form for some time after the decomposition of the hexacarbonyl.   It is concluded that in presence of a monocarboxylic acid inhibitor chromium hexacarbonyl solutions decompose on exposure to light forming a chromium compound which is soluble in hydrocarbon solvents and is active as a fuel "combustion modifier".   This compound subsequently decomposes slowly to another, soluble in hydrocarbon solvents but ineffective as a combustion modifier.   The nature of these intermediate chromium compounds is unknown but the initial intermediate appears to be formed by interaction between equimolecular proportions of chromium hexacarbonyl and stearic acid.   A way has thus been found of preventing the deposition of solid from chromium hexacarbonyl doped fuels exposed to air and light.

Section 111 describes the effect of chromium hexacarbonyl on fuels.   The assembly and testing of a Moore type Spontaneous Ignition Temperature Apparatus is described, the effect of several variables on S.I.Ts. being determined. A series of tests establish the effect of chromium hexacarbonyl on spark-ignition engine fuels.   S.I.T. tests indicate that chromium hexacarbonyl possesses anti-oxidant properties since it raises the S.I.T. of various fuels.   Highest Useful Compression Ratio (H.U.C.R.) tests on a Ricardo E6/S Variable Compression Engine indicate that chromium hexacarbonyl is a pro-knock compound.   The maximum pro-knock effect is

equivalent to a decrease of 5 in the octane number of Pool Petrol. The unusually low concentration of 0.02 g./l. chromium hexacarbonyl is sufficient to cause almost the maximum effect. A series of tests establish the effect of chromium hexacarbonyl on a Diesel engine fuel. A very small concentration of hexacarbonyl raises the cetane number of a Diesel fuel by approximately 3. Increase in additive concentration does not increase the effect. Tests on benzene indicate that chromium hexacarbonyl lowers the S.I.T. and raises the H.U.C.R. (14.5 to 15.6) of the fuel. The results of Section lll are discussed in Sub-Section E (p.109). The effect of chromium hexacarbonyl on the H.U.C.R. of benzene is attributed to the fact that it is inhibiting pre-ignition. The rather anomalous behaviour of chromium hexacarbonyl in the other tests is explained on the basis of both of the current theories on knock.

Section lV deals with compounds of chromium other than chromium hexacarbonyl. Reasons are given for confining the combustion tests to the hexacarbonyl. There are few petrol soluble chromium compounds, and most of them are unstable. The reason for the title of the thesis is discussed.

Section V studies the engine deposits caused by the use of chromium hexacarbonyl as a fuel additive. A 10 cc. model engine is used for the tests. When using fuel containing over 1 g./l. chromium hexacarbonyl, green chromium sesquioxide deposits appear in the combustion chamber. These deposits can be reduced but not eliminated by incorporating small concentrations

of ethylene dichloride or ethylene dibromide in the fuel.
Chromium hexacarbonyl does not cause excessive corrosion or
erosion effects on an engine.

Appendix 1 refers to the Ricardo E6/S Variable
Compression Engine.   The engine and test equipment are
described and the method of determining H.U.C.Rs. is set forth.

Appendix 11 gives the boiling ranges and specific
gravities of the heterogeneous fuels referred to in the thesis.

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"Engines"

... generate by the explosion
... working ... In
... engine combustion is furnished by an
... spark which causes a flame ... to move through the
... as fast ...
... in turn ... mechanical work
... In the "compression ignition" or "Diesel" ...
air is heated to a suitable temperature by compression and the
fuel ... high temperature
... to ignite spontaneously thus liberating ...

INTRODUCTION.

... circumstances ... this
... in both ... ignition ... compression
... although the ... completely different
... is a spark ...
... ignition starting at ... more
... "end gas" ... best ...
flame ... of change ...
combustion ... an indistinguishable ...
... of the whole and the ...
... vary considerably. The more ...

INTRODUCTION.

"Knock in Internal Combustion Engines"

Internal combustion engines operate by the explosion of combustible mixtures which form the working fluid. In the "spark ignition" engine combustion is initiated by an electric spark which causes a flame front to move through the mixture. This converts the inherent energy of the fuel to heat energy which is in turn converted to mechanical work by the engine. In the "compression ignition" or "Diesel" engine air is heated to a suitable temperature by compression and the fuel is injected into the hot air. The high temperature causes the fuel to ignite spontaneously thus liberating heat which the engine converts into mechanical work.

In certain circumstances the character of the combustion changes, accompanied by a knocking sound. This phenomenon is encountered in both spark ignition and compression ignition engines although the causes are completely different.

Engine "knock" in a spark ignition Otto-cycle engine[1] is a form of spontaneous ignition starting at one or more points in the cylinder "end gas" or unburned charge ahead of the flame front. The amount of charge entering into knocking combustion may vary from an indistinguishably small portion to at least three quarters of the whole and the intensity of the knock may also vary considerably. The knock flame seems to sweep through the remaining unburned charge with a velocity of approximately 1000 feet per second - [2] a value far greater than

that of the normal flame but less than would be calculated
for a true detonation wave in similar air-fuel mixtures.
This very rapid combustion causes a rapid pressure rise which
in turn results in the setting up of pressure waves which
induce the emission of sound waves from the engine.   This
causes dissipation of energy and a consequent loss of efficiency.
In addition, severe knock may damage the engine by overheating
and excessive vibration.   The tendency towards knock increases
with increased compression ratio in the engine, and this
prevents the compression ratio being raised beyond a certain
point.   Since the efficiency of an engine rises with increased
compression ratio the existence of knock imposes a limit on
engine efficiency.

    "Knock" as described above, could not possibly occur
in the compression ignition engine since here spontaneous
ignition is not undesirable but necessary.   In a Diesel engine
there is a time-lag between the commencement of the injection
of the fuel and its ignition.   After the start of the ignition
the fuel ignites and burns as it enters the combustion chamber.
If the "ignition delay" is too prolonged a large proportion of
the charge will have entered the combustion chamber before
ignition occurs, the resultant combustion and pressure rise
will be very rapid, and this may cause vibration (audible as
"Diesel knock") and increased stresses in engine parts[3].

    The incidence of knock in internal combustion engines
is influenced by a number of factors, the ignition characteristics
of the fuel being one of the most important.   In a spark

ignition engine a fuel which readily ignities spontaneously
is less suitable from the knock point of view than one which
is less liable to ignite.   The reverse is true of the
compression ignition engine.

Metallic Anti-knock Compounds.

Originally the only way of improving the anti-knock
properties of fuels for spark-ignition engines was by blending
them in suitable proportions but in 1920 Midgley[4] discovered
that the addition of very small amounts of lead tetraethyl to
a fuel effected a great improvement in its anti-knock properties.
The amount of lead tetraethyl added need only be of the order
of one gram per litre of fuel.   Since then numerous metallic
"dopes" have[5] been added to petrol to improve its anti-knock
characteristics but none has been found which can compete
with lead tetraethyl in efficiency, convenience and economy[6].
The organometallic compounds of a great many metals possess anti-
knock properties but very few are superior to lead tetraethyl.
Iron pentacarbonyl and nickel carbonyl have anti-knock properties
comparable with those of lead tetraethyl but their employment
is not practicable due to the harmful effects of their combustion
products on the engine[7].

The requirements of a good metallic anti-knock
additive are

(a) Solubility in petrol.

(b) Ability to effect a considerable improvement in the anti-
     knock properties of a fuel at very low concentrations
     (1 - 4 grams per litre).

(c) Absence of appreciable corrosion, erosion, or deposition effects in the engine.

(d) Stability when in solution in hydrocarbon fuels.

The anti-knock property of an organometallic compound appears to depend principally on the metallic atom although the radicle to which it is attached is also important.

In 1926, Sims and Mardles[8] established that the metal was the active constituent of an anti-knock compound when they discovered that a colloidal dispersion of lead in petroleum produced an effect similar to that of lead tetraethyl. It has been suggested recently[9] that in some cases the radicle attached to the metal has actually a pro-knock effect which to some extent counteracts the effect of the metal itself.

The object of the research described in this thesis was to study organometallic compounds of chromium with a view to determining whether they possessed anti-knock properties.

Causes of Knock and Mode of Action of Anti-knock Compounds.

The causes of knock and the mode of action of anti-knock compounds are not yet fully understood. Until recently it was almost universally accepted that knock was due to preflame reactions of a homogeneous nature in the part of the combustion chamber not yet reached by the flame front. These reactions are believed to be propagated by substances called "chain carriers", the molecules of which can acquire oxygen in the elemental form and then part with it to a relatively stable hydrocarbon molecule. This initiates the oxidation

and decomposition of the hydrocarbon. The chain carrier is subsequently regenerated by acquiring elemental oxygen. In this way relatively few molecules of the chain carrier could activate a very large number of hydrocarbon molecules causing a very rapid increase in the reaction rate and eventually leading to spontaneous ignition and knock. Most workers believe the chain carriers to be organic peroxides although this has not been conclusively proved. According to this theory metallic anti-knock compounds operate by destroying or deactivating these chain carriers. This explains why such a small concentration of anti-knock compound is effective in delaying the onset of knock.

The above theory of the causes of knock and the mode of action of anti-knock compounds has been supported by most of the leading workers in this field including Egerton and Beatty & Edgar who published comprehensive reviews of the subject in 1938[10]. As recently as 1949, Cramer & Campbell[11] published a paper giving a slight variation of the chain reaction theory.

Since 1947, however, R.O. King has been publishing a series of papers on "The Oxidation, Ignition, and Detonation of Fuel Vapours and Gases"[12] which throw considerable doubt on the accepted theories on knock. King maintains that combustion reactions in an engine cylinder are essentially of a heterogeneous character. The conditions required for detonation are governed by the temperature and pressure of the cylinder end gas and the concentration in it of carbon nuclei. The almost simultaneous

commencement of combustion at the surfaces of the carbon particles in the end gas is the cause of detonation[13]. The carbon particles are formed by the pyrolysis of the fuel or lubricating oil.

King believes that metallic anti-knock compounds act by the continuous deposition of a fine layer of active metal on the combustion chamber walls. This metal catalyses the preflame oxidation of some of the fuel to carbon dioxide and steam both of which have strong anti-knock properties[14]. In the absence of metallic anti-knock compounds there would be a greater tendency for the preflame reactions to yield intermediate products such as carbon monoxide and aldehydes, neither of which exhibit the anti-knock properties of carbon dioxide and steam. King thus maintains that anti-knock compounds operate by promoting rather than deterring oxidation.

Testing of Anti-knock Compounds.

(a) Engine Tests.

The efficacy of an anti-knock compound is determined by studying its effect on the knocking characteristics of a suitable fuel. It is not, however, easy to assess the exact knocking tendency of a fuel. The same fuel does not behave in exactly the same manner in different engines in which the fuel mixture may be exposed to somewhat different conditions. Therefore, however carefully the fuel may be compared with a standard fuel in a particular engine, its comparative behaviour may be different in another engine[15].

It has been found that the determination in a
variable compression engine of the compression ratio at which
knock becomes audible (critical compression ratio) does not
give very consistent results, partly because of the difficulties
of measurement of the audibility and partly also because of the
fact that the moment when feeble knock first occurs is sensitive
to change of conditions.   Co-operative efforts, therefore,
have been made to standardise the methods of rating the knock
tendency of fuels[16] and a variable compression engine (known
as the C.F.R. engine from its development by the Co-operative
Fuel Research Committee) has been designed specially for knock
rating.   The generator to which it is coupled absorbs the
load and controls the speed.   A "bouncing pin"[17] acts as an
indicator of the intensity of knock.   When owing to the shock
of the knock the pin bounces from the diaphragm on which it
rests it causes an electric current to pass through a small
resistance, the change of temperature of which is recorded by
a thermocouple connected to a millivoltmeter.

Fuels are matched against one another to give the
same intensity of knock and are referred to a standard scale
called the octane scale.   This scale is based on the knocking
characteristics of two pure hydrocarbons, n-heptane which has
high knocking tendency and iso-octane (2,2,4-trimethylpentane)
which knocks only at very high compression ratios.   Most fuels
come within the range of knock rating of these two hydrocarbons.
An octane number of 60 means that the fuel, when tested in the

C.F.R. engine under standard conditions gives the same intensity
of knock as that given by a mixture of 60 volumes of octane and
40 volumes of heptane.

A slightly different form of test engine was developed
by Ricardo[18] who studied the variation in power output at fixed
speed as the compression ratio of the engine was raised.   When
the compression ratio of an engine is raised the power output
rises until appreciable knock occurs, when it begins to fall.
There is thus a compression ratio corresponding to maximum
power, the value of which will depend on the knocking properties
of the fuel.   This is known as the "Highest Useful Compression
Ratio" (H.U.C.R.).   Ricardo has determined the H.U.C.R. of a
large number of fuels by this method.

The higher the H.U.C.R. of a fuel, the better are its
anti-knock characteristics.   By determining the H.U.C.R. of a
series of n-heptane - iso-octane mixtures it is possible to
relate H.U.C.R. to octane number.   Octane numbers obtained
from H.U.C.R. determinations will not always be exactly the
same as those obtained by the official C.F.R. method but the
difference is unlikely to be very great.   The H.U.C.R. method
is completely satisfactory if it is only required to compare
the knocking properties of a series of fuels but if an absolute
octane number is required it is necessary to use the C.F.R.
method.

(b) Spontaneous Ignition Temperature Determinations.

In studying the efficacy of a substance as an anti-
knock agent it is dissolved in petrol in a known concentration

and its effect on the knocking characteristics of the fuel
observed.   This method has the disadvantage of being slow
and may also be harmful to the engine if anti-knock agents of
hitherto unknown properties are being used.

A fair indication of the knocking characteristics of
a petroleum can, however, be gained from its Spontaneous
Ignition Temperature (S.I.T.)[19].   The Spontaneous Ignition
Temperature of a substance is the lowest temperature at which
the substance, surrounded by air at the same temperature, will
burst into flame without the application of any spark or other
local high temperature.   The S.I.T. of a particular petroleum
is not absolute, its value depending considerably on the
conditions of the experiment and the dimensions of the apparatus
used[20].   It is impossible to draw any reliable conclusions
concerning anti-knock properties by use of this apparatus, but
it has invariably been found that small proportions of efficient
anti-knock compounds raise the S.I.T. of petroleum, by about
100 centigrade degrees.   Thus if a compound is found which
raises the S.I.T. of a petroleum by a considerable amount there
are good grounds for assuming that it will be an anti-knock
agent, and the extent of its utility in this direction can be
established in a test engine[21].   An advantage of the S.I.T.
test is that very little fuel (c. 5 cc.) is required for each
test while at least a litre is required for an engine test.

Numerous types of S.I.T. apparatus have been devised,
differing mainly in detail.   The earliest published S.I.T.

determinations were made by Holm in 1913.[22] By allowing drops
of liquids to fall upon a heated porcelain surface the
temperature of which was measured by a thermocouple, the S.I.T.s
of a number of common liquid fuels were determined.   Soon
after the publication of Holm's work the value of such
determinations as a means of testing fuels for their suitability
in engines was pointed out by Constam & Schlaepfer[23] who
allowed drops of liquid fuels to fall into a platinum crucible
in a gas heated sand bath.

In 1917 Moore[24] developed an S.I.T. apparatus
consisting of a platinum crucible embedded in a steel block
heated by a gas burner.   Dry, preheated air or oxygen was
delivered at a constant rate to the crucible, the preheating
being accomplished by a small coil in the steel block, through
which the air or oxygen passed.   This type of apparatus has
been used extensively by subsequent workers although various
modifications have been made[25].

Various workers have developed more elaborate types
of S.I.T. apparatus[26], incorporating features for determining
ignition temperatures under increased pressures and for
determining the time lag before ignition.   Since the test is
by no means absolute it is doubtful if such refinements are of
any great advantage for the purposes of this research.   The
only reliable method of assessing the knocking characteristics
of a fuel is in a test engine and if only a qualitative indication
of knocking properties is required the Moore type of apparatus
is sufficiently accurate.

A modified form of the Moore apparatus was therefore used in this work.

Chromium Compounds as Anti-knock Additives.

There are very few published records of chromium compounds being tested for anti-knock properties. This is probably partly due to the difficulty of obtaining petrol soluble chromium compounds.

In 1926 Sims & Mardles[27] tested the effect of what they believed to be a mixture of chromium phenyls and chromium phenyl bromides on the anti-knock properties of petroleum. They mixed phenyl magnesium bromide (PhMgBr) with a suspension of anhydrous chromic chloride ($CrCl_3$) in benzene, added the mixture to an appropriate volume of petrol, allowed the mixture to stand overnight and decanted off the clear petrol layer which was then used in the test. They found that the metal appeared to exhibit a reasonably good anti-knock effect. The concentration of chromium in the "doped" petrol was believed to be approximately 0.35 grams. per litre and an increase in H.U.C.R. of 8.3 per cent relative to the undoped fuel was obtained. This compared with an increase of 40 per cent in the H.U.C.R. caused by 2.0 grams of lead per litre, the lead being in the form of lead tetraethyl. There is, however, considerable doubt as to the actual composition and concentration of the compounds present in the petrol and the result obtained by Sims and Mardles cannot be taken as absolute reliable.

In 1926 also, Charch, Mack & Boord[28] investigated

the effect of chromium pentaphenyl bromide (Ph_5CrBr) on the
knocking properties of petroleum. They were unable to find
a suitable fuel in which the compound would dissolve readily
but obtained a solution of "less than 0.1% by weight". This
is equivalent to approximately 0.07 grams chromium per litre.
This solution had no measurable effect on the knocking
characteristics of the fuels tested.

This result throws doubt on the observations of Sims
& Mardles. They believed they had prepared a mixture of
chromium phenyls and chromium phenyl bromides. Chromium phenyls
are, however, highly unstable[29] and would be unlikely to remain
undecomposed after standing overnight. Chromium pentaphenyl
bromide is the most readily formed of the phenyl chromium
bromides and is the one most likely to have been present in the
mixture prepared by Sims & Mirdles. Since, however, Charch,
Mack & Boord failed to produce a solution of even 0.07 grams
chromium per litre in any convenient fuel when using chromium
pentaphenyl bromide, it seems doubtful if the petrol sample
treated by Sims & Mardles contained as much chromium as they
believed (0.35 grams per litre). It is possible that the anti-
knock effect observed by Sims & Mardles was due to the benzene
present in their mixture.

In 1927 Weerman[30] determined the effect of chromium
hexacarbonyl ($Cr(CO)_6$) on the S.I.T. of petrol. The carbonyl
caused a rise of 80 centigrade degrees in S.I.T. at a concentration
of 4.0 grams per litre compared with a rise of 105 centigrade

degrees for 0.50 grams lead tetraethyl per litre. This indicated that the compound was likely to exhibit anti-knock properties.

No further mention of chromium compounds being tested for anti-knock properties is found in the literature until 1948 when Ogilvie, Davis, Thomson, Grummitt & Winkler[31] published a study of the pro-knock activity of a large number of substances in petrol, among them being chromium naphthenate which gave a decrease of 4.2 octane numbers at a concentration of 3.0 grams per litre. This result is in direct contradiction to the observations of previous workers.

In none of the cases mentioned above was any attempt made to vary the concentration of chromium compounds in the fuel being tested. An arbitrary concentration was taken and the effect determined. The reason for this is that many of the workers on this subject tested large numbers of possible anti-knock compounds in a rather empirical way rather than investigated thoroughly a single compound.

The published data on chromium compounds as anti-knock additives for petroleum is therefore very contradictory and a more detailed study of the subject seems justified.

Organic Chromium Compounds.

One of the necessary properties of an anti-knock compound is that it should be soluble in hydrocarbon solvents. This prevents the use of the common inorganic compounds of chromium which are unsoluble in non-polar solvents. Many anti-knock compounds are organometallic in character and the

literature on organometallic compounds of chromium was
therefore studied.

Most of the work on these compounds has been performed
by a German school of workers under Hein[32]. Hein and his co-
workers have prepared compounds of the phenyl chromium halide
type (eg. $Ph_5CrBr, Ph_4CrBr, Ph_3CrBr$). These compounds are
rather unstable thermally and are sensitive to light and oxygen.
Tetraphenyl chromium (Ph_4Cr) and triphenyl chromium (Ph_3Cr) have
also been prepared but they are even more unstable than the
phenyl chromium halides. Alkyl chromium compounds are unknown
and appear to be too unstable to exist. The stability of
organometallic compounds of chromium has been found to depend
to an extraordinary extent on the degree of saturation of the
carbon atom directly linked to the chromium[33], stability
decreasing with increasing saturation. Thus alkyl chromium
compounds appear to be too unstable to exist although numerous
aryl compounds have been prepared. It has been found that
substitution in the benzene ring lessens the stability of the
aryl chromium halides.

Chromium Carbonyl.

The importance of the carbon atom directly linked
to the chromium having a high degree of unsaturation suggested
the possibility of chromium carbonyls being suitable and the
appropriate literature was studied. The only carbonyl of
chromium recorded in the literature is chromium hexacarbonyl
($Cr(CO)_6$), a colourless crystalline compound which sublimes

slowly at room temperature[34]. It is very stable chemically, being unaffected by concentrated hydrochloric or sulphuric acid at room temperature. Chromium hexacarbonyl melts at 149-150°C. on a sealed tube, is stable to bromine and iodine, yields chromic chloride with chlorine, and decomposes with fuming nitric acid. Chromium hexacarbonyl is sparingly soluble in most organic solvents. Despite its chemical stability its solutions are somewhat unstable to light. The above properties indicated that chromium hexacarbonyl might be a suitable medium for introducing chromium into a hydrocarbon solvent and the various methods of preparing the compound were studied.

Preparation of Chromium Hexacarbonyl.

Unlike the carbonyls of nickel and iron chromium hexacarbonyl cannot be obtained by reacting the metal with carbon monoxide under high pressure and temperature. Five groups of workers have described methods of preparing the compound.

(a) Method of Job and Cassal.

The existence of chromium hexacarbonyl was first established by two French workers, Job & Cassal[35], in 1927 when they obtained small quantities of the compound during a study of the reaction between carbon monoxide and phenyl magnesium bromide (PhMgBr) activated by anhydrous chromic chloride ($CrCl_3$). Job & Cassal later adapted this reaction to obtain improved yields of carbonyl[34].

The method consists of adding phenyl magnesium bromide to a violently agitated suspension of anhydrous chromic chloride in ether-benzene mixture in presence of carbon monoxide.   The reaction is exothermic and the temperature is maintained at 0-5°C. by means of a suitable cooling bath.   The reaction is controlled by the rate of addition of the Grignard.   Under these conditions carbon monoxide is absorbed.   The quantities used are

 Anhydrous Chromic Chloride ... 10 g. (1/15 mole)

 Benzene ...   50 c.c.

 Ether ...   50 c.c.

 Grignard Solution ... 200 c.c. (1/3 mole)

 Approximately 8 litres (c. 1/3 mole) of carbon monoxide are absorbed, the amount being in direct proportion to the amount of Grignard reagent used.

 When absorption ceases the reaction mixture is hydrolised with ice and dilute sulphuric acid.   The ether-benzene layer is decanted, neutralised with sodium bicarbonate, and dried over anhydrous magnesium sulphate.   The ether is then distilled off and the residual red liquid allowed to cool. A mixture of chromium hexacarbonyl and organic products crystallises out from this liquid, and after filtering, the carbonyl is removed by vacuum distillation and collected in a U-tube immersed in ice-salt mixture.   The carbonyl is further purified by recrystallisation from benzene and resublimation. Job & Cassal obtained a yield of "about 2 grams" by this method

and claimed that this represented a 22 per cent yield reckoned on the chromium. A simple calculation, however, reveals that their yield is equivalent to about 14 per cent of the theoretical.

Job & Cassal also describe a simplified method of preparation involving the use of ethyl magnesium bromide instead of the corresponding phenyl compound. When using ethyl magnesium bromide the organic products of the reaction are liquids and it is possible to separate the carbonyl from the ether-benzene layer left after hydrolysis. This is done by distilling off the ether and allowing the solution to cool. Job & Cassal do not state what yields they obtained by this method.

(b) Method of Windsor & Blanchard.

In 1934 two Americans, Windsor & Blanchard[36] attempted to duplicate Job's reaction. They failed to obtain any product and assumed that the carbonyl was being carried over with the ether during the removal of the ether from the ether-benzene layer. They therefore chilled with solid carbon dioxide and alcohol the ether-benzene layer remaining after hydrolysis. Under these conditions chromium hexacarbonyl crystallised from the solution and was purified as described by Job & Cassal. The yields obtained were about 1% of the theoretical. Windsor & Blanchard determined the vapour pressure of chromium hexacarbonyl at different temperatures and established that the vapour was monomolecular.

(c) Method of Hieber and Romberg.

In 1935 two German workers, Hieber & Romberg[37] published an adaptation of Job's method using ethyl magnesium bromide as the Grignard reagent. They simplified the separation of the carbonyl by steam distilling the whole reaction mixture after hydrolysis and concentrating the ethereal portion of the distillate by further distillation. The yield of carbonyl obtained was very uncertain, the maximum being 14% of the theoretical (based on chromium).

(d) Method of Anissimov & Nesmeyanov.

In 1940 two Russian workers, Anissimov & Nesmeyanov[38] published another variation of Job's method. They mixed phenyl magnesium bromide in ether with a stirred suspension of anhydrous chromic chloride in ether and added the reaction mixture to a rocking autoclave where they introduced carbon monoxide at 115 atmospheres pressure. Anissimov & Nesmeyanov claimed that temperature had little or no effect at this pressure and so conducted the reaction at room temperature. The subsequent treatment of the reaction mixture was the same as that used by Hieber & Romberg. Yields of up to 22% of the theoretical were claimed by this method.

(e) Method of Owen, English, Cassidy, & Dundon.

The most recent method of synthesising the carbonyl was published in 1947 by an American, Owen, and his co-workers[39]. In this method pure anhydrous chromic chloride was suspended in dry ether in a glass bomb liner with stirring and in an atmosphere of nitrogen. The vessel was cooled to about -70°C. and a solution of phenyl magnesium bromide in ether was added slowly

to the cold suspension. The liner was then removed from the cooling bath and transferred to a bomb capable of being rocked mechanically. Carbon monoxide was admitted and the pressure raised to 50 atmospheres. As the temperature of the bomb and its contents rose absorption of carbon monoxide took place and this was allowed to proceed for about two hours, during much of which time the bomb was at room temperature. Thereafter the procedure followed that described by Hieber & Romberg. Yields as high as 67% of the theoretical were claimed.

Owen et al. also published a low pressure method of preparing chromium hexacarbonyl. A suspension of 12 grams of anhydrous chromic chloride in ether was stirred at about 5000 r.p.m. and cooled to - 70°C. in a carbon dioxide-acetone bath. Without interrupting the stirring 210 cc. of 2.7N. phenyl magnesium bromide in ether was added over a period of one hour. The carbon dioxide-acetone bath was then replaced by an ice bath and carbon monoxide was introduced through the gas inlet at a rate of 220 litres per hour. After about 10 minutes the mixture warmed up to - 10°C. at which temperature the reaction began as evidenced by a change in colour. The reaction was allowed to proceed 15-30 minutes longer, the temperature being 0°C. during most of this period. Thereafter the method followed that of Hieber & Romberg. Yields of up to 24% of the theoretical were obtained. Lower stirring speeds, lower rates of gas flow, and more concentrated solutions were found to decrease the yield.

When the work reported in this thesis was started
the existence of the recent American method of Owen et al.
was not known to the author and the other methods were
therefore studied to decide which was most suitable for the
preparation of a supply of chromium hexacarbonyl.   The method
described by Job & Cassal was rejected since both Windsor &
Blanchard and Hieber & Romberg had failed to obtain reasonable
yields when attempting to duplicate the method.   The method
of Hieber & Romberg was considered preferable to that of
Anissimov & Nesmeyanov since it was deemed that the increase
in yield from 14% to 22% claimed by the latter workers was
insufficient to justify the increased risk and inconvenience
of working with carbon monoxide at high pressures.   It was
therefore decided to duplicate the method of Hieber & Romberg
and to attempt to improve it.

PREPARATION OF CHROMIUM HEXACARBONYL.

Preparation of Intermediates.

The following substances are required in the

chromium hexacarbonyl

Anhydrous chromic chloride ($CrCl_3$).

Pure dry carbon monoxide.

A Grignard reagent:- either ethyl magnesium bromide ($EtMgBr$) or phenyl magnesium bromide ($PhMgBr$).

Pure dry ether and pure dry benzene.

these Intermediates is now described.

SECTION I. Chromic Chloride ($CrCl_3$)

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found to be a basic salt of empirical

where x= y = 3. None of these forms of

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the anhydrous chloride by passing a stream

chromium sesquioxide at 440°C. and by heating

chloride in a stream of dry hydrochloric

SECTION I.

PREPARATION OF CHROMIUM HEXACARBONYL.

A. Preparation of Intermediates.

The following substances are required in the preparation of chromium hexacarbonyl.

1) Anhydrous chromic chloride ($CrCl_3$).

2) Pure dry carbon monoxide.

3) A Grignard reagent:- either ethyl magnesium bromide (EtMgBr) or phenyl magnesium bromide (PhMgBr).

4) Pure dry ether and pure dry benzene.

The preparation of these intermediates is now described.

1)...Preparation of Anhydrous Chromic Chloride ($CrCl_3$)

The readily available commercial forms of chromic chloride are mostly hydrates such as $CrCl_3 \cdot 6H_2O$.   Several firms supply "dry chromium chloride" and this was obtained and examined.   It was found to be a basic salt of empirical formula $Cr(OH)_x Cl_y$ where $x + y = 3$.   None of these forms of chromium chloride can be dried by heating since they undergo auto-hydrolysis to hydrochloric acid and chromium sesquioxide. Attempts to prepare the anhydrous chloride by passing a stream of chlorine over chromium sesquioxide at 440°C. and by heating hydrated chromic chloride in a stream of dry hydrochloric acid gas, failed to produce the substance in a pure state.

The method finally adopted was to heat metallic chromium in a stream of dry chlorine[4c].   For complete purity

chromic chloride requires to be sublimed and the method of preparation used was devised to effect the formation and sublimation of the substance in one operation.

Procedure:- Five to ten grams of finely powdered chromium metal (99.5% pure) was weighed and sprinkled along the bottom of a silica tube (30 ins. long x 1 in. diam.) as shown in Figure 1. The tube was filled with dry chlorine and a steady flow of dry chlorine maintained through it. The middle portion of the tube was then heated in an electric furnace to over 1000°C. Under these conditions the chromium combined with the chlorine and the chromic chloride thus formed sublimed from the hot section of the silica tube and condensed in the cooler sections outside the furnace as shown in Figure 1. Some of the chromic chloride (about a tenth) condensed in the form of a very fine powder which was carried out of the tube and collected in a flask known as the sublimate receiver.

When the furnace had cooled the product was collected and weighed, the product from the sublimate receiver being stored separately. The product from the sublimate receiver was a light pink-purple powder which showed no apparent sign of crystalline form. The product from the silica tube consisted of a mixture of deep violet lustrous flaky crystals and apparently amorphous violet powder.

A considerable number of batches of anhydrous chromic chloride were prepared by this method, a total of 500 g. being obtained. The yields varied from 85 to 95%.

FIGURE I

PREPARATION OF ANHYDROUS CHROMIC CHLORIDE
DIAGRAM OF SILICA TUBE.

FURNACE.

CHLORINE IN

TO SUBLIMATE RECEIVER

ORIGINAL POSITION OF CHROMIUM POWDER

FINAL POSITION OF CHROMIC CHLORIDE.
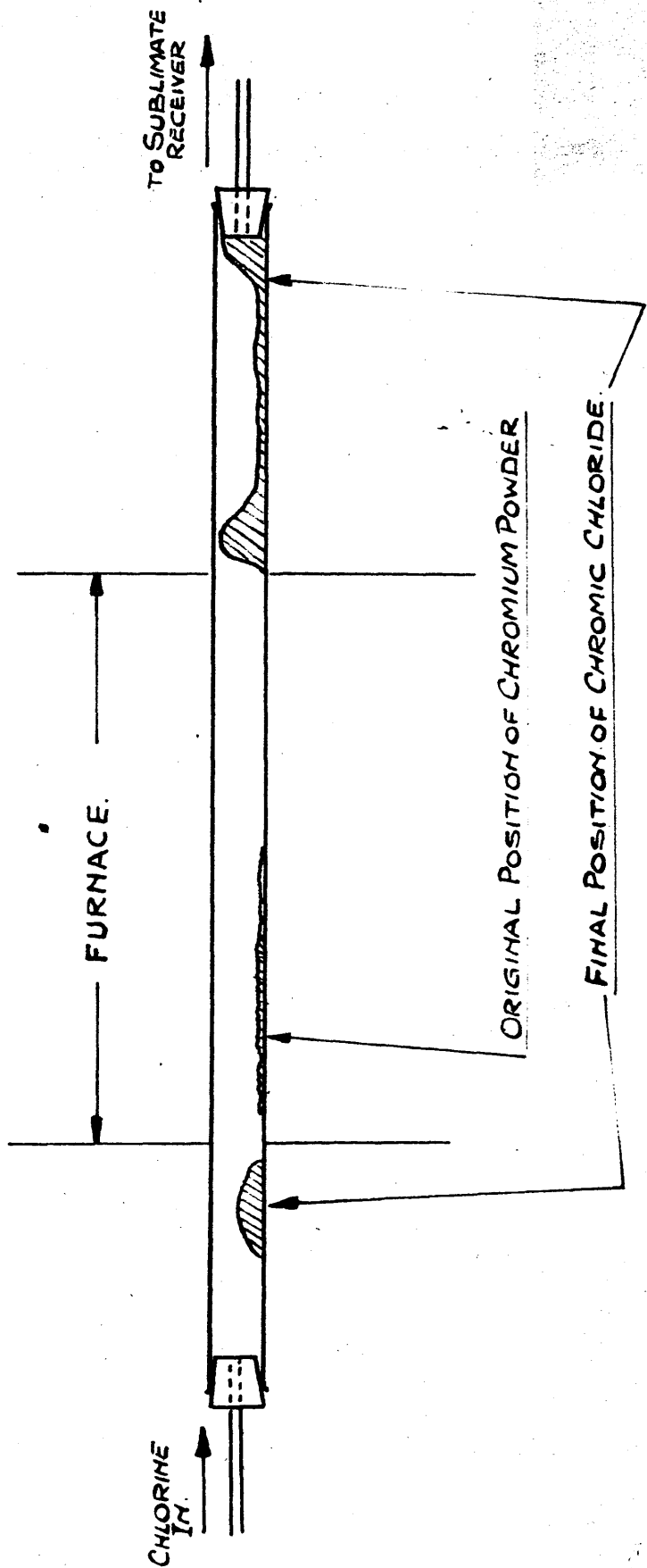
Properties of anhydrous chromic chloride:

      Colour:- Varies from pale pink to deep violet
                  according to crystalline form.

   Solubility:- Insoluble in aqueous or organic solvents,
                though the presence of a trace of chromous
                salt renders it soluble in aqueous solvents.
                Unlike hydrated chromic chloride the salt
                is non polar in character.

Sublimation
Temperature:- 1065°C.

2) Preparation of Pure Dry Carbon Monoxide.

      This was originally prepared by adding formic acid
to concentrated sulphuric acid and applying gentle heat, the
gas being subsequently stored over water in a 50 litre capacity
gas holder and dried before use by passing through anhydrous
calcium chloride. The carbon monoxide prepared in this way
was at least 99.95% pure as indicated by absorption over
ammoniacal cuprous chloride.

      Latterly pure carbon monoxide was obtained direct
from a high pressure cylinder.

3) Preparation of Ethyl Magnesium Bromide (EtMgBr) and Phenyl
Magnesium Bromide (PhMgBr).

      The Grignards were prepared by adding ethyl bromide
(EtBr) or bromobenzene (PhBr) to a flask containing dry
Magnesium and dry ether, the reaction being controlled by the
rate of addition of bromide and by a cooling bath surrounding
the flask. The reaction was conducted in an atmosphere of

nitrogen.

4) Preparation of Pure Dry Ether and Pure Dry Benzene.

Pure "Anaesthetic Ether" and "Analar Benzene" were each dried by calcium chloride followed by sodium metal.

B. Preparation of Chromium Hexacarbonyl by the Method of Hieber & Romberg.

The method has already been outlined in the introduction to this thesis (p.18). The apparatus had the form shown in Figure 2. Slight alterations to the apparatus were made during the course of the work. These variations are detailed below and will be referred to later.

Apparatus A. The carbon monoxide came from a gas-holder in which it was stored over water. Several additional U-tubes containing anhydrous calcium chloride were used to dry the gas before it entered the reaction flask. The capacity of the reaction flask was 1 litre. The importance of rigid temperature control was not fully realised at the commencement of the work and the thermometer was in the ice-bath and not in the reaction flask itself.

Apparatus B. The carbon monoxide came from a high pressure cylinder and one U-tube containing anhydrous calcium chloride was sufficient to dry the gas. In other respects the apparatus was as described in "Apparatus A".

Apparatus C. This is shown in Figure 2. A thermometer was incorporated in the reaction flask which was scaled up to 3 litres capacity. The carbon monoxide came from a high pressure cylinder.

FIGURE 2

PREPARATION OF
CHROMIUM HEXACARBONYL
BY THE METHOD OF
HIEBER AND ROMBERG

GRIGNARD SOLUTION

HIGH-SPEED LINK
STIRRER WITH
MERCURY SEAL

REACTION FLASK.

ETHER

TO OUTSIDE
ATMOSPHERE.

THERMOMETER

ICE-WATER MIXTURE.

CALCIUM CHLORIDE

ETHER

C.O. IN
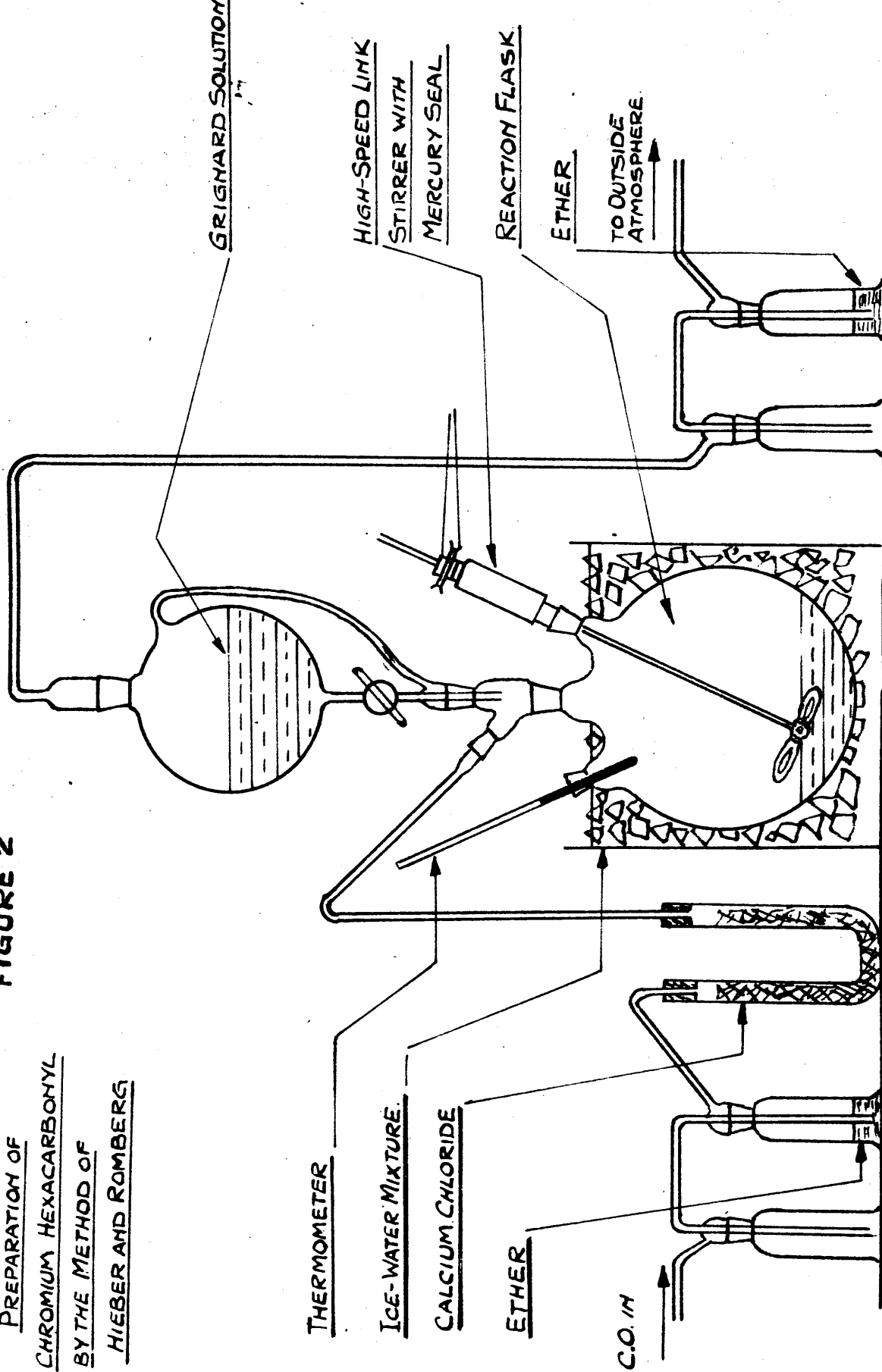
Procedure:-   The chromic chloride and ether
benzene mixture were added to the carefully dried reaction
flask, the apparatus being then assembled as shown in Figure
2.   Carbon monoxide was allowed to flow through the apparatus
until the latter was considered to contain an atmosphere
consisting almost entirely of the gas.   The stirrer was now
started and its speed adjusted to give as intimate contact as
possible between the liquid and gas in the reaction flask.
Approximately 20 cc. of Grignard solution (this quantity applies
to the 3-litre capacity flask used in Apparatus C.   In Apparatuses
A and B the quantity was about 5 cc.) was allowed to drop into
the reaction flask from the funnel.   Very little carbon
monoxide was absorbed for about 15 minutes, after which time
the reaction set in.

After the original addition the Grignard solution was
added in amounts of approximately five cc. at a time.   After
each addition of Grignard the temperature of the reaction
flask rose by about one centigrade degree.   The frequency of
addition of Grignard was adjusted to maintain the temperature
within the required limits - usually 0 - 5°C.   Throughout
the duration of the reaction the ice-water bath surrounding
the reaction flask was maintained at 0°C. by frequent additions
of ice.   The violent stirring of the contents of the reaction
flask was continued until all the Grignard had been added and
thereafter until no further carbon monoxide was absorbed.

The contents of the reaction flask, a dark brown
liquid containing suspended solids, were then poured for

hydrolysis into a mixture of ice and 25% sulphuric acid. During the hydrolysis a heavy yellow floculent precipitate appeared with each addition of the reaction mixture to the acid-ice mixture. This precipitate, however, disappeared on stirring until about half the reaction mixture had been added to the acid. Thereafter the precipitate persisted.

When hydrolysis was complete the whole hydrolysis mixture was steam distilled. The product which came over first in the steam distillate consisted mainly of ether and contained no chromium hexacarbonyl. The bulk of the hexacarbonyl did not distil until the ethereal layer in the distilland had almost disappeared: it then came over fairly rapidly, the white crystals almost blocking the condenser. Soon after this the water in the distilland boiled and thereafter no further chromium hexacarbonyl distilled over.

After the steam distillation the ether-benzene layer of distillate was separated and the aqueous layer extracted several times with ether. The combined ethereal extract was concentrated by distillation, the temperature not being allowed to exceed 60°C. After the distillation the concentrate was allowed to stand in an ice bath overnight to complete crystallisation. The liquid was then filtered, the white solid obtained being immediately put into a stoppered bottle.

The chromium hexacarbonyl thus obtained is associated with strongly smelling organic products from which it must be separated by vacuum resublimation. The sublimation was conducted at 100°C. and 20 cm. mercury pressure, the

hexacarbonyl being condensed on a surface maintained at 5 - 10°C.

Results:-

Details of the various attempts to prepare chromium hexacarbonyl are given in Table 1 overleaf.

In the first nine experiments (using Apparatus B) a study was made of the effects on the reaction of variation in the quantity and exact composition of the Grignard employed. It was found that if a large excess of ethyl bromide was used in preparing the Grignard the onset of carbon monoxide absorption was delayed and the subsequent reaction was unsuccessful. It was very difficult to draw any definite conclusions from the other results since even if the conditions were reproduced as accurately as possible the resultant yields often differed considerably:- viz. Preparations (1), (2) and (6); and Preparations (8) and (9). There did not appear to be any advantage in using excess Grignard. Thus the yields in Preparations (9) and (11) are actually slightly higher than in Preparation (3).

During these initial experiments it was realised that the effect of small variations in temperature was even more striking than had been originally supposed. It was therefore decided that a closer control of temperature was advisable and this was achieved by including a thermometer within the reaction flask. Preparations (10) to (14) were all carried out in Apparatus C. The results shown in Table 1

Table I

Preparation of Chromium Hexacarbonyl by the Method of Hieber & Romberg.

Preparation No.	Apparatus used. (v.p)	Grignard		Weight of CrCl$_3$ (g.).	Vol. of ether-benzene mixture (cc.).	Molar ratio of Mg to Cr.	Grams CrCl$_3$ per l. of suspension.	Temp. of reacn. flask (°C.).	Duration of reacn. (mins.).	Time for reacn. to start (after addition of Grignard) (mins.).	Yield (g.).	Yield % based on Cr.	COMMENTS.
		Weight of EtBr (g.).	Weight of Mg (g.).										
1	B	54	12	10	220	8:1	45	–	–	–	Nil	Nil	Grignard added too rapidly. Temp. in reacn. flask rose. Exothermic reacn. set in. No further CO absorbed and no chromium hexacarbonyl obtained.
2	B	54	12	10	220	8:1	45	–	–	–	0.019	0.14	Reacn. apparently normal but subsequent hydrolysis seemed to cause rise in temp. due to insufficient ice having been added to the sulphuric acid. This may be responsible for the low yield.
3	B	67	15	10	220	10:1	45	–	–	–	1.20	8.6	Slightly more Grignard used. Reacn. successful.
4	B	102	15	10	220	10:1	45	–	–	–	Nil	Nil	In previous Grignard preparations some unreacted Mg always remained. Accordingly 50% excess halide was used in preparing the Grignard. The reaction was much slower in starting than usual and more Grignard was added. After about 2 litres CO had been absorbed an exothermic reacn. set in, a gas being given off and the reacn. mixture boiling. This may have been due to over rapid addition of Grignard.
5	B	66	13.2	10	220	8.7:1	45	–	–	–	0.40	2.9	12% excess EtBr used in preparing Grignard. Reacn. apparently normal though rather slow in starting. The temp. rose rather higher than usual during hydrolysis.
6	B	54	12	10	220	8:1	45	–	–	–	0.77	5.6	Reacn. successful. No excess EtBr in Grignard. Mg to Cr ratio back to 8:1.
7	B	67	15	10	220	10:1	45	–	–	–	0.15	1.1	Grignard added too rapidly. The temp. of the reacn. flask is believed to have risen above 5°C.
8	B	57	12	10	220	8:1	45	–	–	–	0.42	3.0	" " " " "
9	B	57	12	10	220	8:1	45	–	–	–	1.32	9.5	Reacn. successful. EtBr was used in slight excess of stoichiometric quantities to allow for the loss of the compound as vapour. The Grignard was added more slowly than in previous preparations.
10	C	162	36	30	420	8:1	71	0 – 5 Average c. 4.5	90	5	3.04	7.3	Reacn. successful. More accurate temp. control achieved. After each addition of Grignard to the reacn. flask a very rapid absorption of CO occurred. No excessive heat was developed during the hydrolysis.
11	C	216	48	40	560	8:1	71	0 – 4.5 Average c. 4	170	5	4.90	8.8	" " " " "

Table I

(continued)

Preparation No.	Apparatus used. (v.p)	Grignard Weight of EtBr (g.).	Weight of Mg (g.).	Weight of CrCl₃ (g.).	Vol. of ether-benzene mixture (cc.).	Molar ratio of Mg to Cr.	Grams CrCl₃ per l. of suspension.	Temp. of reacn. flask (°C.).	Duration of reacn. (mins.).	Time for reacn. to start (after addition of Grignard) (mins.).	Yield (g.).	Yield %. based on Cr.	COMMENTS.
12	C	216	48	40	560	8:1	71	0 – 6 Average $\underline{c}$. 4.5	240	15	0.92	1.7	This reacn. was conducted on a very hot day, the temp. of the lab. being 31°C. It was especially difficult to keep the temp. of the reacn flask low and the Grignard entering it was also unusually warm. In addition the stopper of the flask in which the Grignard was stored blew off overnight exposing the solution to air. The temp. also rose too high during the hydrolysis. The sludge on the bottom of the reacn. flask after the completion of the reacn. was much greater than was found in Preparations Nos. 10 and 11.
13	C	216	48	40	560	8:1	71	0– 4 Average $\underline{c}$. 3	115	15	2.28	4.1	Reacn. fairly successful. The absorption of CO after each addition of Grignard was not quite so rapid as in Preparations 10 and 11. The chromic chloride was ground by a coffee mill and not by hand as previously. The chloride was more finely and evenly ground but may have become slightly hydrated and hydrolised in the process.
14	C	216	48	40	560	8:1	71	0 – 4.5 Average $\underline{c}$. 3.5	170	70	Nil	Nil	Chromic chloride again ground by coffee mill. The reacn. mixture became very viscous and the stirrer could not work efficiently. The reason for the apparent increase in viscosity is not known. The reacn. took more than an hour to start and even then absorption of CO was very slow.
15	B	54	12	10	220cc. ether - chloroform.	8:1	45	–	–	–	Nil	Nil	Ether-chloroform mixture was used in place of ether-benzene mixture without success.
16	B	54	12	10	220	8:1	45	$\underline{c}$. –10°C.	–	–	Nil	Nil	In this reacn. the cooling bath was maintained at –12°C. The reacn. does not appear to proceed at temperatures below 0°C. Very little CO was absorbed and no chromium hexacarbonyl was obtained.
17	B	54	12	10	220	8:1	45	$\underline{c}$. –10°C.	–	–	Nil	Nil	
18	A	54	12.	10	220	8:1	45	–	300	5	1.03	7.4	The vol. of CO absorbed was recorded by measuring the level of the gasholder before and after the reacn. Vol. of CO absorbed = 8.6 l. (corrected to N.T.P.) = 0.38 mole. EtMgBr present = 0.50 mole; CrCl₃ present = 0.063 mole.

indicate that it is important not to exceed 5°C. and it seems possible that less than 3°C. may be rather low. Despite the similarity of conditions in Preparations (10) to (14) there was considerable variation in the yields obtained. The low yield obtained in Preparation (12) can be accounted for by assuming that the temperature in the reaction flask reached too high a level. Similarly the failure of Preparations (16) and (17) is probably due to too low a temperature. This however does not explain the anomalous result in Preparation (14).

An attempt to replace ether-benzene by ether-chloroform as the suspension medium (Preparation (15)) was unsuccessful, the yield of chromium hexacarbonyl being negligible.

Preparation (18) was performed to determine the quantity of carbon monoxide absorbed.

C. Preparation of Chromium Hexacarbonyl by the Method of Owen, English, Cassidy and Dundon.

A summary of Owen's method has already been given in the introduction to this thesis (p.18). Owen described two methods of preparing the carbonyl, one at atmospheric pressure and the other at 50 atmospheres. An attempt was made to duplicate and, if possible, improve the low pressure method.

A diagram of the apparatus is shown in Figure 3.

Procedure:- Finely powdered anhydrous chromic chloride (12 grams) and pure dry ether (700 cc.) were added to the reaction flask C, the apparatus then being assembled as shown in Figure 3. The stirrer was started and its speed adjusted to give

FIGURE 3

PREPARATION of CHROMIUM HEXACARBONYL BY THE METHOD of OWEN ET. AL.

High Speed Metal Stirrer with Mercury Seal

Condenser

Acetone Solid CO2 Mixture.

Thermometer

Reaction Flask

Ether.

To Outside Atmosphere.

Grignard Solution.

Cooling Bath

Acetone Solid CO2 Mixture.

Calcium Chloride.

Ether.

Coin.
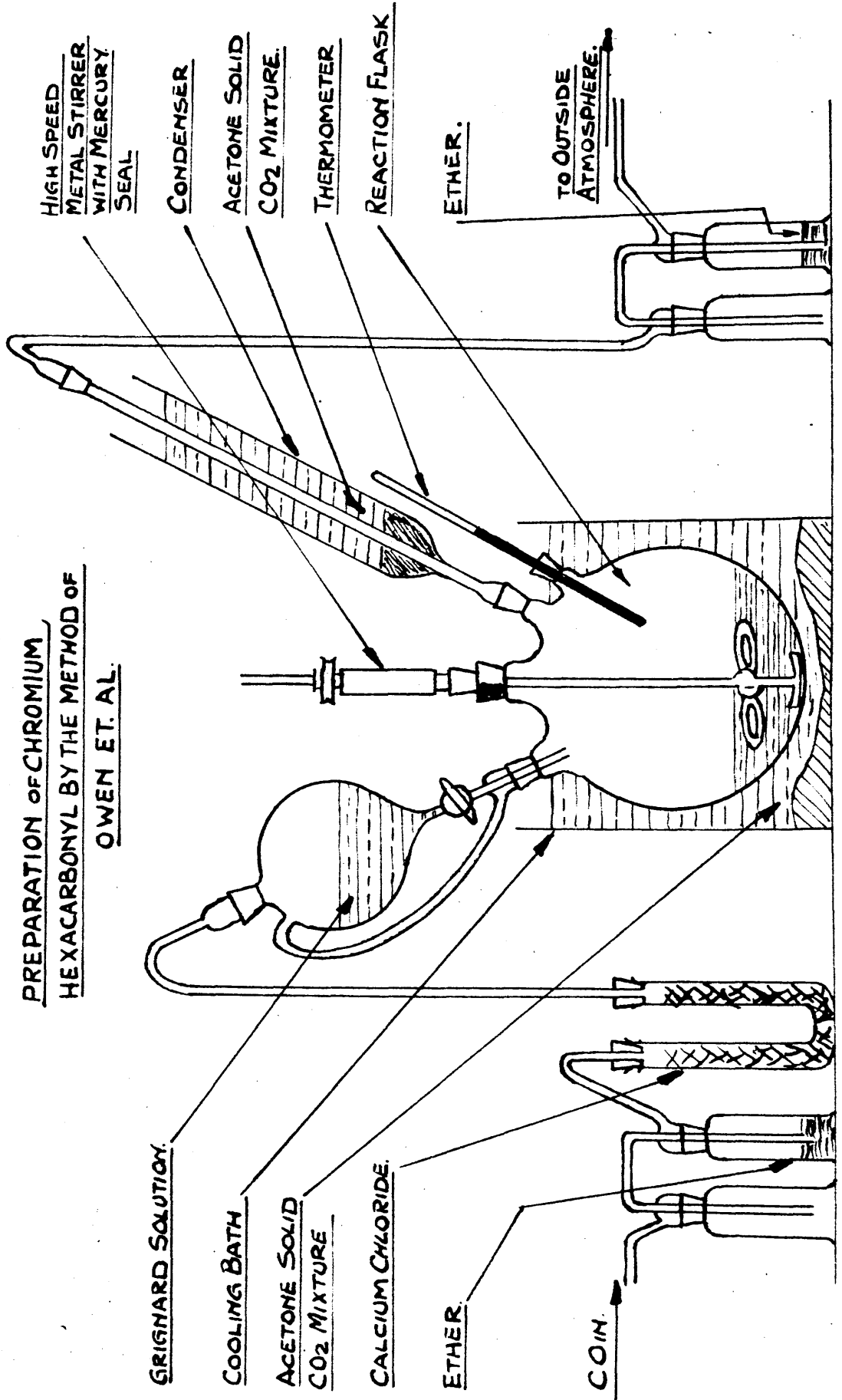
maximum agitation and gas-liquid contact within the flask.

Freshly prepared 2.7N. phenyl magnesium bromide
was placed in the dropping funnel F and slowly added to the
reaction flask over a period of one hour.   Each addition of
Grignard (c. 5 cc.) was accompanied by a temporary rise
in temperature of about 5 centigrade degrees indicating that
an exothermic reaction was taking place.   When about half
the Grignard had been added the liquid in the flask became
so viscous that the stirrer slowed down and tended to stop.
Further additions of Grignard reduced the viscosity and
improved the efficiency of the stirring.   When all the Grignard
had been added carbon monoxide was introduced, through the
gas inlet, at a high rate of flow and the cooling-bath was
replaced by an ice-water bath.   The stirring was not
interrupted.   No absorption of carbon monoxide took place
until the reaction flask warmed to -10°C. at which temperature
the reaction began as indicated by a change in colour of the
reaction mixture.   The absorption of carbon monoxide continued
for 20 to 30 minutes, during which time the colour of the
liquid in the reaction flask changed from deep violet to blood
red and finally to dark brown.   The temperature was at 0 - 3°C.
during most of this period.

At the finish of the reaction the contents of the
flask consisted of a dark brown liquid containing suspended
solids whose colour was masked by that of the liquid.   There
was also a solid deposit at the bottom of the flask.   This
appeared to consist partly of violet crystals of unreacted

anhydrous chromic chloride. The contents of the flask were poured for hydrolysis into a beaker containing ice, and 35 cc. of 6N. sulphuric acid was added. Before the hydrolysis no chromium hexacarbonyl could be extracted from the reaction mixture. The mixture was thoroughly stirred to ensure adequate contact of the ethereal and aqueous portions. Yellow and brown precipitates formed in the ethereal layer which remained brown in colour.

The separation of the carbonyl from the hydrolysis mixture was performed according to the method of Hieber & Romberg (p.26). During the concentration by distillation of the ethereal solution of carbonyl the temperature was not allowed to exceed 45°C, as compared with 60°C. in the method of Hieber & Romberg. The reason for the difference is the absence of benzene from the reaction mixture in the method of Owen et al.

One disadvantage of Owen's method was that the low temperatures at which the reaction was performed led to increased viscosity of the ethereal suspension with consequent difficulty in stirring. The stirrer must keep the solid in the suspension from settling and at the same time give good gas-liquid contact to encourage rapid absorption of the carbon monoxide. It was found that a propellor type stirrer gave good agitation of the suspension and prevented the solid from settling but did not give good gas-liquid contact. A link stirrer gave good gas-liquid contact but did not prevent the solid from settling. Owen et al. do not state what type of stirrer they used other

than that it was metal and operated at 5000 r.p.m. The stirrer finally devised was a combination of the link and propellor types (see Figure 4) which was operated at 3000 r.p.m. and proved satisfactory in giving good gas-liquid contact and in preventing settling of the solid on the bottom of the reaction flask. It was made of brass because it was found that glass stirrers broke under the high speed, high viscosity conditions.

Results:- Seven attempts were made to prepare chromium hexacarbonyl by Owen's method, the details being given below.

Preparation No. 1......An ordinary brass link stirrer was used in this preparation. A considerable quantity of anhydrous chromic chloride settled at the bottom of the flask and remained unreacted at the conclusion of the experiment.

Yield of chromium hexacarbonyl = 0.06 g. (0.36%)

Preparation No. 2......The stirrer shown in Figure 4 was used in this and all subsequent preparations. During the addition of the Grignard the stirrer stopped and about five minutes elapsed before it could be restarted. By this time some of the suspended solid had settled at the bottom of the flask in a solid lump and the remainder was sticking to the sides. When the stirrer was restarted it could neither wash the solid from the sides of the flask nor break up the lumps. The solid, presumably a compound of the Grignard and the chromic chloride, was thus rendered very unreactive and no absorption of carbon monoxide took place.

FIGURE 4

BRASS STIRRER

LINKS

PROPELLOR.
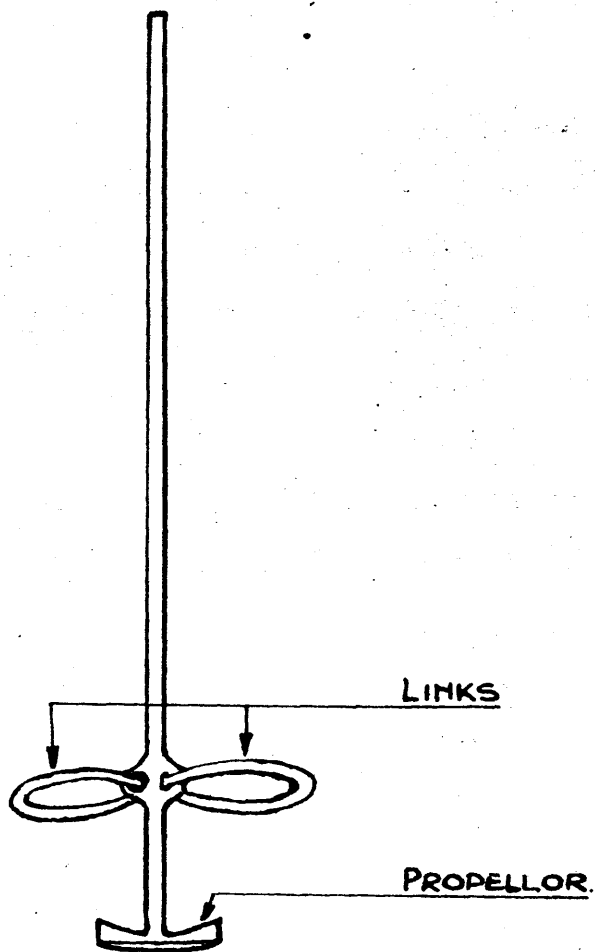
Yield of chromium hexacarbonyl = Nil

Preparation No. 3......The only apparent fault in this preparation was a temporary decrease in the speed of the stirrer when about half the Grignard had been added.   Some unreacted chromic chloride remained after the reaction but a considerable quantity of carbon monoxide was absorbed.

Yield of chromium hexacarbonyl = 0.31 g. (1.9%)

Preparation No. 4......The stirrer stopped for about 30 seconds during the addition of the Grignard and the reaction mixture behaved as in Preparation No. 2.

Yield of chromium hexacarbonyl = Nil.

Preparation No. 5......The stirring was extremely good throughout the addition of the Grignard but for no apparent reason the suspended solid again adhered to the sides of the flask, leaving the liquid clear.   No absorption of carbon monoxide took place at 0-5°C. and an attempt to obtain absorption by increasing the temperature failed.

Yield of chromium hexacarbonyl = Nil.

Preparation No. 6......The stirring remained extremely good during the addition of the Grignard, which was added more frequently and in smaller portions.   A considerable quantity of carbon monoxide was absorbed.

Yield of chromium hexacarbonyl = 0.56 g. (3.4%)

Preparation No. 7......The apparently amorphous chromic chloride from the sublimate receiver (see page 22) was used in this preparation.   The finer particle size of this form of the chloride was expected to give greater reactivity and higher

yields of hexacarbonyl.   Unfortunately the solid coagulated
into lumps after a little of the Grignard had been added.
This took place despite good stirring and gradual addition of
the Grignard.   It occurred more readily than with the crystalline
chromic chloride used in previous preparations.

Yield of chromium hexacarbonyl = Nil.

In an attempt to improve on the yields obtained in the
preparations described above, various modifications were made
in Owen's method, the details being given below.

Preparation No. 8......The Grignard used in this preparation
was ethyl magnesium bromide instead of phenyl magnesium bromide.
No rise of temperature was observed after each addition of the
reagent but an unusual phenomenon occurred when about three
quarters of the Grignard had been added: the suspended solid
suddenly adhered to the walls of the flask, leaving a clear
solution.   This was accompanied by a rise in temperature of
about ten centigrade degrees, indicating that an exothermic
reaction of some sort must have occurred.   The absorption of
carbon monoxide did not commence until the temperature of the
reaction flask rose to 0°C;   this compared with -10°C. when
using phenyl magnesium bromide.   Some of the deposited solids
re-entered the liquid as a suspension and carbon monoxide was
absorbed for about 65 minutes.   The quantity of carbon
monoxide absorbed was not very large compared to previous
preparations (eg. Preparation No. 6).

Yield of chromium hexacarbonyl = 0.050 g. (0.30%)

Preparation No. 9......The carbon monoxide was introduced at the beginning of the reaction, i.e. before the addition of Grignard.   Very slight absorption of carbon monoxide occurred after each addition of Grignard, even at the low temperature of -70°C.   Absorption became rapid when the temperature of the flask was allowed to rise to 0°C. and a considerable quantity of the gas was absorbed.

Yield of chromium hexacarbonyl = 1.15 g. (6.9%)

Preparation No.10......In previous preparations it had been observed that the suspended solid tended to coagulate when the reaction was performed at -70°C.   Some lumps of solid always formed and it is likely that the solid would be less reactive in this form.   As appreciable absorption of carbon monoxide did not begin until the temperature of the reactants rose to -10 -0°C. it was decided to carry out the whole reaction at approximately 0°C.   It was not found possible to add all the Grignard and then introduce the carbon monoxide as this caused a very rapid absorption of the latter accompanied by a sudden rise in temperature.   The carbon monoxide was therefore introduced from the start of the experiment and the Grignard was added at a sufficiently slow rate to maintain the temperature below 5°C. The method was thus similar to that employed by Hieber & Romberg, the differences being in the strength and composition of the Grignard and the use of ether instead of ether-benzene mixture as the suspension medium.

Yield of chromium hexacarbonyl = 0.78 g. (4.6%).

Preparation No. 11......This was a repetition of Preparation 10

with the exception that the fine amorphous chromic chloride
was used.   The coagulation observed when using this form
of chromic chloride at -70°C. did not occur at 0 - 5°C.

Yield of chromium hexacarbonyl = 1.77 g. (10.6%)
Preparation No. 12......This preparation was carried out in
order to establish whether commercial "dry chromium chloride"
(see p.21) could be used in place of the anhydrous variety.
The reaction was unsuccessful, no carbon monoxide being absorbed.

Yield of chromium hexacarbonyl = Nil.

Table II summarises the various attempts made to
prepare chromium hexacarbonyl by the method of Owen et. al.
(with and without modifications), the yields obtained being
given.   For convenience, the following abreviations are used:-

A.G.   After the addition of the Grignard.

B.G.   Before the addition of the Grignard i.e. From the start
       of the reaction.

C.   Crystalline anhydrous chromic chloride.

A.   Apparently amorphous anhydrous chromic chloride.

B.   Commercial "pure dry chromium chloride" - Probably basic.

Results.

(a)   The maximum yield of chromium hexacarbonyl
obtained by Owen's method was 3.4% of the theoretical.   (Yield
claimed by Owen et al. = 24%).

(b)   It is essential to maintain continuous fast
stirring during the carbon monoxide absorption stage of the
preparation.

(c)   Introduction of the carbon monoxide before the

Table II

Preparation of Chromium Hexacarbonyl by the Method of Owen et al.

Preparation No.	Grignard used.	Temp. at which Grignard added.	Time of introduction of CO.	Type of $CrCl_3$ used.	Yield %	Remarks.
1	PhMgBr	-70°C.	A.G.	C	0.36	Ordinary link stirrer used. Stirring poor.
2	"	"	"	"	Nil	Stirrer stopped.
3	"	"	"	"	1.9	Stirrer slowed down.
4	"	"	"	"	Nil	Stirrer stopped.
5	"	"	"	"	Nil	Stirring good. Reason for failure unknown.
6	"	"	"	"	3.4	Stirring good. Grignard added in smaller portions than previously.
7	"	"	"	A	Nil	Suspension coagulated into lumps.
8	EtMgBr	"	"	C	0.30	EtMgBr not suitable for low temps.
9	PhMgBr	"	B.G.	"	6.9	This modification improves the yield.
10	"	0°C.	"	"	4.6	Suspension did not coagulate into lumps.
11	"	"	"	A	10.6	No coagulation. 'A' type of $CrCl_3$ best at 0°C.
12	"	-70°C.	A.G.	B	Nil	No absorption of CO. Reaction unsuccessful.

addition of the Grignard improves the yield considerably.
This is probably due to the resultant exclusion of air.

(d) The cooling of the chromic chloride suspension
to -70°C before the addition of the Grignard was found to be
of no advantage, better yields being obtained when the whole
reaction was carried out at approximately 0°C.

(e) The apparently amorphous finely powdered
anhydrous chromic chloride is unsuitable for the preparation
of chromium hexacarbonyl when the reaction is conducted at -70°C
but gives better yields than the crystalline variety when the
reaction temperature is 0°C.

(f) Phenyl magnesium bromide cannot be successfully
replaced by ethyl magnesium bromide when the Grignard is added
at -70°C.

(g) No yield of chromium hexacarbonyl is obtained if
the anhydrous chromic chloride is replaced by commercial "pure
dry chromium chloride".

D. Attempt to Prepare Chromium Hexacarbonyl by the Method of
Kocheshkov, Nesmeyanov, Nadj, Rossinskaya, and Borissova.

Kocheshkov et al.[41] prepared molybdenum and tungsten
hexacarbonyls by a modification of the method of Hieber &
Romberg in which they replaced the Grignard reagent with
powdered zinc. They stated that at the time of publication
of their paper they had not attempted to apply the method to
chromium hexacarbonyl. In view of the similarities between
previous methods of preparing chromium, molybdenum and tungsten

hexacarbonyls this seemed rather strange.   Nevertheless, the author made several attempts to prepare chromium hexacarbonyl by this method.   The procedure followed that of Hieber & Romberg (p. 24) with the exception that, instead of adding small portions of Grignard to the reaction flask, an equivalent quantity of powdered zinc (Molar ratio Zn/Cr = 10/1) was added in five portions.   Ether benzene mixture was used as the suspension medium and the reaction was conducted at 0-5°C. The pressure of carbon monoxide in the reaction flask was maintained slightly above atmospheric during the addition of each portion of zinc, in order to prevent air entering the flask.   No carbon monoxide was absorbed and no chromium hexacarbonyl obtained.

Result.

The method of Kocheshkov et al., for preparing molybdenum and tungsten hexacarbonyls from zinc and anhydrous chromic chloride in ether-benzene suspension exposed to carbon monoxide, is not applicable to chromium hexacarbonyl.

E.   Discussion of Reaction Mechanism.

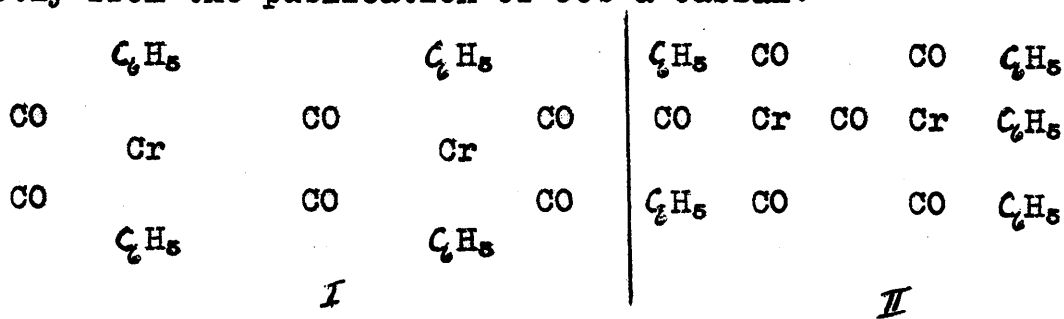All the groups of workers who have published literature on the preparation of chromium hexacarbonyl disagree regarding the reaction mechanism.

1)   Job & Cassal[35] studied the organic compounds formed by the Grignard reagent, phenyl magnesium bromide in presence of chromic chloride and carbon monoxide.   By involved processes of fractional crystallisation and fractional distillation they isolated the following compounds from the

reaction product:-

(1) Chromium hexacarbonyl $Cr(CO)_6$

(2) Phenol $Ph.OH$

(3) Diphenyl $Ph.Ph$

(4) Benzophenone $Ph.CO.Ph$

(5) Benzhydrol $Ph.CH(OH).Ph$

(6) Triphenyl vinyl alcohol $CPh_2:C(OH).Ph$

(7) Triphenyl carbinol $CPh_3.OH$

(8) Benzaldehyde $Ph.CHO$

(9) Benzopinacol $C(OH)Ph_2.C(OH)Ph_2$

(10) Benzoin $Ph.CO.CH(OH).Ph$

(11) Triphenyl methane $CHPh_3$

(12) Benzil $Ph.CO.CO.Ph$

The presence of all these compounds except chromium hexacarbonyl can be accounted for if the initial formation of benzil and benzophenone is assumed. Job & Cassal quote a large number of previously established reactions to support this. On this basis Job & Cassal suggest that the compound originally formed when phenyl magnesium bromide, chromic chloride and carbon monoxide react is a complex of the type shown below, containing chromium, phenyl groups, and at least six carbonyl groups. The structural formulae shown below are reproduced exactly from the publication of Job & Cassal.

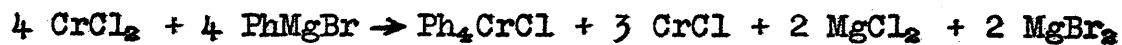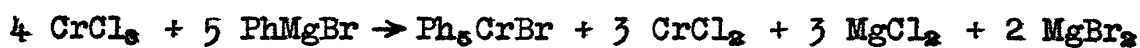|	C_6H_5			C_6H_5			C_6H_5	CO		CO	C_6H_5
CO			CO		CO		CO	Cr	CO	Cr	C_6H_5
	Cr			Cr							
CO			CO		CO		C_6H_5	CO		CO	C_6H_5
	C_6H_5			C_6H_5							

I II

These complexes could then decompose in different ways, giving chromium hexacarbonyl, benzil, and benzophenone as decomposition products.

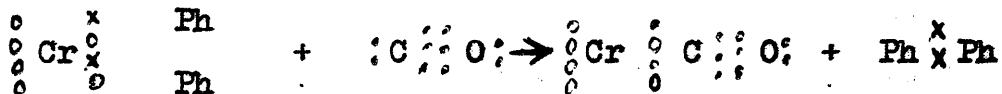Job & Cassal produce no direct evidence of the existence of these intermediate complexes.

2) Hieber & Romberg[87] studied methods of improving and simplifying Job's reaction. They found that ethyl magnesium bromide could be used instead of phenyl magnesium bromide without affecting the yield of carbonyl. They also obtained molybdenum hexacarbonyl and tungsten hexacarbonyl by a similar method and established that the three compounds were isomorphous.

They believe that the Grignard first reduces the chromium to a lower valency state and quote two equations given by Hein when discussing his work on phenyl chromium halides.

$$4 \ CrCl_3 + 5 \ PhMgBr \rightarrow Ph_5CrBr + 3 \ CrCl_2 + 3 \ MgCl_2 + 2 \ MgBr_2$$
$$4 \ CrCl_2 + 4 \ PhMgBr \rightarrow Ph_4CrCl + 3 \ CrCl + 2 \ MgCl_2 + 2 \ MgBr_2$$

Chromium in this lower valency state is more reactive and may form organometallic compounds, presumably of the type Ph_4Cr, Ph_3Cr or Ph_2Cr. These compounds would react with carbon monoxide forming a carbonyl of the organometallic compound. Such a carbonyl would have a formula of the type $R_xCr(CO)y$ where R is an alkyl or aryl group and $x + y = 6$. Finally the organometallic carbonyl would disproportionate with the formation of the hexacarbonyl. Alternatively, the organometallic compound originally formed might be converted

to a carbonyl directly by the replacement of alkyl or aryl
radicles with carbonyl groups:-

$$\overset{o}{\underset{o}{\overset{o}{_o}}}Cr\overset{x}{\underset{o}{_x}} \quad \overset{Ph}{\underset{Ph}{}} \quad + \quad :C\overset{..}{::}O: \rightarrow \overset{o}{\underset{o}{_o}}Cr\overset{o}{\underset{o}{}}C\overset{..}{::}O: \quad + \quad Ph\overset{x}{\underset{}{}}Ph$$
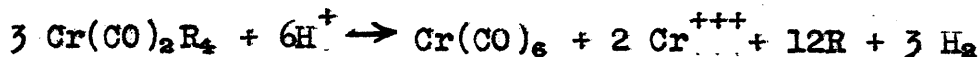
In the above equation the symbols (o), (x) and (·) represent
the electrons belonging to the chromium, phenyl and carbon
monoxide respectively.   The incomplete carbonyl would then
have to disproportionate to form chromium hexacarbonyl.

In support of their theory Hieber & Romberg point
out that disproportionation reactions of the type they assume
have been found to give the hexacarbonyl

$$2\ Cr(CO)_3A_3 + 3H^+ \rightarrow Cr(CO)_6 + Cr^{+++} + 6A + 1.5\ H_2$$
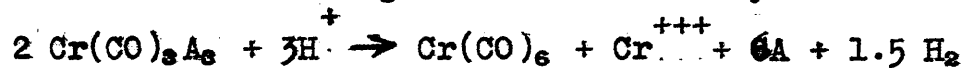
where 'A' is a neutral molecule.

$$3\ Cr(CO)_2R_4 + 6H^+ \rightarrow Cr(CO)_6 + 2\ Cr^{+++} + 12R + 3\ H_2$$

where 'R' is an organic residue capable of undergoing
further reaction.

The poor yield is partly explained by the fact that
in the hydrolysis free carbon monoxide and hydrogen are given
off, presumably due to reactions of the type:-

$$2\ Cr(CO)_3A_3 + 6H^+ \rightarrow 2Cr^{+++} + 6A + 6CO + 3\ H_2$$
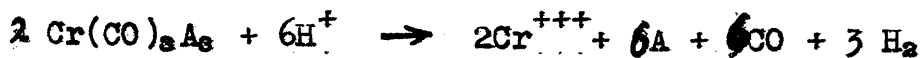
The organic compounds found by Job are said to be
due to the fact that the carbon monoxide combined with chromium
in compounds of the type $R_xCr(CO)_y$ would be exceptionally
active if it were liberated by the decomposition of the complex.
This active carbon monoxide would then combine with other
organic residues.

3) Kocheshkov, Nesmeyanov, Nadj, Rossinskaya & Borissova[41] repeated the experiments of Hieber & Romberg using a zinc suspension instead of a Grignard reagent. Molybdenum and tungsten hexacarbonyls were prepared in this way, the yields actually being superior to those obtained by Kocheshkov et. al. when using the Grignard. Anissimov & Nesmeyanov applied the method to chromium using high pressures and replacing ether-benzene by methyl or ethyl alcohol as a suspension medium. They obtained very small yields of chromium hexacarbonyl in this way.

Kocheshkov et al. do not agree with the theories of Hieber & Romberg or Job & Cassal. They believe that the main function of the Grignard is to reduce the chromic chloride to a lower halide which would then react with carbon monoxide to give chromium hexacarbonyl and chromic chloride.

e.g. $3\ CrCl\ +\ 12\ CO \rightarrow CrCl_3\ +\ 2\ Cr(CO)_6$.
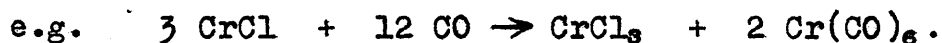
Kochleshkov et al. do not claim to have fully elucidated the mechanism of the reaction.

4) Owen, English, Cassidy & Dundon[89] do not advance any theory for the reaction mechanism but give their opinion that none of the previous theories is correct. They base this opinion on the fact that they have treated a mixture of phenyl chromium bromides with carbon monoxide under pressure and failed to obtain any chromium hexacarbonyl. Compounds of this type were assumed by Hieber & Romberg to be intermediates in the formation of the hexacarbonyl. They also replaced the chromic chloride used in previous methods by chromous chloride

prepared by reducing chromic chloride with hydrogen at
450°C.   They obtained only very poor yields of chromium
hexacarbonyl by this method although Hieber & Romberg and
Kocheshkov et al. had assumed that chlorides of chromium of
lower valency than chromic chloride were intermediates in the
formation of the hexacarbonyl.

Owen et al. also established that a compound formed
by the reaction of equimolecular proportions of Grignard and
chromic chloride appears to be an intermediate in the reaction.

Criticism of the Theories on Reaction Mechanism.

1)   Theory of Job & Cassal.

(i) No experimental evidence is produced to confirm
the constitution or even the existence of the hypothetical
complexes vital to the theory.

(ii) The maximum yield of chromium hexacarbonyl
obtainable from the decomposition of the complex intermediates
postulated by Job & Cassal would correspond to 50% of the
chromium originally present.   Owen et al., however, have
obtained conversion of over 60% of the chromium to the
hexacarbonyl.

(iii) Owen et al. established that the first
intermediate formed was produced by the reaction of one mole
of Grignard with one mole of chromic chloride.   The theory
of Job & Cassal does not explain this.

(iv) The theory does not explain the significant
effect of increased pressure on the yield.

2) <u>Theory of Hieber & Romberg.</u>

(i) This theory claims that phenyl chromium halides of the type prepared by Hein and/or lower valency chlorides of chromium are intermediates in the reaction. Owen <u>et al</u>., however, have attempted without success to react carbon monoxide with the phenyl chromium halides as prepared by Hein. They also failed to obtain any absorption of carbon monoxide when using chromous chloride in place of chromic chloride.

(ii) The theory is based on the formation of intermediate organometallic compounds of chromium; yet tungsten, which gives a higher yield of carbonyl by this method when either chromium or molybdenum has the least tendency to form organometallic compounds.

(iii) As in the theory of Job & Cassal there is an absence of concrete proof of the presence of the intermediates essential to the theory.

3) <u>Theory of Kocheshkov et al.</u>

This theory is much less precise than the previous two and is, therefore, less liable to detailed criticism on specific points.

(i) The complex organic products found by Job & Cassal prove that there is more in the reaction than a simple reduction and substitution.

(ii) Owen <u>et al</u>. failed to obtain a good yield of chromium hexacarbonyl when using chromous instead of chromic chloride. This suggests that the Grignard does not function simply to reduce the chromium to a lower valency state.

(iii) The theory does not explain the intermediate discovered by Owen when one mole of Grignard is allowed to react with one mole of chromic chloride.

The reaction mechanism in the formation of chromium hexacarbonyl is thus very uncertain and it seems unlikely that any of the theories so far advanced is absolutely correct. It is possible that several completely different reaction mechanisms are involved, the mechanism depending on the conditions of the experiment, but this seems unlikely in view of the similarity between the various methods of preparation.

An explanation of the reaction mechanism should be consistent with the following facts:-

1) The reaction is very sensitive to temperature when conducted at atmospheric pressure, the narrow temperature range of 0 - 5°C being essential for optimum yield (Established by Hieber[37] and confirmed by the author (p.27).

2) The nature of the solvent used for suspending the anhydrous chromic chloride is of importance. Ether alone (Owen et al.[39] Anissimov & Nesmeyanov[38]), acetone and methyl and ethyl alcohol (Anissimov & Nesmeyanov[38]) have been used with some success but ether-chloroform appears to be ineffective (author (p.28)).

3) There is an intermediate product formed when one mole of phenyl magnesium bromide and one mole of anhydrous chromic chloride are allowed to react to completion. Treatment of this intermediate with carbon monoxide leads to good yields of chromium hexacarbonyl but if more than one mole of Grignard

is allowed to react to completion with one mole of chromic chloride, the intermediate formed will not readily absorb carbon monoxide and very poor yields of the hexacarbonyl are obtained.   The intermediate is soluble in ether and is not chromous chloride ($CrCl_2$), pentaphenyl chromium bromide (Ph_5CrBr), tetraphenyl chromium bromide (Ph_4CrBr) or triphenyl chromium bromide (Ph_3CrBr). (Owen et al.[39]).

4) When preparing the carbonyl by Owen's low pressure method the introduction of carbon monoxide from the beginning of the reaction gives better yields than if it is not introduced until after the addition of the Grignard (Author (p.35)).

5) Continuous fast stirring is a vital factor in the low pressure methods of preparing the carbonyl (Owen et.al.[39]; confirmed by the author (p. 35)).

6) The reaction product is liable to contain numerous organic reaction products of the type described on p.38 of this thesis. (Job & Cassal[85]).

7) The molar ratio of Grignard to chromic chloride must be greater than 5:1 for optimum yield (Owen et al.[39])

8) The yield is not sensitive to small changes in the above ratio provided it is greater than 5:1. (Owen et al.[39]; confirmed by the author (p.27)(and Table I)).

9) The yield is influenced by the pressure at which the absorption of the carbon monoxide is conducted, higher yields being obtained with increased pressure. (Owen et al.[39])

10) The maximum yield obtained corresponds to a conversion of

67% of the chromium to hexacarbonyl (Owen et al.[39]).

11) No chromium hexacarbonyl can be obtained from the reaction mixture until it has been hydrolised by dilute sulphuric acid.   This is agreed by all workers on the subject.

12) The volume of carbon monoxide absorbed appears to depend on the amount of Grignard used.   Job & Cassal stated that carbon monoxide was absorbed in equimolecular proportion to the quantity of Grignard used[35].   Hieber & Romberg[37] found that the amount of carbon monoxide absorbed was roughly proportional to the amount of Grignard used but did not agree that the proportion was necessarily equimolecular.   In a confirmatory determination the author (Table I) found that the molar ratio of carbon monoxide absorbed to Grignard present was approximately 3/4.

13) The presence of ethyl bromide in the reaction mixture delays the onset of carbon monoxide absorption in the method of Hieber & Romberg. (Author (p. 27)).

14) It is possible to obtain very small yields of chromium hexacarbonyl by reacting chromic chloride and carbon monoxide under pressure in presence of zinc dust, the suspension medium being methyl or ethyl alcohol. (Anissimov & Nesmeyanov[38]).

        All these facts can be accounted for if the existence of an unstable intermediate alkyl or aryl chromium halide of formula $RCrCl_2$ is assumed. (R is an alkyl or aryl group, its composition depending on the Grignard used).   In the following discussion the Grignard compound is taken to be phenyl magnesium

bromide (PhMgBr) but the proposed reaction mechanism could
be applied to any other suitable Grignard.

The initial reaction would then be between equimolecular
proportions of Grignard and chromic chloride

$$2\ PhMgBr + 2\ CrCl_3 \rightarrow 2\ PhCrCl_2 + MgBr_2 + MgCl_2 \qquad (1)$$
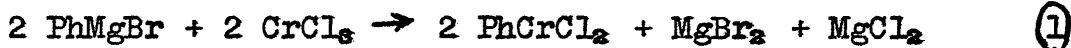
The existence of such an intermediate would explain the
sensitivity of the reaction to temperature (Fact 1). Presumably
temperatures above 5°C. would decompose it. The importance of
the solvent used for suspending the chromic chloride is also
explained. It is presumably essential that the intermediate
be soluble in the solvent (Fact 2). It also seems likely that
the intermediate discovered by Owen et al. (Fact 3) could only
be a compound of this type. The intermediate (PhCrCl_2) would
almost certainly be unstable to oxygen since similar compounds
prepared by Hein[32] showed this instability. This would explain
the improvement in yields, obtained by the author when using
Owen's method, if air was excluded from the reaction mixture
by introducing carbon monoxide from the start of the reaction
(Fact 4). Reaction of the intermediate with further Grignard
reagent would probably lead to the formation of the type of
phenyl chromium halides observed by Hein[42] (Ph_5CrBr,Ph_4CrBr,Ph_6
CrBr), This would explain the deleterious effect on the yield
of hexacarbonyl of reaction to completion between the
intermediate and further Grignard observed by Owen (Fact 3).
The importance of continuous fast stirring would be in the
prevention of the accumulation of local high concentrations of
Grignard (Fact 5).

The intermediate phenyl chromium dichloride ($PhCrCl_2$) would then react with further Grignard in presence of carbon monoxide to give a phenyl chromium carbonyl of the type $Ph_xCr(CO)y$ where $x + y = 6$.   A typical reaction of this sort would be:-

$$PhCrCl_2 + 2\ PhMgBr + 4\ CO \longrightarrow Ph_2Cr(CO)_4 + MgBr_2 + MgCl_2 + Ph \qquad ②$$
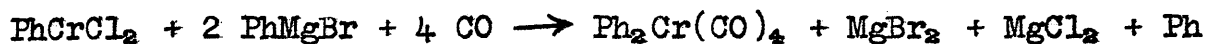
The free phenyl groups formed could react with each other and with carbon monoxide to give benzophenone ($Ph.CO.Ph$) benzil ($Ph.CO.CO.Ph$) and diphenyl ($Ph.Ph$). The benzophenone and benzil could then react with additional Grignard in the manner described by Job & Cassal[35] (Fact 6).   Side reactions of the type studied by Hein[43] would of course be liable to occur throughout the carbon monoxide absorption stage of the preparation and the predominance of these would contribute to the low yields obtained by many workers.

$$5\ PhMgBr + 4\ CrCl_3 \longrightarrow Ph_5CrBr + 2\ MgBr_2 + 3\ MgCl_2 + 3\ CrCl_2 \qquad ③$$
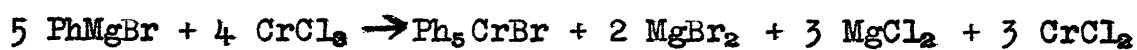
In the final hydrolysis the phenyl chromium carbonyls ($Ph_x Cr(CO)y$, $x + y = 6$) would disproportionate to form chromium hexacarbonyl.

e.g. $$3\ Ph_2Cr(CO)_4 + 3H^+ \longrightarrow 2\ Cr(CO)_6 + Cr^{+++} + 1.5H_2 + 6\ Ph \qquad ④$$
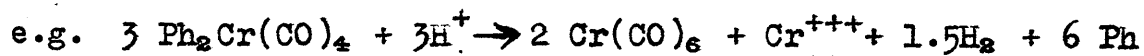
The existence of compounds of the phenyl chromium carbonyl type is known, Hieber & Mühlbauer[44] having prepared tripyridine chromium tricarbonyl ($C_5H_5N)_3\ Cr\ (CO)_3$ and dipyridine chromium tetracarbonyl ($C_5H_5N)_2\ Cr\ (CO)_4$.   Moreover disproportionation reactions of the type shown in Equation (4) have been found to yield the carbonyl[37]

$$2(C_5H_5N)_3\ Cr\ (CO)_3 + 3H^+ \longrightarrow Cr(CO)_6 + Cr^{+++} + 6C_5H_5N + 1.5H_2$$
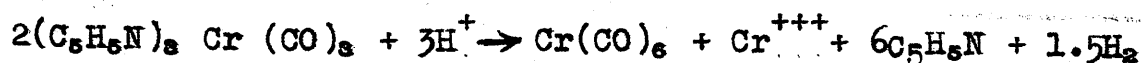
The reaction mechanism suggested above would explain

the fairly high molar ratio of Grignard to chromic chloride (5:1) necessary for optimum yield (Fact 7).   For the reactions shown in Equations (1) and (2) a molar ratio of at least 3:1 would be essential.   The existence of side reactions between the Grignard and compounds such as benzil (Ph.CO.CO.Ph) would consume additional Grignard:-

$$\text{Ph.CO.CO.Ph} + 2\ \text{PhMgBr} \longrightarrow \underset{\substack{| \\ \text{OMgBr}}}{\overset{\substack{\text{Ph} \\ |}}{\text{Ph}-\text{C}}} \underline{\hspace{2cm}} \underset{\substack{| \\ \text{OMgBr}}}{\overset{\substack{\text{Ph} \\ |}}{\text{C}}} \underline{\hspace{2cm}} \text{Ph} \qquad \text{(5)}$$
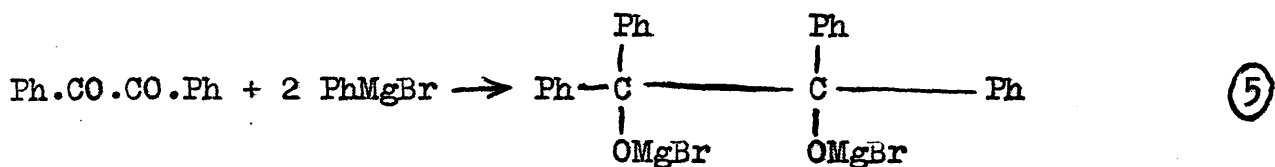
Job & Cassal[35] have shown that such reactions almost certainly do take place.   When sufficient Grignard is present to conduct reactions of the type shown in Equations (1), (2) and (5) the addition of still further Grignard would be unlikely to affect the yield of hexacarbonyl (Fact 8).

Reactions of the type shown in Equation (2) produce phenyl chromium carbonyls of formulae $Ph_xCr(CO)y$ where $x + y = 6$. The composition of the phenyl chromium carbonyls is likely to depend on pressure, the carbon monoxide content increasing with increasing pressure.   The higher the carbon monoxide content of the complex the greater is the possible yield of chromium hexacarbonyl when it disproportionates during the hydrolysis (Fact 9).   The formation of chromium hexacarbonyl by the disproportionation of phenyl chromium carbonyls imposes a limit on the yield, the limit depending on the composition of the phenyl chromium carbonyl.   If the compound were $Ph_5Cr(CO)$ as it might well be at low pressures of carbon monoxide the maximum possible conversion of chromium to hexacarbonyl would

be approximately 16%; if the compound were $PhCr(CO)_5$ the theoretical maximum conversion of chromium to hexacarbonyl would be approximately 84%. Since the maximum conversion of chromium to hexacarbonyl obtained by Owen was 67% it seems possible that the principal phenyl chromium carbonyl present in this case would be $Ph_2Cr(CO)_4$ (Maximum conversion would correspond to 67%) (Fact 10).

The formation of phenyl chromium carbonyls also explains why it is impossible to obtain any chromium hexacarbonyl from the reaction mixture until after it has been hydrolised (Fact 11). The hexacarbonyl is not formed until the phenyl chromium carbonyl disproportionates during the hydrolysis.

If it is assumed that the composition of the phenyl chromium carbonyl is determined by pressure rather than by availability of Grignard the amount of carbon monoxide absorbed will depend on the amount of Grignard present (Fact 12). This would only apply to concentrations of Grignard corresponding to a molar ratio Grignard/Chromic Chloride of 5/1 or less.

If excess Grignard were available the amount of carbon monoxide absorbed would depend on the composition of the phenyl chromium carbonyl complex. Thus if the complex were $Ph_5Cr(CO)$ the molar ratio of CO absorbed/chromic chloride would be approximately 1.5/1 allowing for the absorption of some carbon monoxide by free phenyl groups. Similarly if the complex were $PhCr(CO)_5$ the molar ratio would be approximately 7/1. The carbon monoxide absorption quoted by Job & Cassal corresponds

to a value for the ratio of 5.9/1 while Hieber & Romberg found that the ratio averaged about 4.5/1 with a maximum of 6/1. The author obtained values varying from 0 to 6/1. Owen et al., Kocheshkov et al., and Anissimov & Nesmeyanov did not measure the quantity of carbon monoxide absorbed. The theory thus gives values for the ratio which are in accord with the experimental results.

The delay in the onset of carbon monoxide absorption caused by the presence of excess ethyl bromide when using ethyl magnesium bromide as the Grignard can also be accounted for by this theory. The unstable initial intermediate, ethyl chromium dichloride ($EtCrCl_2$) is presumably decomposed by the ethyl bromide.

$$EtCrCl_2 + EtBr \longrightarrow CrCl_2Br + 2\ Et.$$

The free ethyl radicles would presumably undergo further reaction. Until the ethyl bromide has been destroyed as indicated above the ethyl chromium dichloride cannot react with further Grignard (Fact 13).

Finally, the reaction of Anissimov & Nesmeyanov must be considered (Fact 14). They obtained very small yields of chromium hexacarbonyl by using zinc dust in place of a Grignard. It is significant that they carried out the reaction in a methyl or ethyl alcohol medium instead of the usual ether or ether-benzene medium. The author attempted to conduct their reaction in an ether-benzene medium and failed to obtain any yield of hexacarbonyl. It is possible that a different

intermediate is formed in this case and that it is soluble in alcohol but not in ether.   It is also conceivably possible that reactions of the type shown below were taking place:-

$$2 CrCl_3 + 2 Zn + 2 MeOH \rightarrow 2 MeCrCl_2 + ZnCl_2 + Zn(OH)_2$$

$$2 MeCrCl_2 + 3 Zn + 8 CO + 2 MeOH \rightarrow 2 Me_2Cr(CO)_4 + Zn(OH)_2 + 2ZnCl_2$$

$$3 Me_2Cr(CO)_4 + 3 H^+ \rightarrow 2 Cr(CO)_6 + Cr^{+++} + 6 Me + 1.5 H_2$$
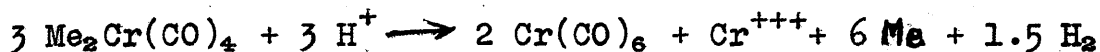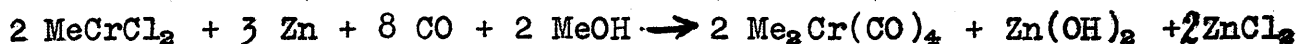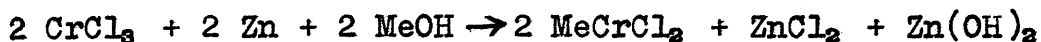
Only a very small proportion of the reactants would require to react as above since the final yields were very small.

The foregoing explanation of the reaction mechanism in the formation of chromium hexacarbonyl is based on the results of all the workers on this subject, including the author. It is not claimed that the theory has been proved but it is believed to be the only one which accords with all the known facts on the subject.

F. Analysis of Chromium Hexacarbonyl.

A sample of combined product from the various methods of preparation was analysed for chromium content by the method described by Job & Cassal[34]. The carbonyl was decomposed by fuming nitric acid and the resultant product ignited to chromium sesquioxide (Cr_2O_3). The analysis was done in duplicate, the results being given below.

Found: Cr 23.5%, 23.3% : $Cr(CO)_6$ requires Cr 23.6%.

The results of the analyses are in good agreement with the theoretical figure.

CONCLUSIONS - Section 1.

1) Chromium hexacarbonyl can be prepared by the method of Hieber & Romberg and the method of Owen, English

Cassidy & Dundon though the yields obtained by the author were less than those quoted by the original workers.

Method of Preparation	Yield quoted by original workers.	Yield obtained by author
Hieber & Romberg	14%	9.5%
Owen et al.	24%	3.4%

The essential difference between the two methods is that Owen et al. conduct a stage of the reaction at - 70°C while Hieber & Romberg conduct the whole reaction at temperatures over 0°C.   The low temperatures used by Owen et al. appear to reduce rather than increase the yield.   The author obtained a yield of 10.6% when following a modification of Owen's method which eliminated the low temperature stage.   It is of interest to note that Kocheshkov et al.[41] obtained yields of less than 6% when attempting to duplicate Hieber's method of preparing the hexacarbonyls of chromium, molybdenum and tungsten.

2)   In order to obtain satisfactory yields from either of the above methods of preparation the following conditions must be achieved during the carbon monoxide absorption stage of the preparation:-

1) .. Continuous fast stirring.

2) .. Rigid temperature control (0-5°C).

3) .. Exclusion of air from the reaction flask.

4) .. The chromic chloride must be of the anhydrous variety and should preferably be in the form of a fine amorphous powder.

3)   The method of Kocheshkov et al. for the preparation

of molybdenum and tungsten hexacarbonyls is not applicable to
chromium hexacarbonyl.

4) A reaction mechanism for the formation of chromium
hexacarbonyl which is in accord with the known facts can be
propounded if the existence of an intermediate compound $(PhCrCl_2)$
is assumed.   It is proposed that chromium hexacarbonyl is formed
by reactions of the type shown below:

$2\ PhMgBr + 2\ CrCl_3 \longrightarrow 2\ PhCrCl_2 + MgBr_2 + MgCl_2$

$PhCrCl_2 + 2\ PhMgBr + 4\ CO \longrightarrow Ph_2Cr(CO)_4 + MgBr_2 + MgCl_2 + Ph$

$3\ Ph_2Cr(CO)_4 + 3\ H^+ \xrightarrow{\text{hydrolysis}} 2\ Cr(CO)_6 + Cr^{+++} + 1.5\ H_2 + 6\ Ph.$

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CHROMIUM HEXACARBONYL

Chromium Hexacarbonyl.

... the pure product as it, the ... colourless, orthorhombic crystals, up to 1 cm. in length.

Solubility:- Chromium hexacarbonyl is slightly soluble in benzene, ether, alcohol, acetic acid, chloroform and ... but is insoluble in aqueous solvents.

Melting Point:- The compound sublimes slowly at room temperature and pressure (a small quantity left exposed ... disappeared overnight). On heating the crystals ... sublime more and more rapidly until at 130°C **SECTION II.** ... violently, leaving a residue ... "explosive." If heated in a sealed tube ... melts at 149-150°C. under its own vapour ... at that temperature.

Specific gravity: The specific gravity of chromium hexacarbonyl at ... is 1.77.

... The effect of heating in air has already ... described (Property). If heated in an inert atmosphere ... sealed tube chromium hexacarbonyl vapourises at 150°C and ... about 200°C shows signs of decomposition. At 230°C. it

Section II

STABILITY OF CHROMIUM HEXACARBONYL.

A. Properties of Chromium Hexacarbonyl.

1) Crystalline Form:- The pure product is in the form of colourless, orthorhombic crystals up to 1 cm. in length.

2) Solubility:- Chromium hexacarbonyl is slightly soluble in benzene, ether, alcohol, acetic acid, chloroform and carbon tetrachloride but is insoluble in aqueous solvents.

3) Melting Point:- The compound sublimes slowly at room temperature and pressure (A small quantity left exposed on a watch glass disappeared overnight). On heating the crystals in air they sublime more and more rapidly until at 210°C. they burst into flame and decompose violently, leaving a residue of chromium sesquioxide. If heated in a sealed tube chromium sesquioxide melts at 149-150°C. under its own vapour pressure at that temperature.

4) Specific Gravity:- The specific gravity of chromium hexacarbonyl at 18°C. is 1.77.

5) Heat:- The effect of heating in air has already been described (Property 3). If heated in an inert atmosphere in a sealed tube chromium hexacarbonyl vapourises at 150°C and at about 200°C. shows signs of decomposition. At 230°C. it forms a metallic mirror on the surface of the tube and carbon monoxide can be recovered when the tube is opened.

6) Stability:-

(i) Water or dilute acids have no action on chromium hexacarbonyl.

(ii)   Concentrated nitric acid causes decomposition only
         after a considerable time.

(iii)   Bromine and iodine have no action although they readily
         decompose nickel carbonyl.

(iv)   Fuming nitric acid (48° Baume) attacks the compound
         forming chromium nitrate, carbon monoxide and carbon
         dioxide being evolved.

(v)   When in solution the compound slowly decomposes if
         exposed to light, a brown floculent precipitate being
         formed.

B. Decomposition of Chromium Hexacarbonyl Solutions.

         Although chromium hexacarbonyl is very stable to
most chemical reagents, its solutions were found to decompose
on standing, a gelatinous precipitate, usually brown in colour,
being formed.   The exact reason for this decomposition was
uncertain but light seemed to promote the reaction.   If
chromium hexacarbonyl is to be a suitable petroleum additive it
is important that its solutions be as stable as possible.   It
was therefore decided to study the decomposition of chromium
hexacarbonyl solutions with a view to delaying or preventing
decomposition.   The composition of the gelatinous precipitate
formed when solutions of chromium hexacarbonyl decompose, is
not known.   The precipitate varies from pale green to dark
red-brown depending on the conditions and tends to darken in
colour on further exposure to light.   If the precipitate is
filtered and allowed to dry it appears as a dark brown amorphous
powder which, if strongly ignited, leaves a green residue of

chromium sesquioxide thus proving chromium to be present in the precipitated decomposition product(s).

A study was made of the factors influencing the decomposition of chromium hexacarbonyl solutions.

1) Effect of Solvent.

Chromium hexacarbonyl was dissolved in 10 cc. of various solvents at a concentration of 1 gram per litre, the solutions being placed in corked test tubes and exposed to sunlight. The results are given in Table III. During this, and all subsequent exposure tests, the solutions were examined every 5 minutes for the first 30 minutes, every 15 minutes for the following 90 minutes, and thereafter at intervals of 60 minutes. Only those examinations which revealed any significant change in the appearance of the solutions are recorded in the Tables. The following abbreviations are used in the Tables:-

ac.	...	acid
cls.	...	colourless
col.	...	colour
P.C.	...	precipitation complete
gel.	...	gelatinous.

The results in Table III indicate that the nature of the solvent does not appear to affect the course of the decomposition although the rate of decomposition may vary from one solvent to another. Of the solvents tested benzene, chloroform, n-heptane, iso-octane and pool petrol appeared to permit decomposition at approximately equal rates, while with

Table III

The Decomposition of Solutions of Chromium Hexacarbonyl in Various Solvents.
(Concentration of Solutions = 1g./l.)

Solvent	Appearance of Solution after Exposure to Sunlight. Duration of Exposure (minutes).									
	0	5	10	20	30	60	120	180	240	3000
Benzene	Clear, colourless.	Clear, colourless.	Pale straw colour.	Straw col. Small brown ppte.	Ppte. becoming heavier.	Soln. clear cls. Ppte. becoming darker in colour.	P.C.	—	—	—
Carbon tetrachloride	"	"	"	Straw col. No ppte.	Straw col.	Colour deepening but no ppte.	Colour deepening. Becoming cloudy	Heavy brown gel. ppte.	Soln. clear cls. Ppte. becoming darker in colour.	P.C.
Chloroform	"	Very faint yellow colour.	Faint yellow colour.	Brown gel. ppte. Soln. yellow.	Ppte. becoming heavier.	Soln. clear cls. Ppte becoming darker in colour.	P.C.	—	—	—
Diethyl ether	"	Bright yellow colour.	Yellow colour becoming brighter.	Bright yellow col. Gel. ppte.; col. masked by soln.	Ppte. becoming heavier.	No visible change.	Soln's col. diminishing. Ppte. now green-brown in colour.	Ppte. darkening in colour.	Soln. clear cls. Brown gel. ppte.	P.C.
n-Heptane	"	Clear, colourless.	Pale straw colour.	Brown gel. ppte.	Ppte. becoming heavier.	Soln. clear cls. Ppte. darker in colour.	P.C.	—	—	—
iso-Octane	"	"	"	"	"	"	"	—	—	—
Pool Gas Oil	Yellow, viscous.	No visible change.	No visible change.	No visible change.	No visible change.	No visible change.	No visible change.	No visible change.	No ppte. but soln. becoming darker in colour.	Brown gel. ppte.
Pool Petrol	Clear, yellow.	Clear, yellow.	Clear, yellow.	Brown gel. ppte.	Ppte. becoming heavier.	Ppte. becoming darker in colour.	No visible change.	P.C.	—	—

carbon tetrachloride and Pool Gas Oil the rate of decomposition was considerably less.   Ether solutions decomposed in a slightly different way, the initial decompositon product being soluble and imparting a bright yellow colour to the solution.

In subsequent tests only hydrocarbon solvents were used.

2) The Stability of a Chromium Hexacarbonyl Solution under Total Exclusion of Light and Oxygen.

A stoppered 'Quickfit' test tube completely full of a saturated solution of chromium hexacarbonyl in n-heptane was placed in a closed, light-tight container, and left for one year.   When re-examined, the solution was still clear and free of precipitate, indicating that no decomposition had occurred during the period.   A similar result was obtained with a solution of the hexacarbonyl in ether.

3) The Stability of a Chromium Hexacarbonyl Solution under Total Exclusion of Light but in Presence of Air.

The above conditions were achieved by slowly bubbling air through an n-heptane solution of chromium hexacarbonyl in complete darkness.   Air was drawn through the solution by an aspirator at a rate of 1 litre per hour.   The rate of flow of air was maintained at this low value because a high rate of flow might have entrained appreciable quantities of chromium hexacarbonyl and n-heptane.

After running the test continuously for seven days

the solution was examined and found to be clear and free of precipitate. That this was not due to the entrainment of all the chromium hexacarbonyl by the air was proved by exposing to light the clear solution after the test. Decomposition soon set in, a red-brown precipitate forming.

A solution of chromium hexacarbonyl is therefore stable in presence of oxygen provided that light is excluded.

4) The Effect of the Presence or Absence of Oxygen on the Stability of a Chromium Hexacarbonyl Solution Exposed to Light.

Two cubic centimetres of a freshly prepared saturated solution of chromium hexacarbonyl in n-heptane were added to each of two test tubes fitted with ground glass necks and stoppers. The dead space in one of the test tubes (A) was filled with nitrogen and the stopper quickly inserted to minimise any possible leak in of oxygen from the atmosphere. No grease was used in the ground glass joint because n-heptane dissolved a yellow component from the grease giving a yellow colouration to the solution. This colour might mask the formation of a decomposition product. Sealing of the joint was effected by sliding the stopper home with both ground glass surfaces dry and sealing the top of the joint with acetone soluble varnish which resisted n-heptane successfully after it had hardened. The dead space in the second test tube (B) was filled with oxygen and sealed in a similar manner. Both test tubes were then exposed to daylight and examined at intervals. Details are given in Table IV.

Table IV.

The Effect of the Presence or Absence of Oxygen on the Stability of

a Chromium Hexacarbonyl Solution Exposed

to Light.

Time of exposure.	A Appearance of chromium hexacarbonyl solution in contact with nitrogen.	B Appearance of chromium hexacarbonyl solution in contact with oxygen.	Remarks.
0	Clear, colourless.	Clear, colourless.	
1 hour	Very small green gelatinous ppte.	Fairly heavy brown gelatinous ppte.	Ppte in 'B' much heavier than in 'A'.
24 hours	Green ppte. no longer evident but might have adhered to side of tube when tube was shaken.	Ppte. slightly heavier and darker brown.	During 6 hours of this time the tube would be in comparative darkness (overnight).
At this point both solutions were placed on a slow speed mechanical agitator to improve the contact between gas and liquid within the tube.			
2 days	No appreciable change.	no appreciable change.	
5 days	No appreciable change. Soln. still appeared clear.	Ppte. appeared very slightly heavier and darker.	Agitator now only operated for 1 hour per day.
10 weeks.	No further change.	No further change.	

After ten weeks the stoppers were removed from the
two test tubes, the clear solution in test tube (A) being
thus exposed to the atmosphere.   In a few hours a light
brown precipitate formed and gradually darkened.   The liquid
containing the brown precipitate in test tube (B) was filtered,
the filtrate being then exposed to oxygen and light.   No
further precipitation occurred in the solution thus indicating
that precipitation was already complete.

This test indicated that a solution of chromium
hexacarbonyl in n̄-heptane is unstable to light in presence of
oxygen but in absence of oxygen very little if any decomposition
occurs.   The small green precipitate noticed when chromium
hexacarbonyl in n̄-heptane was exposed to light in presence of
nitrogen may have been due to traces of oxygen in the tube.

5) The Effect of Temperature on a Chromium Hexacarbonyl
    Solution Exposed to Light and Air.

Five cubic centimetres of a saturated solution of
chromium hexacarbonyl in n̄-heptane were added to each of two
test tubes (C) and (D) which were then partially immersed in
two beakers containing respectively ice cold water (C) and
water at 28°C.(D).   Thermometers in the two solutions recorded
the temperatures.   The solutions were then exposed to air and
light and observed at suitable intervals, the results being
given in Table V.

This test showed that the colour of the decomposition
product varied with the temperature, being green to green-brown

Table V.

The Effect of Temperature on the Stability of a Chromium Hexacarbonyl

Solution.

Time of exposure (hours).	Temp. of 'C' (°C.)	Temp. of 'D' (°C.)	Appearance of 'C'	Appearance of 'D'	Remarks.
0	1	27	Clear, colourless	Clear, colourless.	
0.5	2	26	Very small green gelatinous ppte.	Small light brown gelatinous ppte.	Pption. very slight but approx. equal in 'C' & 'D'.
1	4	25	Heavier ppte. Colour now green-brown.	Heavier ppte. Colour now brown-red.	Ppte. in 'D' slightly heavier than in 'C'.
2	4	28	Ppte. increasing slightly. Colour unchanged.	Ppte. increasing slightly. Colour unchanged.	Ppte. in 'D' still slightly heavier than in 'C'.
3	3	25	Ppte. increasing very slightly. Colour slightly darker.	Ppte. increasing very slightly. Colour unchanged.	"
4	3	27	Further slight pption. Colour unchanged.	Further slight pption. Colour unchanged.	"

at 0 - 4°C. and brown to brown-red at 25 - 28°C. The
rate of decomposition appeared to be slightly greater at
the higher temperature.

6) Additional Observations.

(a) It was noticed that when a test tube was nearly
filled with a solution of chromium hexacarbonyl in n-heptane
and then tightly corked, the decomposition product on exposure
to light was a gelatinous precipitate - purple in colour.
This change in colour from that noticed in previous tests may
have been due to the limited amount of oxygen available.

(b) When a solution of chromium hexacarbonyl was
left exposed to the atmosphere it was noticed that decomposition
invariably occurred at the surface of the liquid, the brown
gelatinous precipitate forming there and sinking when the
containing vessel was tapped. This confirmed the result of
Test 4 (p. 60); i.e. that oxygen was necessary for the
decomposition.

A summary of the results in Tests 2 - 6 is given in
Table VI.

Conclusions.

The decomposition of chromium hexacarbonyl in
solution is not greatly affected by the nature of the solvent
although the rate of decomposition may be different in different
solvents.

Solutions of chromium hexacarbonyl in n-heptane are
stable at ordinary atmospheric temperatures in absence of light

Table VI.

The Stability of Solutions of $Cr(CO)_6$ in n-Heptane.

Test No.	CONDITIONS OF TEST Exposure to:-			EFFECTS.
	Light	Temp. (°C)	Oxygen.	
2	Nil.	18-22	Nil or trace.	No decomposition
3	Nil.	18-22	Free access to air	No decomposition
4A	Through pyrex glass	18-22	Oxygen available in the ratio:- $\dfrac{\text{Vol. of Oxygen}}{\text{Vol. of Soln.}} = \dfrac{20}{1}$	Fairly heavy brown ppte. in one hour; darkening and increasing on further exposure to light.
4B	Through pyrex glass.	18-22	Nitrogen gas plus possible small traces of oxygen available.	Very small green ppte. in one hour; not increasing appreciably on further exposure to sunlight.
5C	Free access.	0 - 4	Free access to air	Fairly heavy green ppte. after one hour's exposure to sunlight.
5D	Free access.	25-28	Free access to air	Fairly heavy brown ppte. after one hour's exposure to sunlight. Ppte. heavier than in Test 5C.
6a	Through pyrex glass	18-22	Limited amount of air in contact with the solution. Ratio:- $\dfrac{\text{Vol. of air}}{\text{Vol. of Soln.}} = \dfrac{1}{40}$	Small purple gelatinous ppte.; not increasing on further exposure to light through pyrex glass.

whether oxygen is present or not.   In presence of light
chromium hexacarbonyl solutions decompose forming gelatinous
precipitates, the rate of decomposition depending on the
availability of oxygen.   If no oxygen is available the rate
of decomposition is negligible while if unlimited oxygen is
available it is quite fast. (5 mins. - several hours for first
signs of decomposition depending on the intensity and wave
length of the light.).   The amount of oxygen available also
influences the nature of the decomposition product, the colour
varying from purple to green to brown with increasing oxygen.
The rate of decomposition of chromium hexacarbonyl solutions
exposed to air and light increases with increasing temperature,
the decomposition product being a green gelatinous precipitate
at low temperatures (c. 0°C.) and a brown-red gelatinous
precipitate at higher temperatures (c. 25°C.).

C.   Inhibition of Decomposition of Chromium Hexacarbonyl
     Solutions.

          One of the principal disadvantages of chromium
hexacarbonyl as a petroleum additive is the instability of its
solutions when exposed to light.   Solutions of lead tetraethyl
in petroleum also decompose on standing, and various inhibitors
have been used in an attempt to diminish its rate of decomposition.[45]
These include natural cresylic acids, α-naphthol, p-tert-
butylcatechol, N,N'-dimethyl-p-phenylenediamine, hexylresorcinol
and amyl-m-cresol. Solutions of chromium hexacarbonyl, of
concentration 1 gram per litre, in n-heptane each containing
approximately 10 grams per litre of one of the inhibitors were

simultaneously exposed to light.   A solution of chromium
hexacarbonyl containing no inhibitor was exposed at the same
time for purposes of comparison.   The results are given in
Table Vll.

The inhibitor tests described in Table Vll indicate
that none of the substances tested is very suitable for
retarding the decomposition of chromium hexacarbonyl solutions.
Natural cresylic acids, p-tert.-butylcatechol, hexylresorcinol
and amyl-m-cresol appear to retard the decomposition slightly
and certainly have some effect since the character of the
decomposition products is altered.   In the case of p-tert.-
butylcatechol a red colouration develops.

Quinine compounds have been used in inhibiting
decompositions of this sort and the following substances were
therefore tested as inhibitors:- quinine, quinine sulphate,
quinine citrate, quinine salicylate.   These compounds were
not soluble in n-heptane to any appreciable extent and had no
perceptible effect on the decomposition of chromium
hexacarbonyl.

Solutions of iron pentacarbonyl in hydrocarbon solvents
are also unstable to light and various inhibitors have been
used to stabilise the compound.   These include α-naphthylamine-
azo-α-naphthol[46], stearic acid and oleic acid[47].   These
compounds, together with palmitic acid were tested as inhibitors
in the decomposition of chromium hexacarbonyl solutions, the
results being shown in Table Vlll.

Table VII

The Effect of Lead Tetraethyl Decomposition Inhibitors on the Decomposition of Chromium Hexacarbonyl Solutions.

(Concn. of Chromium Hexacarbonyl = 1g./1.)
(Concn. of Inhibitor = 10g./1.)

Inhibitor	Appearance of Solution after Exposure to Light. Duration of Exposure (minutes).			
	0	15	30	60
None.	Clear, colourless.	Pale straw colour.	Brown gel. ppte. Hereafter referred to as 'A'.	Ppte. becoming heavier and darker in colour.
Natural cresylic acids (Sample 1).	Clear. Very pale straw colour	Cloudy. Pale yellow colour.	Dark brown amorphous ppte. Less than 'A' in bulk.	Ppte. becoming heavier.
Natural cresylic acids (Sample 2).	"	Pale straw colour. Small cls. gel. ppte.	Colourless gel. ppte. Less than 'A' in bulk.	Ppte. becoming heavier.
α–Naphthol.	Clear, colourless.	Colourless gel. ppte.	Colourless gel. ppte. More than 'A' in bulk.	Ppte. becoming heavier.
p–tert. butyl-catechol.	Clear, colourless.	Pink colour.	Pink col. deepening. Small brown amorphous ppte.	"
N,N'– dimethyl-p-phenylene diamine.	Pale green colour.	Dark brown col. and gel. ppte.	Gel. ppte., dark in col. Turbid soln.	"
Hexyl-resorcinol.	Clear, colourless.	Colourless gel. ppte.	Pale brown ppte. Less than 'A' in bulk.	"
n–Amyl–m–cresol.	"	Cloudy. Pale yellow colour.	"	"

Table Vlll.

The Effect of Iron Pentacarbonyl Decomposition Inhibitors on the Decomposition of Chromium Hexacarbonyl Solutions.

Concentration of Chromium Hexacarbonyl = 0.2g./l.
Concentration of Inhibitor = 2.0g./l.

Inhibitor	Appearance of Solution after Exposure to Sunlight. Duration of Exposure (minutes).					
	0	5	10	30	60	240
None	Clear, colourless.	Clear, pale yellow.	Pale yellow soln. Light brown ppte.	Solution clear. Dark brown gelatinous precipitate	P.C.	------
α-naphthylamine -azo- -naphthol	Clear, orange coloured solution.	Orange colour deepening.	Dark brown ppte. Heavier and darker than when no inhibitor present.	"	P.C.	------
Stearic acid	Clear, colourless	Very pale straw colour	Very pale straw colour. No ppte.	Straw colour fading. No ppte.	Very pale blue coloured solution. No ppte.	No visible change since previous observation.
Oleic acid	"	"	"	"	"	Very pale blue colour. Slightly cloudy.
Palmitic acid.	"	"	"	"	"	No visible change. Identical in appearance to stearic acid test.

The results in Table Vlll indicate that α-naphthylamine-azo-α-naphthol is ineffective as an inhibitor but stearic, oleic and palmitic acids appear to have the desired effect. In view of the apparent efficacy of fatty acids as inhibitors a series of saturated straight chain monocarboxylic acids of varying chain lengths was tested, the results being shown in Table lX.

In previous tests the light used to promote decomposition was ordinary sunlight. This was quite suitable when negative results were being obtained but when the existence of effective inhibitors had been established it was desirable to have a source of light of constant intensity which would permit comparisons between different series of tests. An ultra-violet lamp using a mercury vapour arc was used in this and all subsequent tests, the solutions being exposed at a distance of 10 inches from the light source.

The results shown in Table lX indicate that saturated monocarboxylic acids do not inhibit the decomposition of chromium hexacarbonyl solutions unless they contain at least four carbon atoms. Thereafter, the efficacy of the inhibitor appears to depend on the number of carbon atoms in the chain, the stabilising property increasing with increased chain length. If it is assumed that the start of decomposition is indicated by the liquid becoming cloudy it is possible to graph "Time required for start of decomposition" against "Number of carbon atoms in inhibitor chain". This is shown in Figure 5.

Table IX

Straight Chain Monocarboxylic Acids as Inhibitors of the Decomposition of Chromium Hexacarbonyl Solutions.
(Concn. of Chromium Hexacarbonyl = 0.2g./l.)   (Concn. of Inhibitor = 10g./l.)

Inhibitor.	No. of C atoms in inhibitor.	Appearance of Solution after Exposure to Ultra-violet Light. Duration of Exposure (minutes).									
		0	5	10	20	40	80	240	360	720	1440
None.	–	Clear, cls.	Clear, yellow.	Yellow col. Brown gel. ppte.	Ppte. heavier and darker.	'Solution clear, cls. Brown gel. ppte.	P.C.	—	—	—	—
Formic acid.	1	〃	Cloudy. Yellow colour.	〃	Ppte. becoming pale blue.	Solution clear, cls. Pale blue gel. ppte.	P.C.	—	—	—	—
Acetic acid.	2	〃	Cloudy. Straw colour.	Cloudy. Straw colour.	Pale blue gel. ppte.	〃	P.C.	—	—	—	—
n-Propionic acid.	3	〃	〃	〃	Very cloudy. Pale blue colour.	Very cloudy. Pale blue colour.	Solution clear, cls. Pale blue gel. ppte.	P.C.	—	—	—
n-Butyric acid.	4	〃	Clear. Straw colour.	Clear. Straw colour.	Clear. Pale greenish-yellow col	Clear. Very pale blue col.	Cloudy. Pale blue colour.	Pale blue gel. ppte.	Solution clear, cls. Pale blue gel. ppte.	P.C.	—
n-Valeric acid.	5	〃	〃	〃	〃	〃	Clear. Very pale blue col.	Cloudy. Pale blue colour.	Pale blue gel. ppte.	Solution clear, cls. Pale blue gel. ppte.	P.C.
n-Caproic acid.	6	〃	Clear. Very faint straw colour.	Clear. Faint straw colour.	Clear. Very pale greenish-yellow col	〃	〃	Clear. Very pale blue col.	Cloudy. Pale blue colour.	Cloudy. Pale blue colour.	Cloudy. Pale blue colour.
n-Caprylic acid.	8	〃	〃	〃	〃	〃	〃	〃	Clear. Blue col. fading.	Cloudy. Very pale blue col.	〃
n-Lauric acid.	12	〃	〃	〃	〃	〃	〃	〃	〃	Cloudy. Very pale blue col.	〃
n-Myristic acid.	14	〃	〃	〃	〃 ^	〃	〃	〃	〃	Solution clear and almost cls.	Clear, cls. No cloudiness or ppte.
n-Palmitic acid.	16	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
n-Stearic acid.	18	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃

FIGURE 5

THE EFFECT OF CHAIN LENGTH ON THE EFFICIENCY OF MONOCARBOXYLIC ACIDS AS INHIBITORS FOR THE DECOMPOSITION OF CHROMIUM HEXCARBONYL SOLUTIONS.

No DECOMPOSITION AFTER 1400 MINS.

Y-axis: TIME REQUIRED FOR START OF DECOMPOSITION (MINS)

X-axis: Nº OF CARBON ATOMS IN INHIBITOR CHAIN
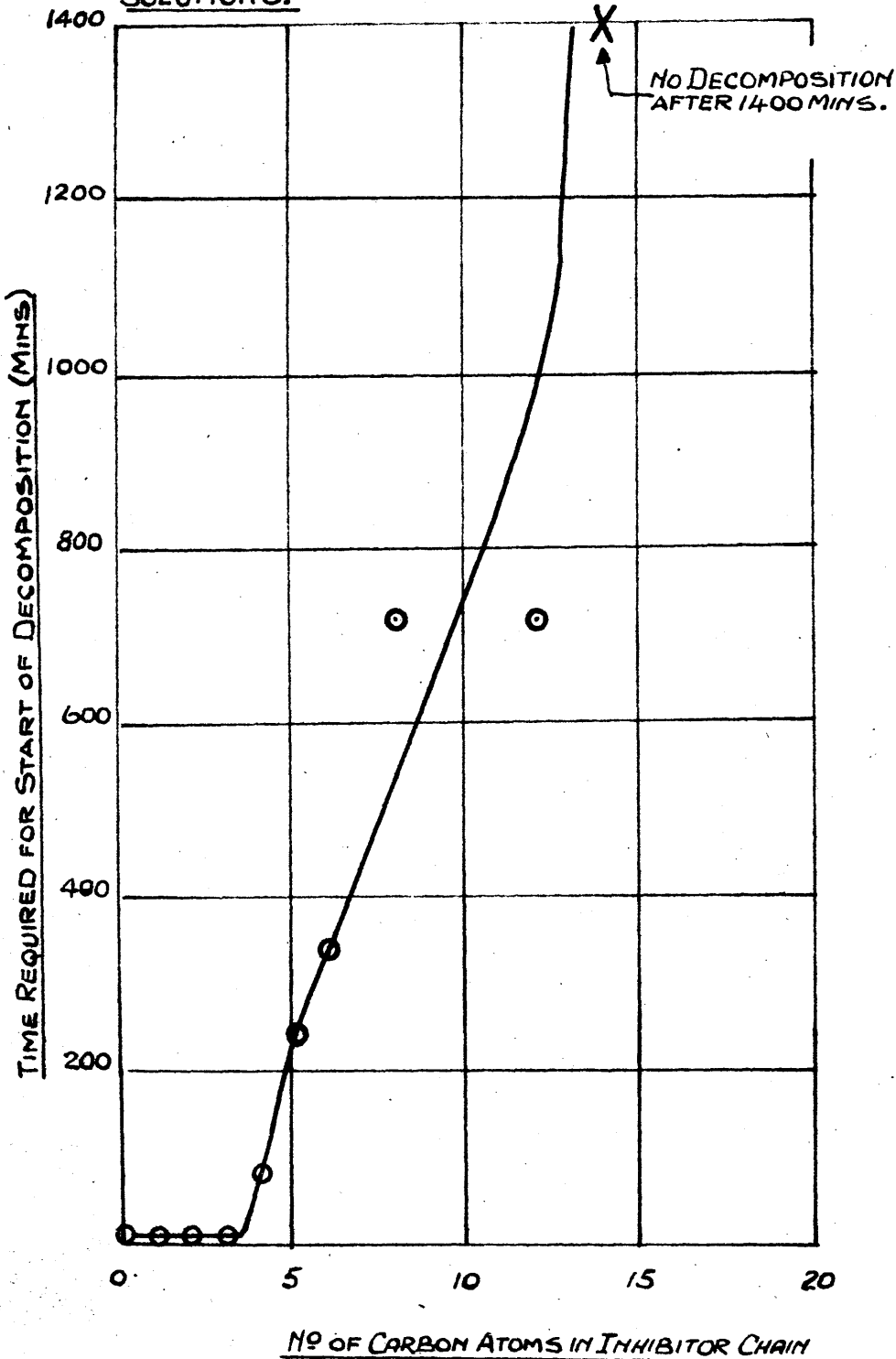
From Figure 5 it is clear that any saturated
monocarboxylic acid with a chain length of fourteen carbons
or more is likely to be a satisfactory inhibitor.

A series of empirical tests on other types of compound
revealed that some alcohols inhibited precipitation and a
number of acids and alcohols were therefore tested for inhibition
properties, the results being shown in Table X. Tests (2) and
(3) show that the presence of one double bond in the inhibitor
molecule does not appear to affect the inhibiting properties to
any great extent. A further test with a solution of oleic acid
in n-heptane (no carbonyl present) showed that the solution
turned cloudy and yellow after exposure to ultra-violet light.
The apparent decomposition observed in Test (2) is therefore
probably due to the decomposition of the oleic acid itself.

Tests (4) and (5) indicate that a straight chain
dicarboxylic acid is much less effective than the corresponding
monocarboxylic acid.

Tests (6) to (10) show that aromatic carboxylic acids
are ineffective for inhibition purposes.

Tests (11) and (12) show that cyclic structures are
ineffective for inhibition purposes.
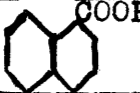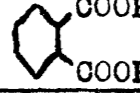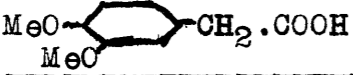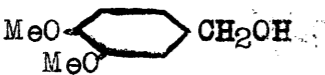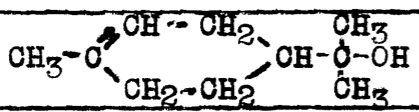
Tests (14) and (15) show that a branched chain compound
appears to be less effective than the corresponding straight
chain compound.

Conclusions.

It has thus been established that long straight chain

Table X

Alcohols and Carboxylic Acids as Inhibitors in the Decomposition of Chromium Hexacarbonyl Solutions.
(Concn. of Chromium Hexacarbonyl = 0.2g./l.)   (Solvent:- n-Heptane.)

Test No.	Inhibitor	Formula of inhibitor.	No. of C atoms in inhibitor.	Concn. of inhibitor (g./l.).	Appearance of Solutions after Exposure to U.V. Light. Duration of Exposure (minutes).					
					0	10	30	60	360	600
1	None	–	–	–	Clear, colourless.	Brown gel. ppte. Brown solution.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
2	Oleic acid.	$CH(CH_2)_7COOH$ $CH(CH_2)_7CH_3$	18	10	"	Clear, colourless.	Clear, colourless.	Clear, colourless.	Slightly cloudy. Colourless.	Cloudy. Very pale yellow.
3	Stearic acid.	$CH_3(CH_2)_{16}COOH$	18	10	"	"	"	"	Clear, colourless.	Clear, colourless.
4	Adipic acid.	$COOH(CH_2)_4COOH$	6	10 (saturated)	"	Brown gel. ppte. Brown solution.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
5	n-Caproic acid.	$CH_3(CH_2)_4COOH$	6	1	"	Clear, colourless.	Clear, colourless.	Clear, colourless.	Cloudy, colourless.	Cloudy, colourless.
6	α-Naphthoic acid.	COOH (naphthalene with COOH)	11	10 (saturated)	"	White gel. ppte. Soln. cloudy.	White gel. ppte. Soln. clear, cls.	P.C.	—	—
7	Phthalic acid.	COOH / COOH (benzene with two COOH)	8	"	"	Brown gel. ppte. Brown solution.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
8	3.4.Dimeth-oxyphenyl-acetic acid.	MeO— (ring) —$CH_2.COOH$, MeO	8+1+1	"	"	"	"	"	P.C.	—	—
9	3.4.Dimeth-oxybenzyl alcohol.	MeO— (ring) —CH_2OH, MeO	7+1+1	"	"	White gel. ppte. Soln. cloudy.	Green gel. ppte. Soln. clear, cls.	P.C.	—	—
10	Caprylic acid.	$CH_3(CH_2)_6COOH$	8	1	"	Clear, colourless.	Clear, colourless.	Clear, colourless.	Clear, colourless.	Clear, colourless.
11	α-Terpineol.	CH_3-C (ring structure with CH-CH$_2$, OH-C-OH, CH$_2$-CH$_2$, CH$_3$, CH$_3$)	10	10	"	Green gel. ppte.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
12	Lactose	$C_{12}H_{22}O_{11}$	6+6	10 (saturated)	"	Brown gel. ppte. Brown solution.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
13	sec-Heptyl alcohol.	$CH_3.CH_2.CH_2$ \ $CHOH$ / $CH_3.CH_2.CH_2$	7	10	"	Yellow, cloudy.	Green gel. ppte. Soln. clear, cls.	P.C.	—	—
14	n-Heptyl alcohol.	$CH_3(CH_2)_5CH_2OH$	7	10	"	Clear, colourless.	Clear, colourless.	Clear, colourless.	Clear, colourless.	Clear, colourless.

monocarbonylic acids are effective as inhibitors for the deposition of precipitate by chromium hexacarbonyl solutions. No other types of compound have been proved effective although there is some indication that long chain alcohols may possess inhibition properties.

D. Mechanism of Inhibition.

1) Visual Examination of Precipitate Tests.

It has already been established (p. 61) that the decomposition of chromium hexacarbonyl in solution takes place only in presence of light and oxygen and it is difficult to understand what effect compounds of the long chain monocarboxylic acid type could have on a decomposition of this sort. It was decided to perform a series of tests with stearic acid to establish the minimum molar ratio of inhibitor to chromium hexacarbonyl consistent with successful inhibition. The results of this test are shown in Table Xl.

Table Xl revealed that the critical concentration of inhibitor was approximately equimolecular to the concentration of the chromium hexacarbonyl. In order to confirm this and to prove that the critical inhibitor concentration was not constant but dependant on the chromium hexacarbonyl concentration, a further series of tests was performed using a concentration of hexacarbonyl five times greater than that employed for the previous test. The results of this series of tests are given in Table Xll.

Table Xll confirms that the inhibitor becomes effective when its molar concentration exceeds that of the

Table Xl.

<u>Stearic Acid as an Inhibitor in the Decomposition of Chromium Hexacarbonyl Solutions.</u>
<u>The Effect of Varying the Molar Ratio Stearic acid/Chromium Hexacarbonyl.</u>
Concentration of Chromium Hexacarbonyl = 0.2g./l   Solvent:- <u>n</u>-Heptane.

Molar Ratio:- Stearic Acid / $Cr(CO)_6$	<u>Appearance of Solutions after exposure to Ultra-violet Light</u>. Duration of Exposure (minutes)				
	0	5	10	60	140
0	Clear, colourless	Brown gel. ppte. Solution cloudy.	Brown gel. ppte. Solution cloudy.	Brown gel. ppte. Solution clear, cls.	P.C.
1.0	"	Clear, colourless	White gel. ppte. Solution cloudy.	"	P.C.
1.1	"	"	Soln. clear. Very pale straw colour.	Brown gel. ppte. Solution cloudy, brown.	Brown gel. ppte. Solution clear, cls.
1.2	"	"	"	Solution clear. Pale straw colour.	
1.5	"	"	"	"	
2	"	"	Straw colour. More pale than with lower molar ratios.	Soln. clear. Straw colour fainter than above.	
3	"	"	"	"	Yellow-brown colouration diminishing in intensity as the molar ratio:- Stearic acid / $Cr(CO)_6$ increases. No ppte. or cloudiness
4	"	"	"	"	
6	"	"	"	"	
8	"	"	"	"	
10	"	"	"	"	

Table XII

Stearic Acid as an Inhibitor in the Decomposition of Chromium Hexacarbonyl Solutions.
The Effect of Varying the Molar Ratio Stearic Acid/$Cr(CO)_6$.
(Concn. of $Cr(CO)_6$ = 1.000g./l.)   (Solvent:- n-Heptane).

Molar Ratio:- Stearic Acid / $Cr(CO)_6$	Appearance of Solutions after Exposure to U.V. Light. Duration of Exposure (minutes).							
	0	15	30	45	60	75	180	1440
0	Clear, colourless.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—	—	—	—
0.200	"	"	P.C.	—	—	—	—	—
0.500	"	Solution clear, pale green.	Green gel. ppte. Soln. cloudy.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—	—
0.750	"	"	Solution clear, pale green.	Green gel. ppte. Soln. cloudy.	Brown gel. ppte. Soln. clear, cls.	P.C.	—	—
0.900	"	"	"	Solution clear, pale green.	Green gel. ppte. Soln cloudy.	Brown gel. ppte. Soln. clear, cls.	P.C.	—
1.000	"	"	"	"	Solution clear, pale green.	Green gel. ppte. Soln. cloudy.	Brown gel. ppte. Soln. clear, cls.	P.C.
1.100	"	"	"	"	"	Solution clear, pale green.	Green gel. ppte. Soln. cloudy.	Brown gel. ppte. Soln. clear, cls.
1.200	"	"	"	"	"	"	Soln. clear. Col. slowly changing from green to brown.	Brown soln. No ppte. or cloudiness.

hexacarbonyl.   If it is assumed that the start of decomposition
is indicated by the appearance of the precipitate it is
possible to graph "Time for start of decomposition" against
"Molar ratio Stearic acid/Cr(CO)$_6$".   This is shown in
Figure 6.

Although it has been established that the critical
threshold concentration of inhibitor is equimolecular with
the chromium hexacarbonyl the mechanism of the inhibition is
still not clear.   If the inhibitor were preventing precipitation
by retaining the chromium in solution as chromium stearate it
would be expected that the critical value of the molar ratio
stearic acid/Cr(CO)$_6$ would be at least 3/1 since it is likely
that chromium would be at least trivalent in presence of oxygen.

It is possible that the stearic acid is acting by
absorbing light of the wavelengths which cause decomposition.
The wavelengths of light causing decomposition must be in the
near ultra-violet.   The light passes freely through ordinary
glass since all tests were carried out in glass test tubes.
A test in which chromium hexacarbonyl solutions were exposed
to an equal intensity of light in quartz and glass test tubes
showed no appreciable variation in the decomposition rate.
This established that the wavelengths causing decomposition
were not less than 3000 Angstrom Units since glass cuts out
a large proportion of the light at shorter wavelengths.   It was
also established that the light causing decomposition would not
pass through brown glass since chromium hexacarbonyl solutions

FIGURE. 6.

STEARIC ACID AS AN INHIBITOR IN THE DECOMPOSITION OF $Cr(CO)_6$ SOLUTIONS.

THE EFFECT OF VARYING THE MOLAR RATIO $\dfrac{STEARIC\ ACID}{Cr(CO)_6}$

WITH MOLAR RATIO 1·2 NO DECOMPOS^N AFTER 1440 MINS.

TIME FOR START OF DECOMPOSITION (MINUTES)

MOLAR RATIO $\dfrac{STEARIC\ ACID}{Cr(CO)_6}$
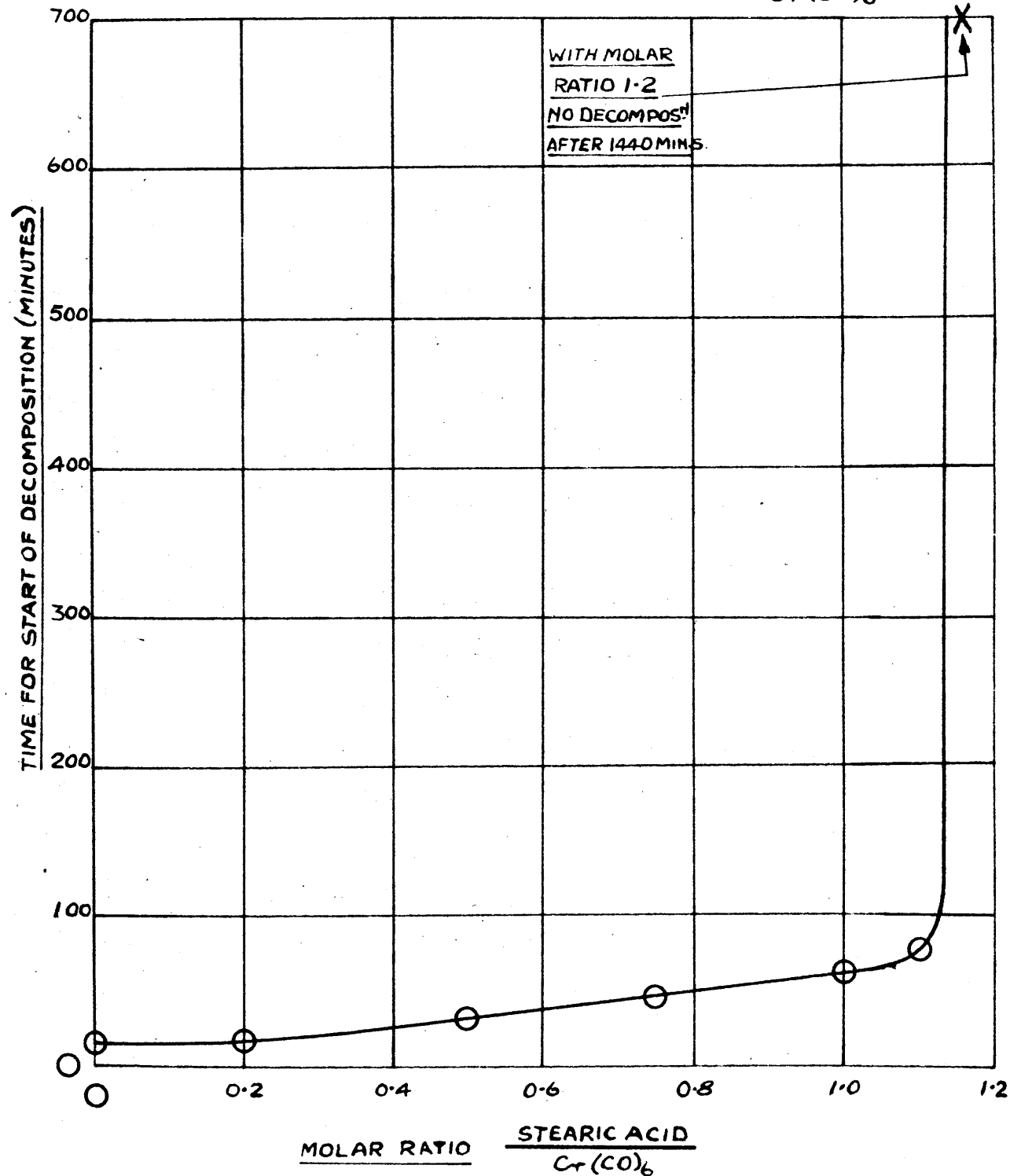
stored in brown glass remained undecomposed after exposure
to sunlight or the ultra-violet lamp.   This proved that
the wavelength was less than 6000A.   Exposure to intense
light from a normal tungsten filament electric bulb caused
decomposition only after very long periods and this indicated
that the important wavelengths were not in the visible region
of the spectrum.   The wavelengths causing decomposition are
therefore somewhere in the region 3000-4000A. and if stearic
acid is acting by absorbing light of the vital wavelengths it
would be expected to give a reasonably strong absorption of
light in the near ultra-violet.

It is also possible that the inhibitor acts by
forming an addition compound with the hexacarbonyl, the addition
complex being stable to light.

2)   Ultra-Violet Absorption Tests.

In an attempt to establish the mechanism of
inhibition it was decided to study the ultra-violet absorption
spectra of chromium hexacarbonyl and stearic acid.   Solutions
of the two compounds were studied in a "Unicam Model SP 500
Quartz Spectrophotometer".   The solvent used in the following
tests was iso-octane (2.2.4. trimethylpentane) since supplies
of this hydrocarbon were available in the specially pure form
necessary for spectroscopic work.

Figure 7 shows the absorption curves for M/50,000
chromium hexacarbonyl and M/5,000 stearic acid.   A series of
empirical tests established these to be the most suitable

FIGURE 7   UV   ABSORPTION SPECTRA OF CHROMIUM HEXACARBONYL
AND STEARIC ACID

○—○ $\frac{M}{50,000}$ Cr (CO)$_6$

×—× $\frac{M}{5,000}$ STEARIC ACID

OPTICAL DENSITY UNITS

WAVELENGTH OF LIGHT (ANGSTROM UNITS)
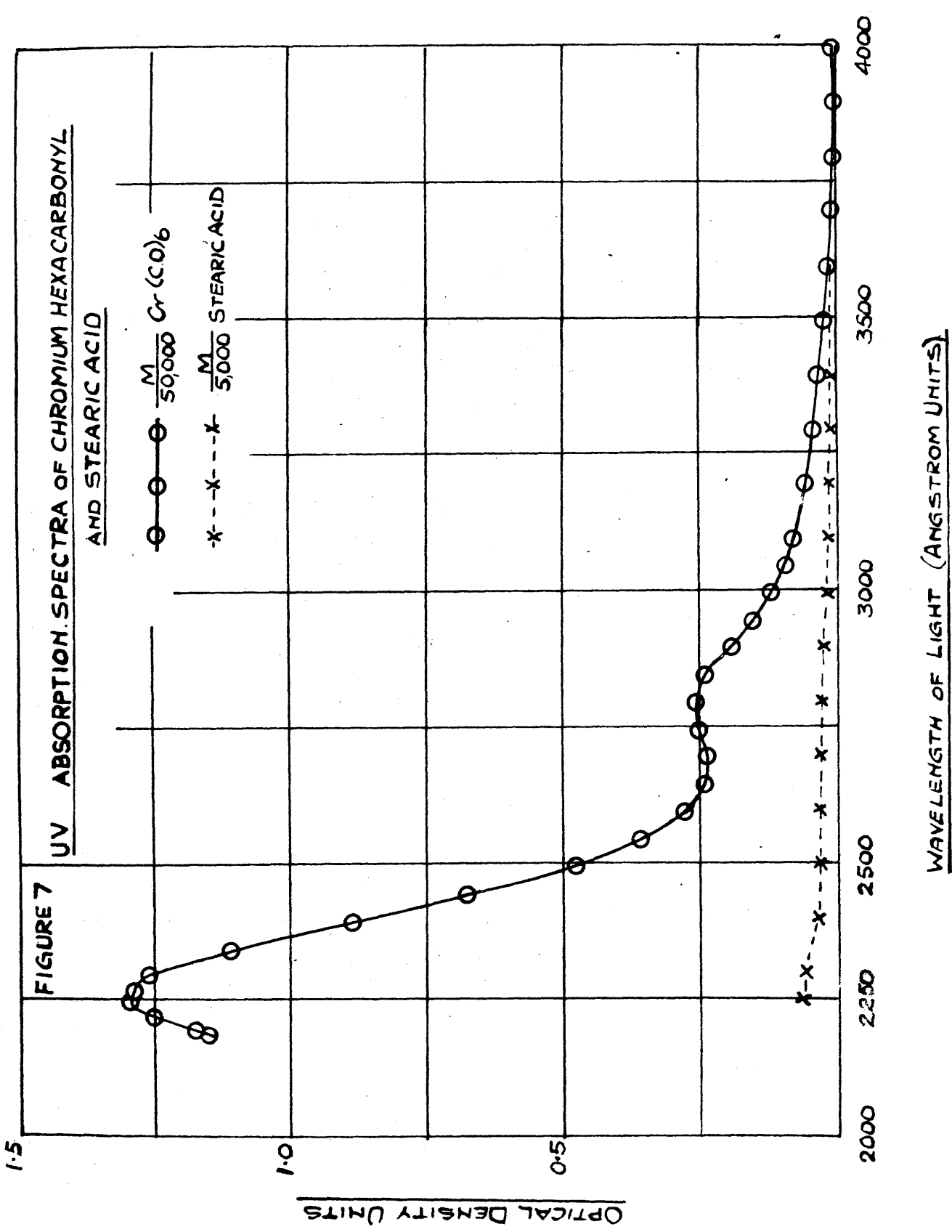
concentrations for the test. Absorption of light by the
solvent has no effect on the graphs as it is cancelled by
a compensating system in the instrument. The abscissae of
this and subsequent graphs correspond to the wavelength of
light while the ordinates show "optical density".

$$\text{Optical Density} = \log_{10} I_o/I_1$$

where I_o = Intensity of incident light

and I_1 = Intensity of light after passage through the
solution.

The value of the optical density thus gives a measure of the
light absorbed by the substance. Figure 7 shows that chromium
hexacarbonyl gives a strong absorption band at 2250 A. and a
weaker one at 2800 A. Stearic acid gives very little absorption
of ultra-violet light in the range 2200-4000 A.

Figure 8 shows the effect on a M/50,000 solution of
chromium hexacarbonyl of exposure to ultra-violet light for
varying periods of time. (The source of light was the mercury
vapour lamp already mentioned (p.64). The ultra-violet light
to which the solutions are exposed in the spectrophotometer is
not of sufficient intensity to cause appreciable decomposition
of the solutions provided the absorption curve is determined
fairly rapidly. This was established by doing two successive
runs on the same solution. The two absorption curves were
almost exactly coincidental.) As would have been expected from
previous stability tests the intensities of the two absorption
bands diminish rapidly indicating that the hexacarbonyl is
decomposing. The graphs in Figure 8 do not show the absorption

FIGURE 8

U.V. ABSORPTION CURVES INDICATING DECOMPOSITION OF CHROMIUM HEXACARBONYL IN SOLUTION AFTER EXPOSURE TO U.V. LIGHT FOR VARYING PERIODS.
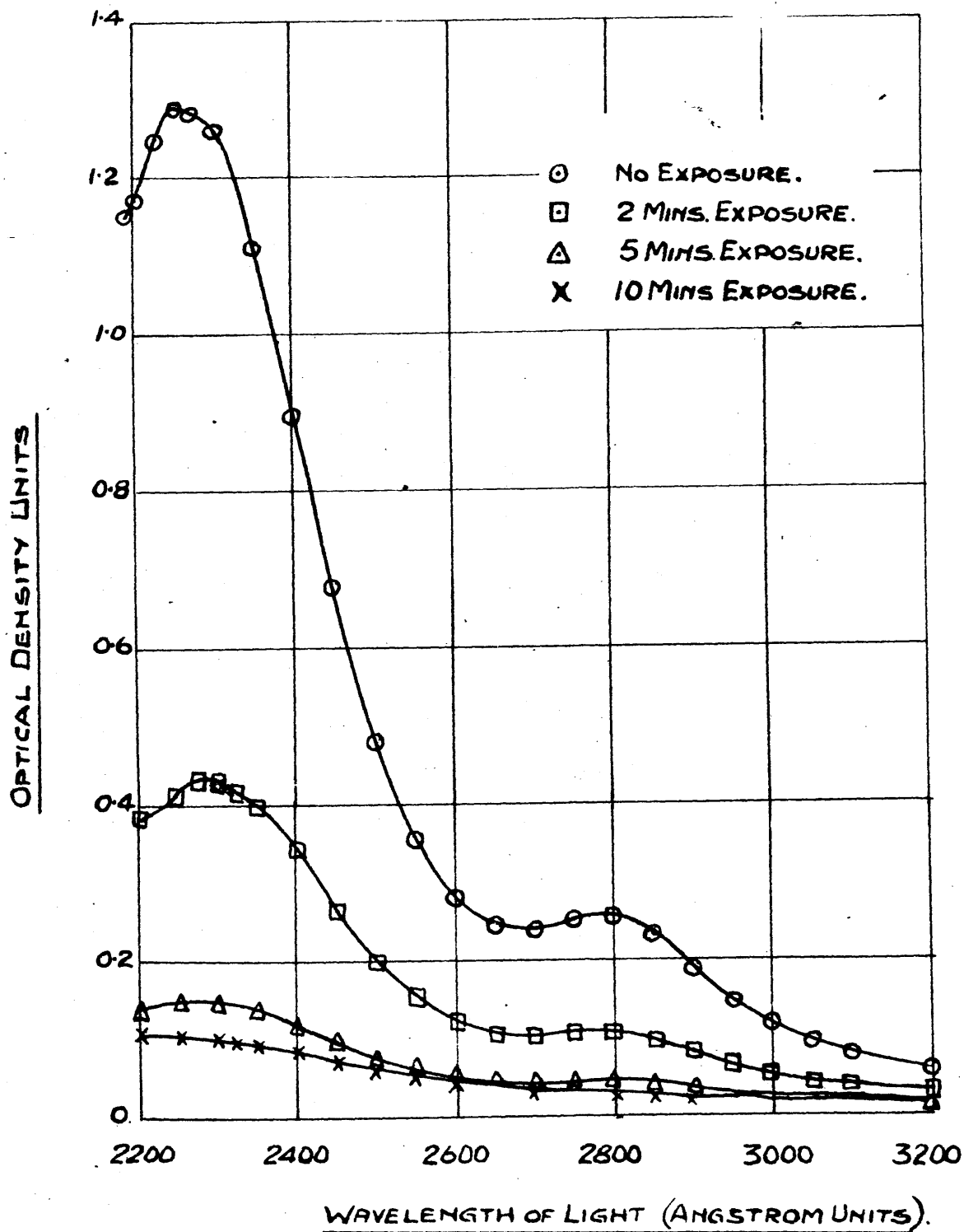
at wavelengths greater than 3,200 A. since no new absorption
bands were detected in this region and the graphs were too
close together to be shown clearly. Figure 9 shows the
ultra-violet absorption curve of a mixture of M/50,000 chromium
hexacarbonyl and M/40,000 stearic acid. The reason for
selecting the concentration M/40,000 for the stearic acid is
that this corresponds to a molar ratio Stearic acid/Cr(CO)$_6$ of
1.25, which would be expected to be effective in inhibiting
decomposition without involving the presence of a large excess
of the stearic acid (v. Figure 6). The graph in Figure 9
is almost identical with the graph on Figure 7 showing the
absorption curve for chromium hexacarbonyl alone. The very
slightly increased absorption can be attributed to the stearic
acid and the absence of any new absorption bands indicates
that if any new compound has been formed it must be a simple
addition compound of chromium hexacarbonyl and stearic acid
in equimolecular proportions.

Figure 10 shows the effect of exposure to ultra-
violet light on M/50,000 chromium hexacarbonyl in presence of
M/40,000 stearic acid. The very small absorption due to
stearic acid has been subtracted from the curve so that the
absorption of the hexacarbonyl only is shown. A comparison
between the curves in Figures 8 and 10 shows that the inhibitor
is delaying decomposition slightly but not to nearly the same
extent as would appear from the visual examination of exposed
inhibited solutions. Thus after exposing to ultra-violet

FIGURE 9

U.V. ABSORPTION SPECTRUM OF A MIXTURE OF $\frac{M}{50,000}$ CHROMIUM HEXACARBONYL AND $\frac{M}{40,000}$ STEARIC ACID.

WAVELENGTH OF LIGHT (ANGSTROM UNITS)
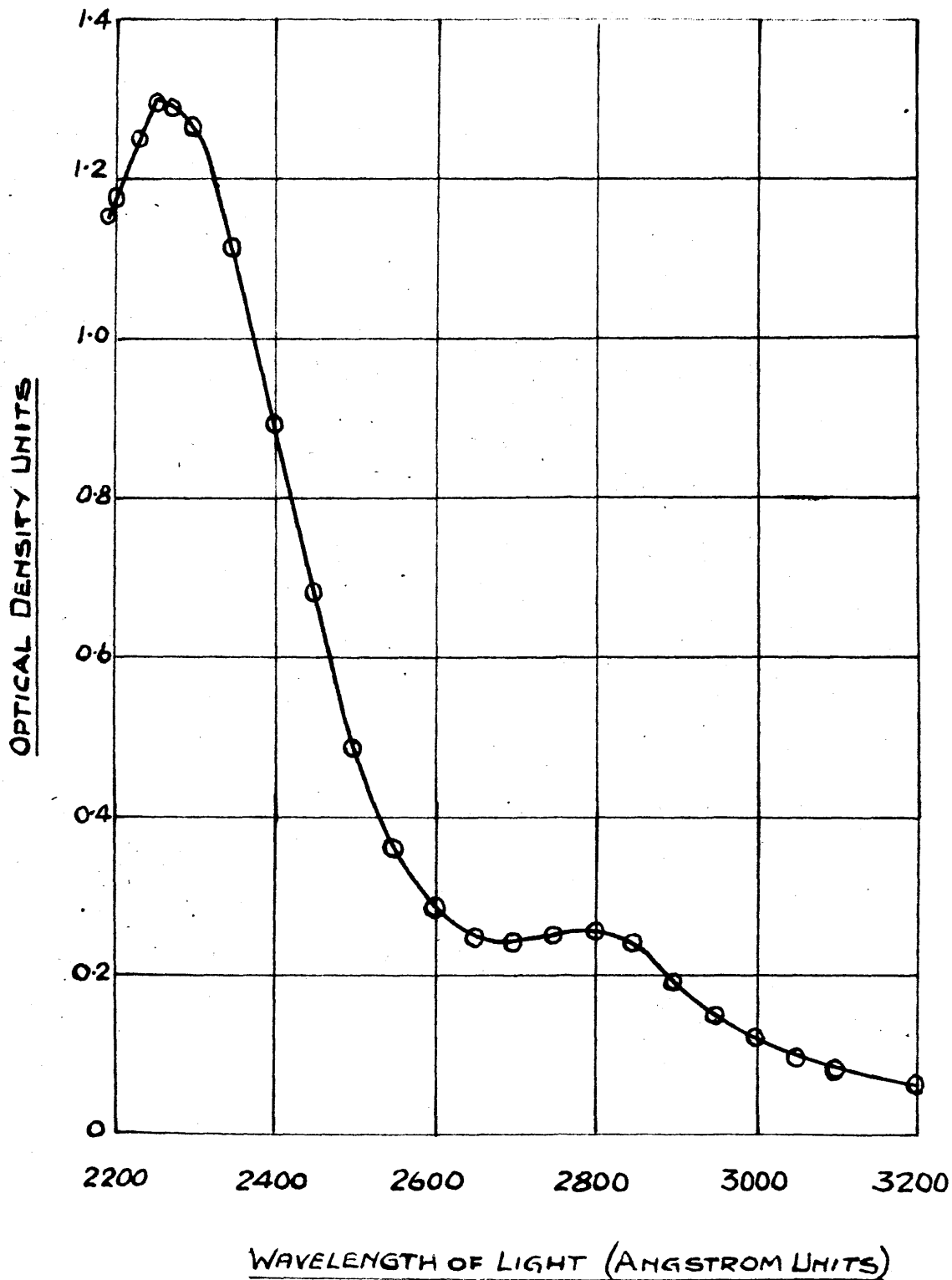
FIGURE 10

UV ABSORPTION CURVES INDICATING DECOMPOSITION
OF $\frac{M}{50,000}$ CHROMIUM HEXACARBONYL IN PRESENCE
OF $\frac{M}{40,000}$ STEARIC ACID.

[STEARIC ACID ABSORPTION SUBTRACTED FROM CURVES]

EFFECT OF EXPOSURE TO UV LIGHT FOR VARYING PERIODS.

⊙ NO EXPOSURE.
⊡ 2 MIN. EXPOSURE
△ 5 MIN " "
✕ 10 MIN " "
▽ 60 MIN " "

OPTICAL DENSITY UNITS

WAVELENGTH OF LIGHT (A°)
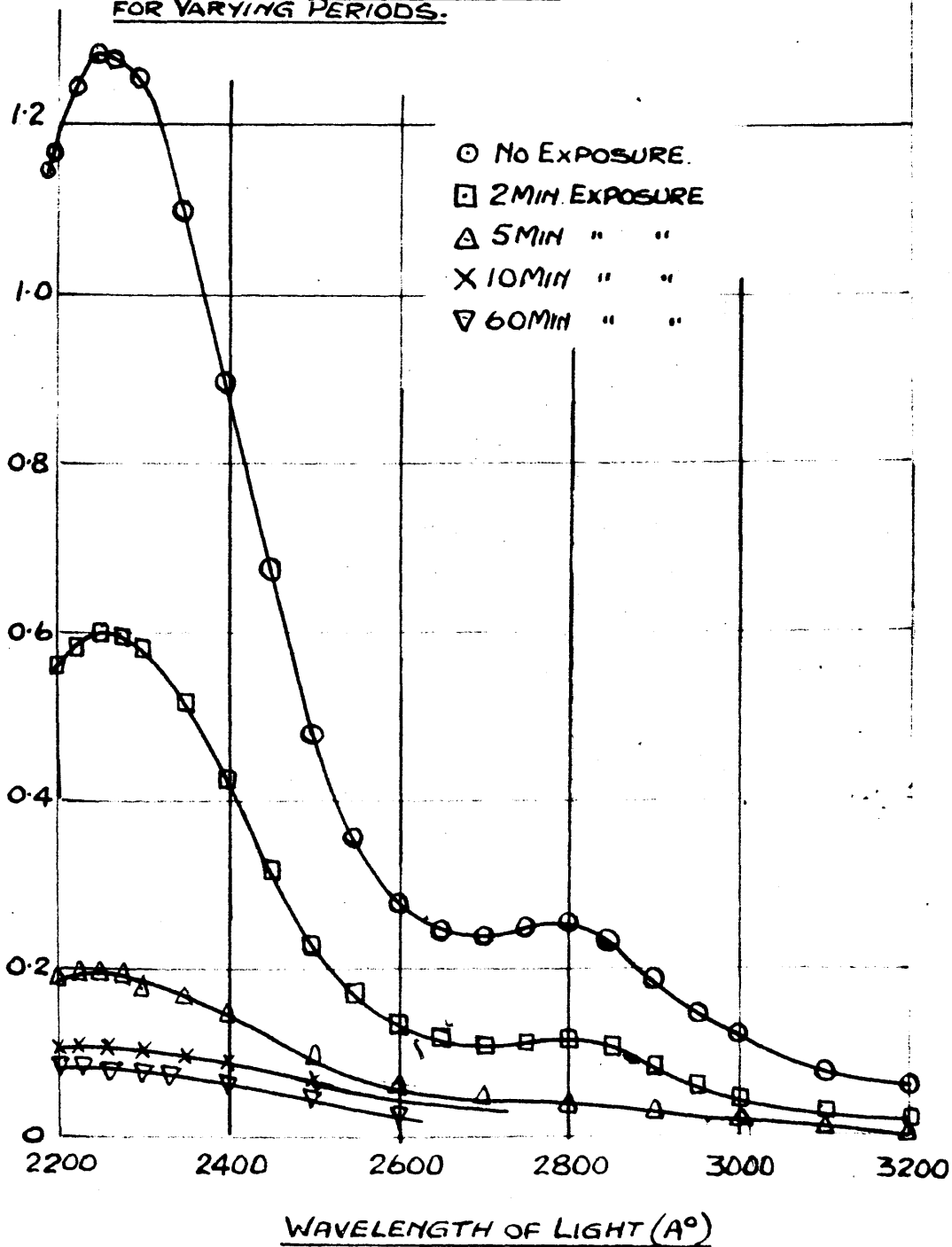
light for one hour an inhibited solution of chromium hexacarbonyl
the absorption band at 2,250 A. is only about 6% of its original
intensity.   There is, however, no precipitation in the solution
although this would occur in a few minutes in absence of the
inhibitor.

The fact that the absorption band did not disappear
completely after the inhibited solution had been exposed for
one hour made it seem possible that a large excess of inhibitor
was necessary to prevent decomposition.   A solution of M/50,000
chromium hexacarbonyl, M/5,000 stearic acid (Molar ratio stearic
acid/$Cr(CO)_6$ = 10/1), was exposed to ultra-violet light for one
hour.   After exposure the absorption band at 2250 A. was found
to be only about 6% of its original intensity thus showing
that the presence of a large excess of inhibitor did not further
reduce the rate of decomposition.

The ultra-violet absorption studies have shown that
long chain monocarboxylic acids do not really inhibit the
decomposition of chromium hexacarbonyl solutions although they
delay the decomposition to some extent.   The inhibitors do,
however, retain the chromium in solution in some way.   The
exact form in which the chromium is retained in solution is
not clear from the ultra-violet absorption curves.   The curves
show that the hexacarbonyl is decomposing and this obviates
the possibility of a stable addition complex being responsible
for the non appearance of a precipitate.   The carbonyl can
hardly be decomposing to chromium stearate since the concentration

of stearic acid required to inhibit precipitation was equimolecular with the chromium hexacarbonyl. If, therefore, the existence of a chromium stearate is postulated it is necessary to assume the stable existence of monovalent chromium. This seems most unlikely.

The fact that a method of inhibiting precipitation has been discovered would, however, make it practicable to use chromium hexacarbonyl as an additive to internal combustion engine fuels. The presence of inhibitor would prevent the formation of solid deposits in the fuel tank, and since there is likely to be very little exposure of the fuel to strong ultra-violet light it seems probable that a large proportion of the hexacarbonyl would remain undecomposed.

3) Spontaneous Ignition Temperature Tests.

Chromium hexacarbonyl causes a considerable rise in the S.I.T. of Pool Petrol: the details are given in Section III of this thesis (p.88). The two series of tests completed so far on the inhibition of the decomposition of chromium hexacarbonyl solutions have given rather surprising results. Visual examination of the precipitates formed on decomposition has indicated that stearic acid was inhibiting precipitation. Ultra-violet absorption studies have shown that though stearic acid inhibits precipitation its effect on the rate of decomposition is relatively slight. The conclusion arrived at was that chromium hexacarbonyl, in presence of stearic acid, was decomposing on exposure to ultra-violet light but the decomposition was to some unusual type of chromium compound. It would be of

interest to see whether this compound produces the same effect on the S.I.T. of Pool Petrol as does chromium hexacarbonyl itself, and the S.I.T. tests described below were designed with this end in view.

(i)   S.I.T. of Pool Petrol   = 424°C.

(ii)   S.I.T. of Pool Petrol containing
         2g./1. Cr(CO)$_6$ = 510°C.

(iii)   S.I.T. of Pool Petrol containing
         3g./1. stearic acid   = 395°C.

(iv)   S.I.T. of Pool Petrol containing
         2g./1. Cr(CO)$_6$, 3g./1. stearic acid   = 503°C.

These tests show that stearic acid lowers the S.I.T. of Pool Petrol but when both stearic acid and chromium hexacarbonyl are present in the fuel the combined effect is to cause a rise in S.I.T. almost equal to that caused by chromium hexacarbonyl alone.

A solution of 2g./1.Cr(CO)$_6$, 3g./1.stearic acid in Pool Petrol was poured into a number of test tubes, each of which was exposed to ultra-violet light for a different period of time.   After exposure the S.I.T.'s of the solutions were determined, the results being shown in Table X111.

The results in Table X111 indicate that chromium is remaining in solution in an active form for about one hour of exposure to intense ultra-violet light: thereafter the activity of the chromium appears to diminish.

Visual precipitation studies showed no sign of a precipitate even after 24 hours while ultra-violet absorption curves showed almost complete decomposition in 10 minutes. The latest results suggest that when chromium hexacarbonyl

Table X111.

The Effect of Exposure to U.V. light on the S.I.T. of Pool Petrol containing 2 g./l. Cr(CO)$_6$ and 3 g./l. stearic acid.

Duration of Exposure. (hours)	S.I.T. (°C.)
Nil.	503
0.5	503
1	500
4	452
8	420

solutions are exposed to light in presence of stearic acid there is a very rapid decomposition of the hexacarbonyl to some other chromium compound.   This compound is soluble in hydrocarbon solvents and is active as a combustion modifier. This intermediate compound appears to be decomposing to another, also soluble in hydrocarbon solvents but ineffective as a combustion modifier.

Conclusions - Section II.

1) Solutions of chromium hexacarbonyl decompose on exposure to light and oxygen, forming an insoluble decomposition product, the exact nature of which depends on the conditions of the decomposition.

2) The wavelength of light causing decomposition is in the near ultra-violet.

3) The presence of monocarboxylic acids containing four or more carbon atoms in a straight chain delays the formation of the insoluble decomposition product. Monocarboxylic acids containing more than thirteen carbon atoms in a straight chain appear to inhibit precipitation completely.

4) In order to inhibit precipitation the concentration of the acid must be greater than equimolecular to the chromium hexacarbonyl.

5) In presence of a monocarboxylic acid of suitable chain length chromium hexacarbonyl solutions decompose forming an unknown chromium compound which is soluble in hydrocarbon solvents.   Like chromium hexacarbonyl this compound modifies

the ignition characteristics of Pool Petrol.   The original decomposition product slowly decomposes to another unknown compound, also soluble in hydrocarbon solvents but without effect on the ignition characteristics of Pool Petrol.

6) Chromium hexacarbonyl can be used as a fuel additive without fear of solid deposition on storage provided that a long chain monocarboxylic acid is also dissolved in the fuel.   The ignition properties of the fuel will not be affected by short periods of exposure to light.

SECTION III.

... the Appendix and the Spontaneous X
... (S.I.T.) tests were performed in a modified
... ure Apparatus constructed by the ...
... Ignition Temperature Apparatus ...
... the low value
of which the substance, surrounded by air at the ...
... flame without the application of ...
on other ... brief review of

SECTION III.

... the introduc-
... the S.I.T. is determined by ...
drop of ... substance to be tested to fall into a ...
which is at a known temperature and into which air
... The apparatus shown in Figure 11 ...
designed to ... with the above conditions and con-
... Mild steel pot containing solder.
... Ignition pot with air preheating coil (Dimensions
...).
... Polished ... disc.
... Wire ...

SECTION 111.

THE EFFECT OF CHROMIUM HEXACARBONYL ON FUELS.

The engine tests described in this section were carried out in a "Ricardo E 6/S Variable Compression Engine" (For description see Appendix) and the Spontaneous Ignition Temperature (S.I.T.) tests were performed in a modified version of the Moore Apparatus[24] constructed by the author.

A. The Spontaneous Ignition Temperature Apparatus.

The S.I.T. of a substance is the lowest temperature at which the substance, surrounded by air at the same temperature, will burst into flame without the application of any spark or other local high temperature.   A brief review of Spontaneous Ignition Temperatures has been given in the introduction to this thesis (p.9).   The S.I.T. is determined by allowing a drop of the substance to be tested to fall into a pot maintained at a known temperature and into which air is flowing at a known rate.   The apparatus shown in Figure 11 was designed to comply with the above conditions and consists of:-

(A) Mild steel pot containing solder.

(B) Ignition pot with air preheating coil (Dimensions of pot : 3" x 1.1/2" D.).

(C) Polished stainless steel disc.

(D) Mild steel thermocouple sheath.

(E) Alundum tube wound with resistance wire.   Current from the mains is passed through the resistance wire thus heating the pot.   The voltage drop across this resistance is varied by an external variable resistance in series thus

FIGURE 11
SPONTANEOUS IGNITION TEMPERATURE
APPARATUS

A
B
C
D
E
G
H
J
K
L
M
N
F

enabling the rate of heating to be controlled.

(F)   Insulated copper flex.

(G)   Asbestos lagging to prevent temperature fluctuations.

(H)   Copper plate casing of furnace.

(J)   Circular "Sundanyo" sheets forming top and bottom of furnace.

(K)   Asbestos sheets.

(L)   Burette containing solution to be tested.

(M)   Chromel-alumel thermocouple.   Readings are taken on a 0-40 mv. millivoltmeter.

(N)   Air line from flow-meter (0-40 l./hr.).

1)   Assembly and Testing of Apparatus.

(a)   The thermocouple was calibrated and the relation between thermocouple temperature and the temperature of the ignition pot established.   The two temperatures agreed to within 5 centigrade degrees over the temperature range 20 - 600°C. Since the method is only accurate to $\pm$ 5°C. this was considered satisfactory.

(b)   In carrying out S.I.T. tests it is important to be able to control the rate of temperature rise.   The settings of the variable resistance corresponding to different rates of temperature rise were determined and noted.   The rate of heating should not rise above 2.5 centigrade degrees/minute[19].

(c)   A burette was selected which gave a drop volume of approximately 0.013 cc. with petrol.   This was the drop volume used by Weerman[19] in an apparatus of similar dimensions.

(d)   The flow meter was calibrated by the water displacement method.

2) Manipulation of Apparatus.

In determining the S.I.T. of a liquid the heating is switched on and the temperature allowed to rise to about 100 centigrade degrees less than the expected ignition temperature. The external resistance is then adjusted to give a rate of temperature rise of 2 centigrade degrees/minute. The resistance is adjusted to maintain this rate throughout the test. The rate of air flow is brought to the desired value and kept constant during the test.

One drop of the liquid to be tested is then allowed to fall from the burette (L) into the centre of the ignition pot (B) and which is watched carefully to observe if ignition occurs. This process is repeated every two minutes until ignition does occur. Ignition is usually indicated by a flame leaping out of the pot but under certain conditions there may only be a faint "pop" and a small flame within the pot.   When ignition occurs the millivoltmeter reading is at once taken and recorded. The furnace is then switched off and the unit allowed to cool to at least 50°C. below the S.I.T. before a repeat determination is carried out.   Ignition tests performed while the unit is cooling are unsatisfactory since previous ignitions have overheated the pot to a higher temperature than that of the surrounding bath.   It is also inadvisable to add the drops of test liquid more frequently than one every two minutes, since each drop removes heat in evaporating and equilibrium must be

re-established.

Since the rate of heating is 2 centigrade degrees/min. and the frequency of drop additions is one every two minutes, the accuracy of the test is to within 4°C.   This can be improved to 2°C. by repeating the experiment as before, except that a drop of liquid is now added at a temperature 2°C. lower than the previous ignition temperature.   This is repeated until ignition no longer occurs, the lowest temperature at which ignition takes place being regarded as the S.I.T..   The test is not absolutely reliable to more than ± 5°C.

3) Characteristics of Apparatus.

Various factors are known to affect the S.I.T. of a substance[48] but few quantitative data are available.   It was therefore decided to test the effect of these variables on certain substances.   The substances selected were n-heptane and iso-octane which were known to have relatively low and high S.I.T.s respectively and Pool Petrol as a typical commercial fuel.   The effects of the following variables were studied:-

(a)   The nature of the metal of the contact disc "C" (v.Figure 11)

(b)   The rate of air flow.

(c)   The volume of the drop of test liquid.

(a)   The Nature of the Contact Disc.

When a drop of the test liquid is allowed to fall into the ignition pot it strikes a thin circular metal disc at the bottom of the pot.   The effect of this variable is very inconclusive.   Egerton and Gates[49] found that the composition

of the discs had a considerable effect on S.I.T.s while Moore[50]
came to the opposite conclusion.

The effect of discs of various metals on the S.I.T.
of n̲-heptane was determined, the conditions of the discs after
a number of ignitions also being noted.   The results are
shown in Table XlV.

Table XlV shows that the metal of the disc has little
effect on the S.I.T. of n̲-heptane.   Similar results were
obtained with iso-octane and Pool Petrol.   A stainless steel
disc was selected as being most suitable from the corrosion
point of view.

(b)   The Rate of Air Flow.

The effects of varying air flow on the S.I.T.s of
n̲-heptane, iso-octane and Pool Petrol were determined, the
results being shown graphically in Figures 12, 13 and 14.   In
determining S.I.T.s at air flow rates under 8 l./hr. the
atmosphere in the pot was purged of residual combustible
material by increasing the air flow temporarily if a drop failed
to ignite.

A study of the graphs in Figures 12, 13 and 14 reveals
that as the rate of air flow is increased from zero to 35 l./hr.
the S.I.T. first rises fairly quickly, then remains almost
constant over a range of air flow rates, and finally increases
again.   Since it is principally changes in S.I.T. with which
this work is concerned it is obviously of advantage to work
in the temperature range corresponding to the straight region

Table XlV.

The Effect of Different Contact Discs on the S.I.T. of n-Heptane.

(Rate of Air Flow = 11 l./hr. Drop Volume = 0.013 cc.)

Metal Disc	S.I.T.(°C)	Condition of Disc after 10 Ignitions.
Aluminium	274	Untarnished
Brass	272	Untarnished
Cast Steel	274	Tarnished
Copper	272	Tarnished
Mild Steel	274	Untarnished
Monel Metal	271	Untarnished
Stainless Steel	272	Untarnished

FIGURE 12

The Effect of Varying Air Flow on the S.I.T. of n-Heptane.

Drop Volume = 0.013 c.c.
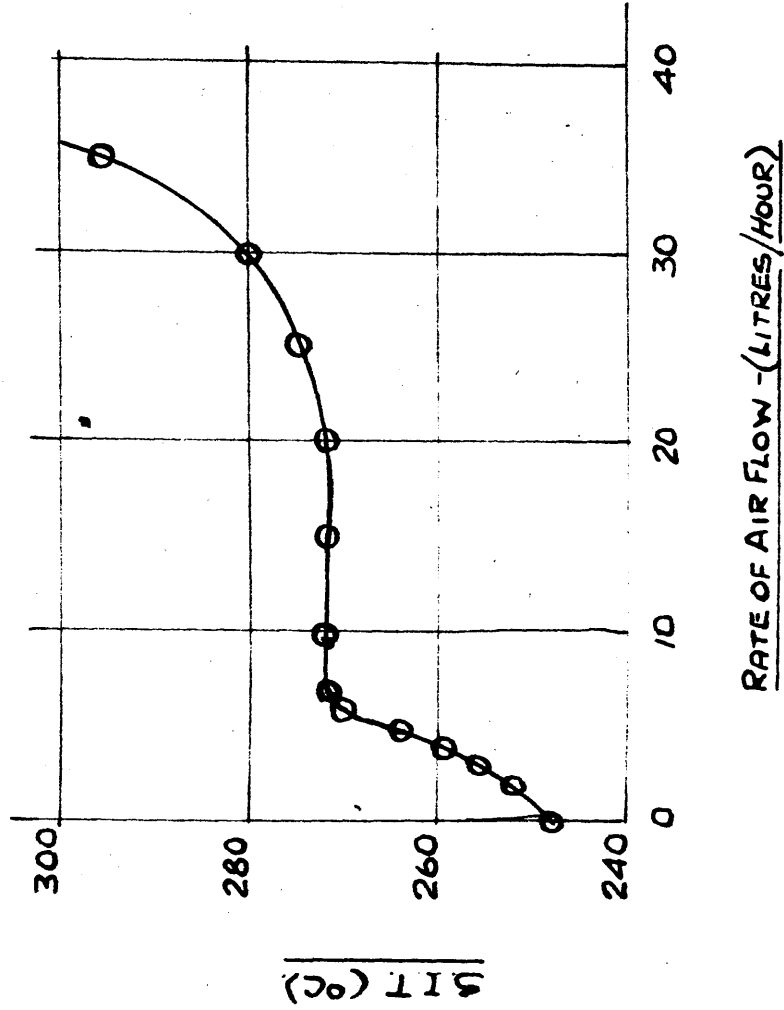
FIGURE 13

THE EFFECT OF VARYING AIR FLOW ON THE S.I.T.
OF 160° OCTANE.

DROP VOLUME = 0.013 CC.
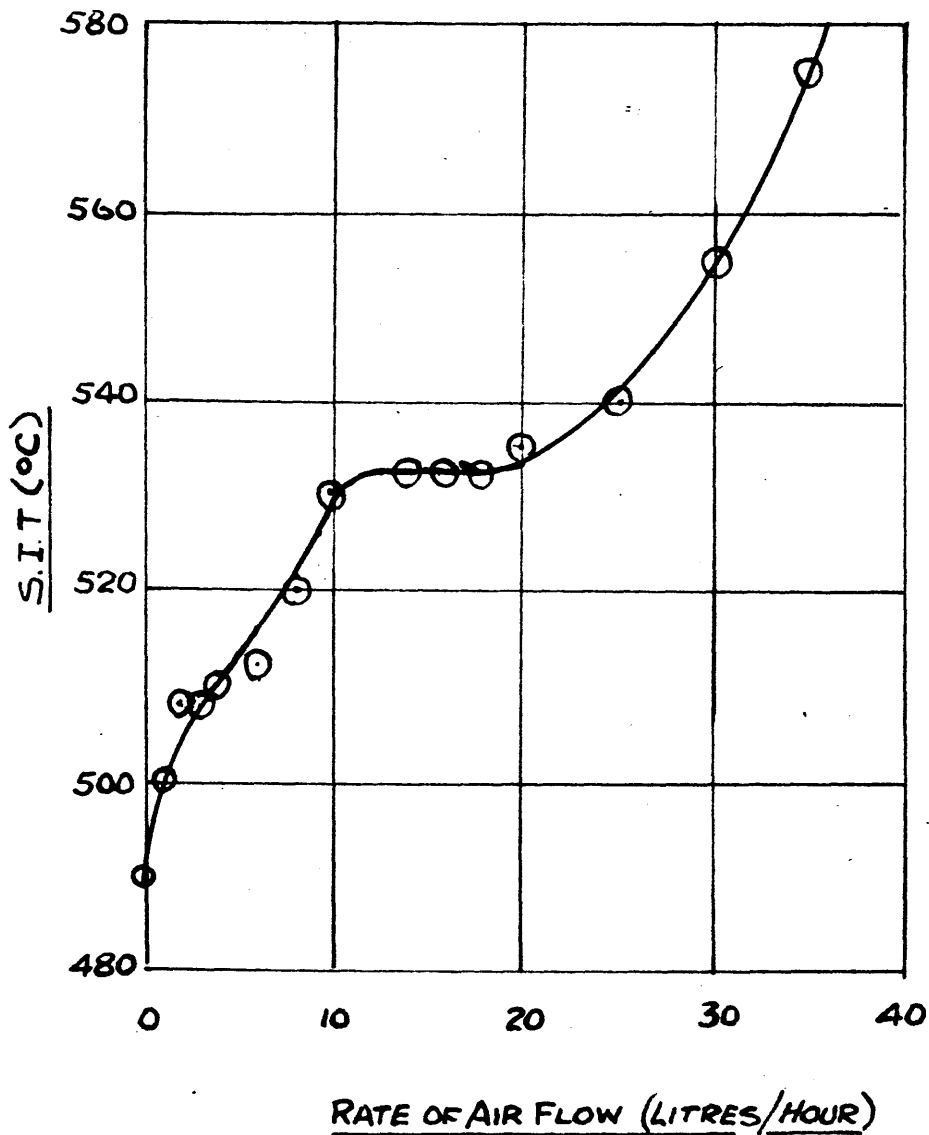
FIGURE 14

THE EFFECT OF VARYING AIR FLOW
ON THE S.I.T. OF POOL PETROL
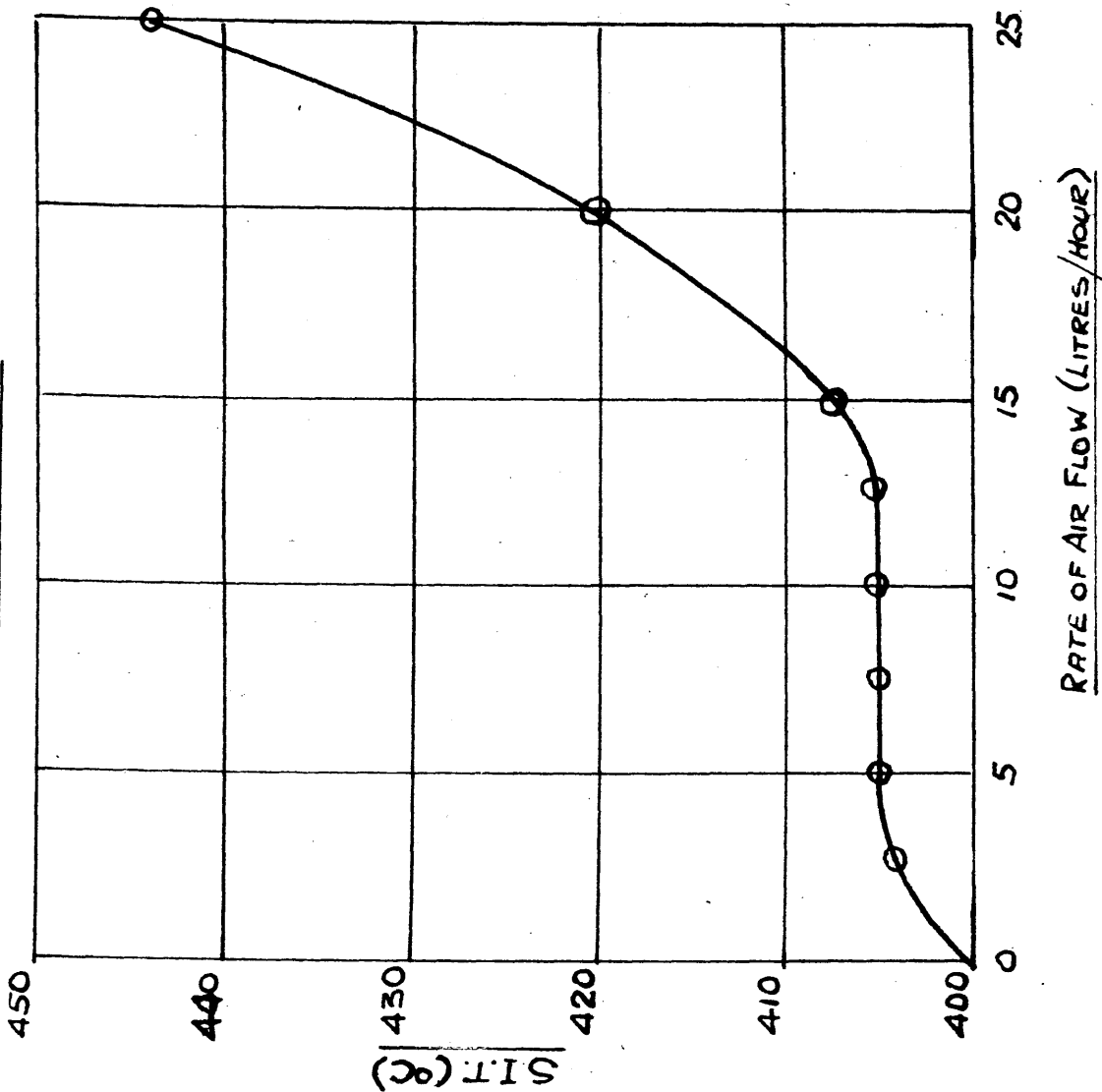
of the graphs, for within this range small changes in air flow will have no appreciable effect on S.I.T.s.   A value for the air flow of 11 l./hr. falls on the straight portion of each curve and this was selected as the standard rate of air flow and used in all subsequent S.I.T. determinations.

The magnitude of the time-lag between the addition of the drop and its ignition has a considerable effect on the S.I.T. but if the air flow is maintained at 11 l./hr the time lag is always 2 - 4 seconds.

(c) The Volume of Test Liquid Added.

The volume of the drop of test liquid added to the pot has a considerable effect on the S.I.T.   In tests performed with n-heptane and iso-octane the effect on the S.I.T. of variation in drop volume was determined for this apparatus, the results being shown in Figures 15 and 16.

From Figures 15 and 16 it can be seen that as the drop volume increases the S.I.T. falls to a minimum and is then considerably increased.   It is, therefore, important to standardise the drop volume used.   A volume of 0.016 cc. gave the lowest S.I.T. for both the substances tested so this was adopted as the standard drop volume for the apparatus and a burette was selected which delivered 0.016 cc. per drop. When testing the effect on the S.I.T. of variation in air flow and of changes in the contact disc metal, the drop volume used was 0.013 cc.   This was the volume used by Weerman in a similar apparatus.   It can be seen from Figures 15 and 16

FIGURE 15

THE EFFECT OF DROP VOLUME ON THE S.I.T.
OF n - HEPTANE
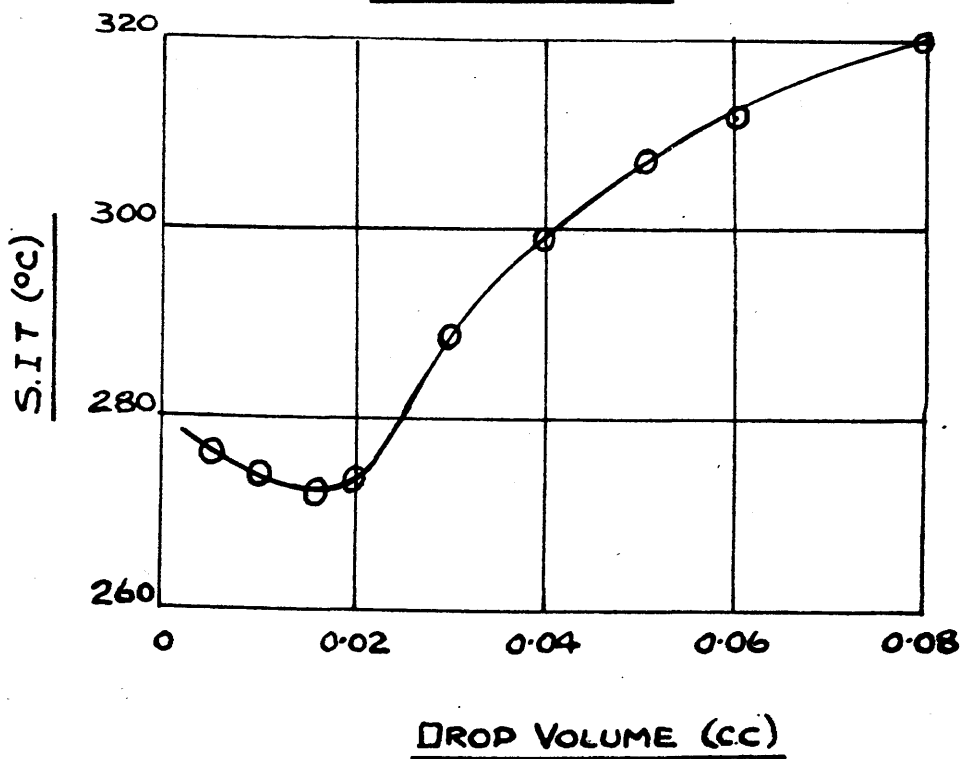
DROP VOLUME (cc)

FIGURE 16

THE EFFECT OF DROP VOLUME ON THE S.I.T OF ISO-OCTANE.
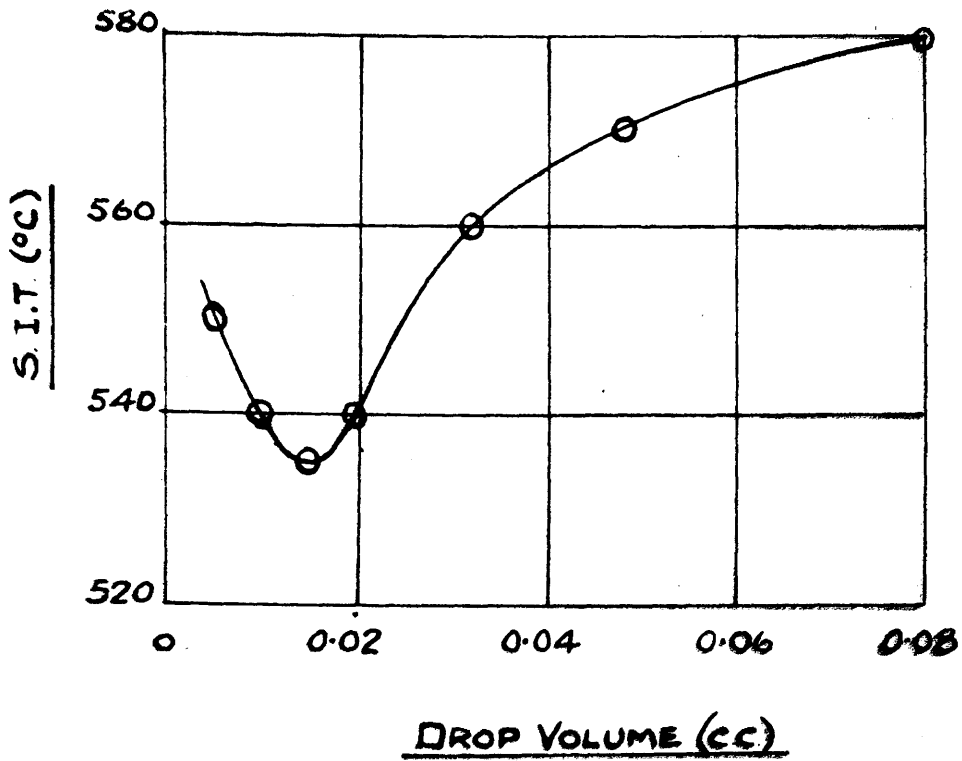
DROP VOLUME (CC)

that the slight change in drop volume does not affect the
reliability of the previous results since the corresponding
change in S.I.T. is only one centigrade degree.   In all
subsequent tests a drop volume of 0.016 cc. is used.   The
drop volume depends on surface tension but the variation is
negligible for the fuels being used in this work.

4) Testing of Apparatus.

The efficacy of the apparatus in distinguishing
between fuels of varying ignition properties was established
by determining the S.I.T.s of a range of n-heptane - iso-octane
mixtures.   This is shown in Figure 17.   Figure 17 shows that
the S.I.T. increases with increasing octane number (p. 7)
although the relationship between the two factors is not a
"straight line" one.

It is of interest to compare the S.I.T.s obtained by
the author on the apparatus just described with the values
obtained by other workers.   This is shown below

Worker	S.I.T. of n-heptane
Author	272
Helmore[51]	451
Tizard & Pye[52]	298
Egerton & Gates[53]	430

The above results show that the S.I.T. of a substance
varies considerably depending on the method by which it is
determined.

B. The Effect of Chromium Hexacarbonyl on Spark-Ignition
Engine Fuels.

1) Comparison Between the Effects of Chromium Hexacarbonyl
   and Lead Tetraethyl on the S.I.T. of n̄-Heptane.

It has been observed by previous workers[54] that
compounds which raise the S.I.T. of a fuel to a considerable
degree passess anti-knock properties.   If, therefore, the
effect of chromium hexacarbonyl is to raise the S.I.T. of
n-heptane there are grounds for assuming that it will be an
effective anti-knock additive for petroleum.   The effects
of varying concentrations of chromium hexacarbonyl on the
S.I.T. of n-heptane were accordingly determined.   Similar
tests were performed with lead tetraethyl for purposes of
comparison.

In preparing a series of solutions of additive of
varying concentration a concentrated solution of known strength
was first prepared and samples of this were suitably diluted
to give the required concentration.   A 5 cc. micro-pipette
graduated at intervals of 0.02 cc. was used for this purpose.

The results of the S.I.T. tests are shown in Figure
18.   It will be noticed that the S.I.T. of "undoped" n̄-heptane
was 314°C. in these tests.   This compares with a value of
272°C. previously obtained (p.82).   The reason for the
discrepancy is that the intitial tests were performed on
purified n-heptane while the tests recorded in Figures 18 and
19 were performed on a commercial grade of the substance.   Since
these tests are comparative rather than absolute the commercial
grade was considered to be quite satisfactory.

FIGURE 17
THE S.I.Ts OF n-HEPTANE – ISO-OCTANE MIXTURES

%ISO OCTANE in n-HEPTANE – ISO OCTANE MIXTURE

(OCTANE NUMBER)
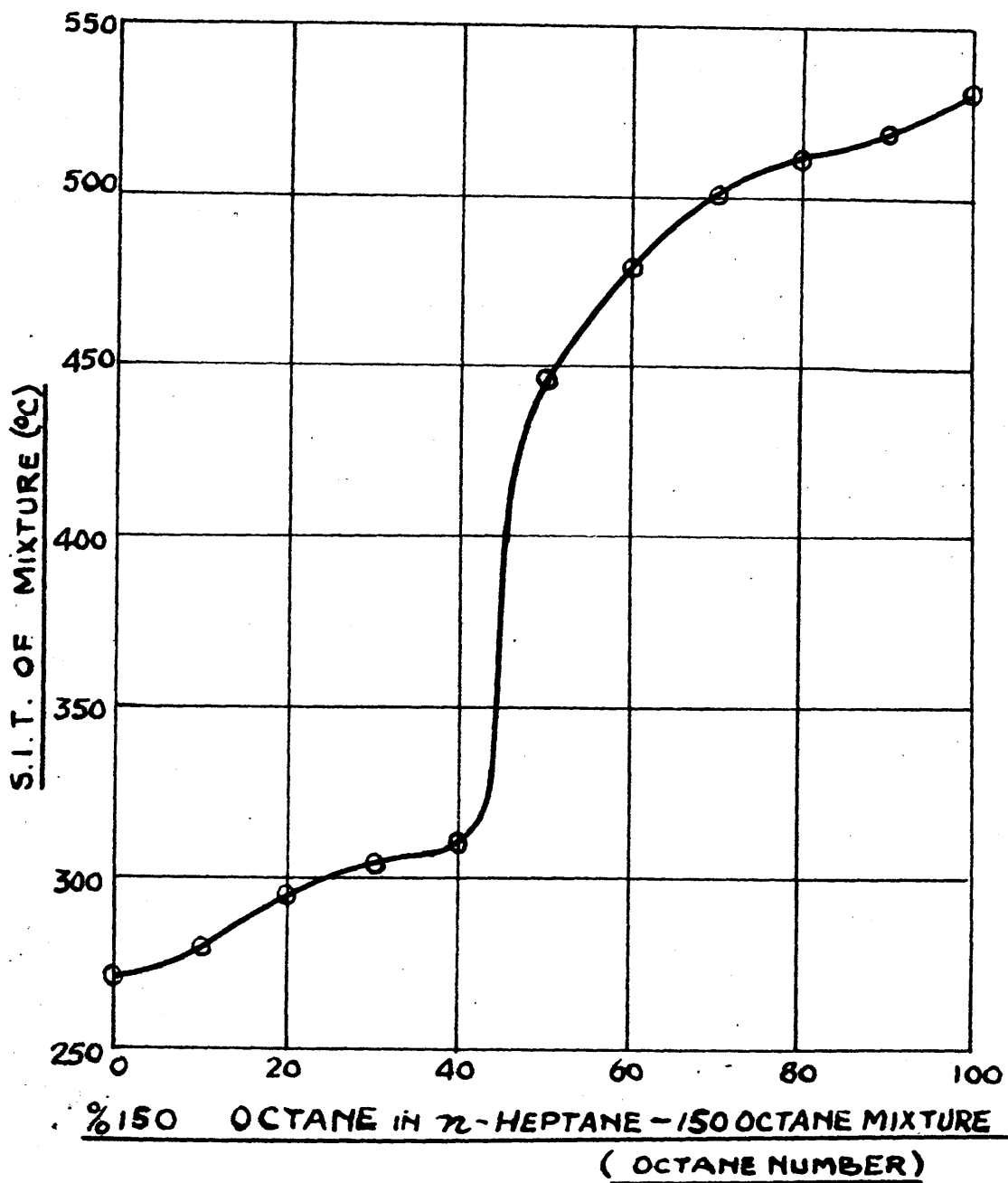
FIGURE 18

COMPARISON BETWEEN THE EFFECTS OF CHROMIUM HEXACARBONYL AND
LEAD TETRAETHYL ON THE S.I.T. OF n-HEPTANE.

CHROMIUM
HEXACARBONYL

LEAD TETRAETHYL

CONCENTRATION OF ADDITIVE (GRAMS/LITRE)

S.I.T. (°C)
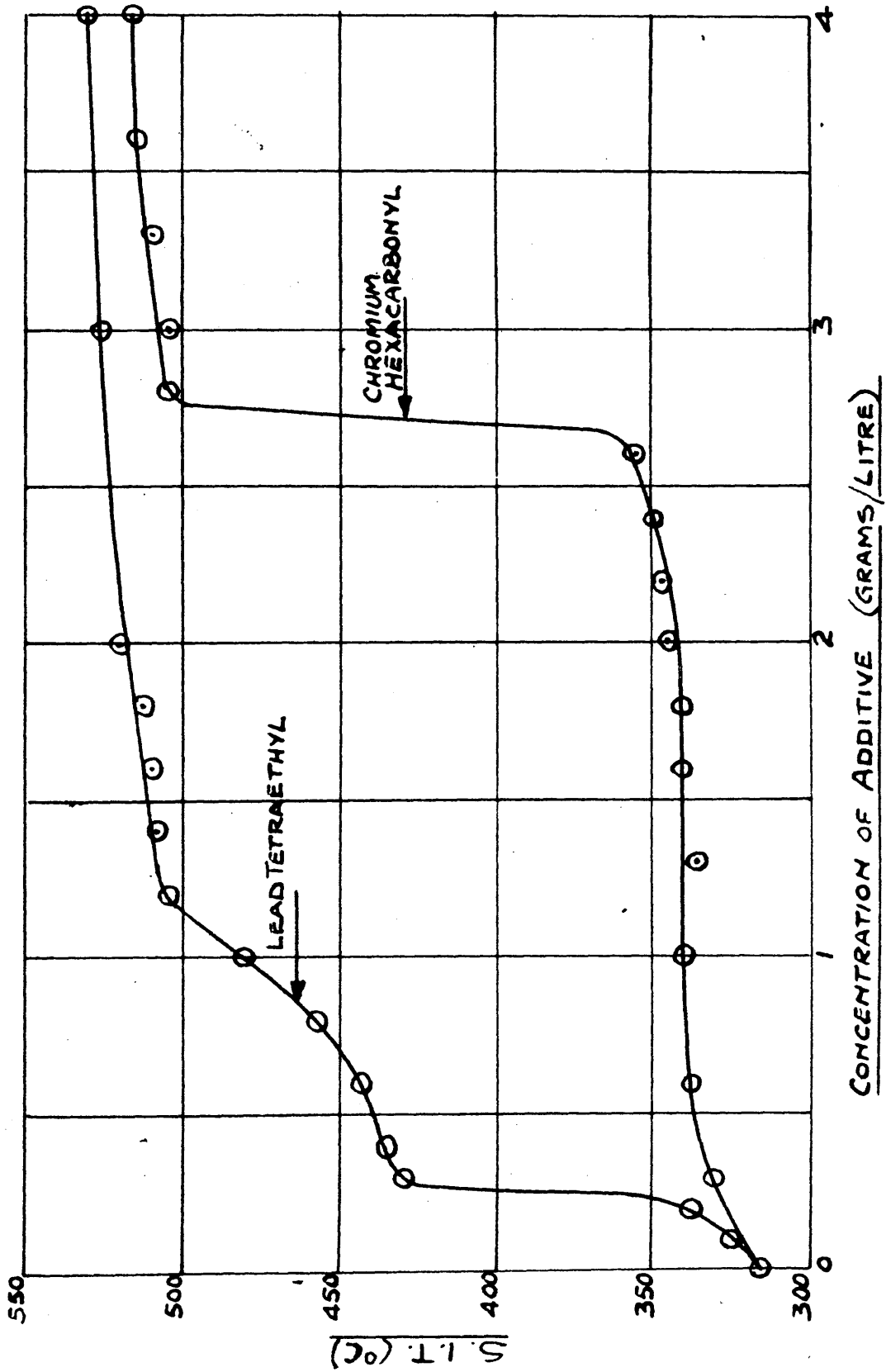
The results show that as the concentration of either petroleum additive is raised the S.I.T. also increases. This increase is not, however, regular, there being a narrow range of concentration within which a comparatively small increase in concentration causes a comparatively large increase in S.I.T. For lead tetraethyl this range is 0.2 - 0.3 g./l. (approx.) while for chromium hexacarbonyl it is 2.6 - 2.8 g./l. The final temperatures attained at concentrations of over 3 g./l. do not differ greatly, though chromium hexacarbonyl is slightly inferior to lead tetraethyl. Lead tetraethyl becomes effective at a much lower concentration than does chromium hexacarbonyl.

The anti-detonant property of an organometallic compound depends principally on the metallic atom so it would be of interest to compare the relative effects of lead and chromium metals. This can be done by expressing the concentration of anti-detonant as the equivalent concentration of lead and chromium respectively. This is shown in Figure 19. At concentrations of metal greater than 0.7 g./l. the effects of chromium and lead on the S.I.T. of n-heptane are approximately equal.

The above tests showed that chromium hexacarbonyl had a very marked effect on the S.I.T. of n-heptane. At very low concentrations the effect was considerably less than that caused by lead tetraethyl but at concentrations of 3 g./l. and over the effects of the two compounds were almost equal.

2) The Effects of Chromium Hexacarbonyl and Aniline on the H.U.C.R. of Pool Petrol.

FIGURE 19

COMPARISON BETWEEN THE EFFECTS OF CHROMIUM AND LEAD ON THE S.I.T OF n-HEPTANE
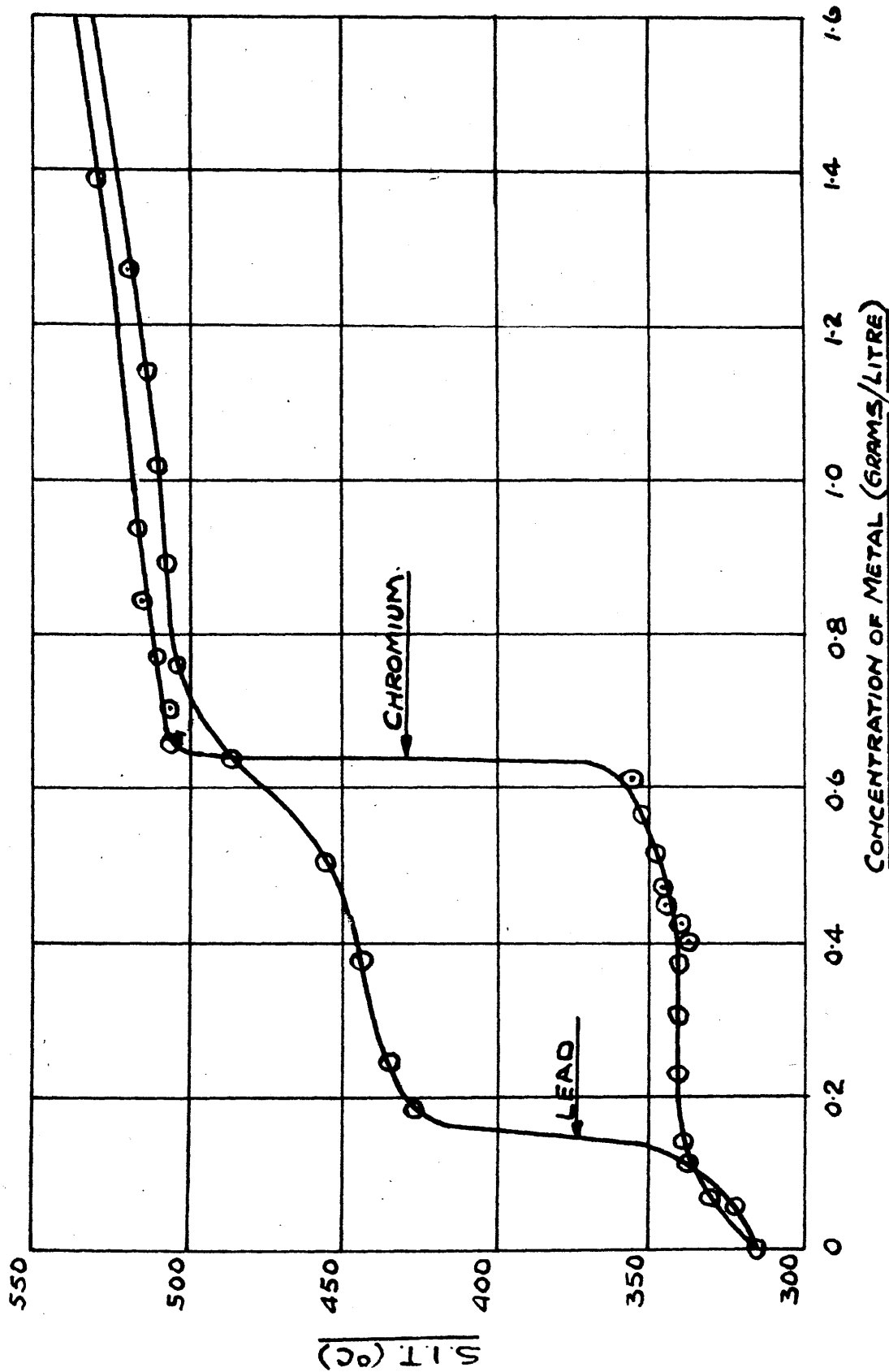
The results obtained in the previous test made
it seem highly probable that chromium hexacarbonyl could
possess anti-knock properties and a series of engine tests
were carried out to evaluate the anti-knock effect. In
these tests aniline was used as the standard anti-knock
additive since it was safer to handle and more readily
available than lead tetraethyl. The fuel used for the tests
was Pool Petrol since this was readily available in adequate
quantities. A bulk sample of the above fuel was obtained and
is hereafter referred to as Pool Petrol A (See Appendix II).

The value of the H.U.C.R. gives a measure of the
knocking properties of the fuel being tested. Fuels with
poor knocking characteristics have a low H.U.C.R. while fuels
with good anti-knock properties have a high H.U.C.R. Thus
the H.U.C.R. of n-heptane is 3.75 while that of iso-octane
is 10.96[55]. For the purpose of this research the H.U.C.R.
of a fuel may be defined as the compression ratio corresponding
to maximum power when the fuel is tested in a Ricardo E6/S
Variable Compression Engine running at 2500 r.p.m., cooling
water temperature 155 $\pm$ 5°F. and with ignition timing and
mixture strength adjusted to give maximum power (See Appendix 1).
Since under constant speed conditions the power is directly
proportional to the Brake Mean Effective Pressure (B.M.E.P.),
the compression ratio is graphed against the corresponding
B.M.E.P. when drawing H.U.C.R. curves.

(a) The effect of varying proportions of aniline

on the H.U.C.R. of Pool Petrol A.

A number of 2 l. samples of Pool Petrol A (See Appendix II) were prepared each containing a different concentration of aniline. A series of H.U.C.R. tests were performed on the fuels, the results being shown in Figure 20. The compression ratio corresponding to the peak of each curve in Figure 20 is the H.U.C.R. of the fuel being tested. A graph of H.U.C.R. against concentration of aniline for Pool Petrol A is shown in Figure 21. This graph provides a standard against which the efficacy of any other anti-knock compound can be judged, provided that Pool Petrol A is used as the "base fuel".

(b) The Effect of Varying Proportions of Chromium Hexacarbonyl on the H.U.C.R. of Pool Petrol A.

Although the solubility of chromium hexacarbonyl in Pool Petrol A at 20°C was approximately 3 g./l. it was advisable to heat the petrol in a flask provided with a reflux condenser when preparing solutions more concentrated than 0.1 g./l. In the absence of heat a considerable amount of agitation was necessary to dissolve the hexacarbonyl.

Solutions of varying concentrations of chromium hexacarbonyl in Pool Petrol A were prepared and tested for H.U.C.R. in the Ricardo E6 engine under conditions exactly similar to those during the "aniline doped" petrol tests. Contrary to all expectations chromium hexacarbonyl was found to reduce the H.U.C.R. of the petrol. It thus proved to be

FIGURE 20

THE H.U.C.R. OF POOL PETROL (A) CONTAINING VARYING PROPORTIONS OF ANILINE.

FIGURE 20
(CONTINUED)

15g Aniline/Litre.

20g Aniline/Litre.

25g Aniline/Litre.
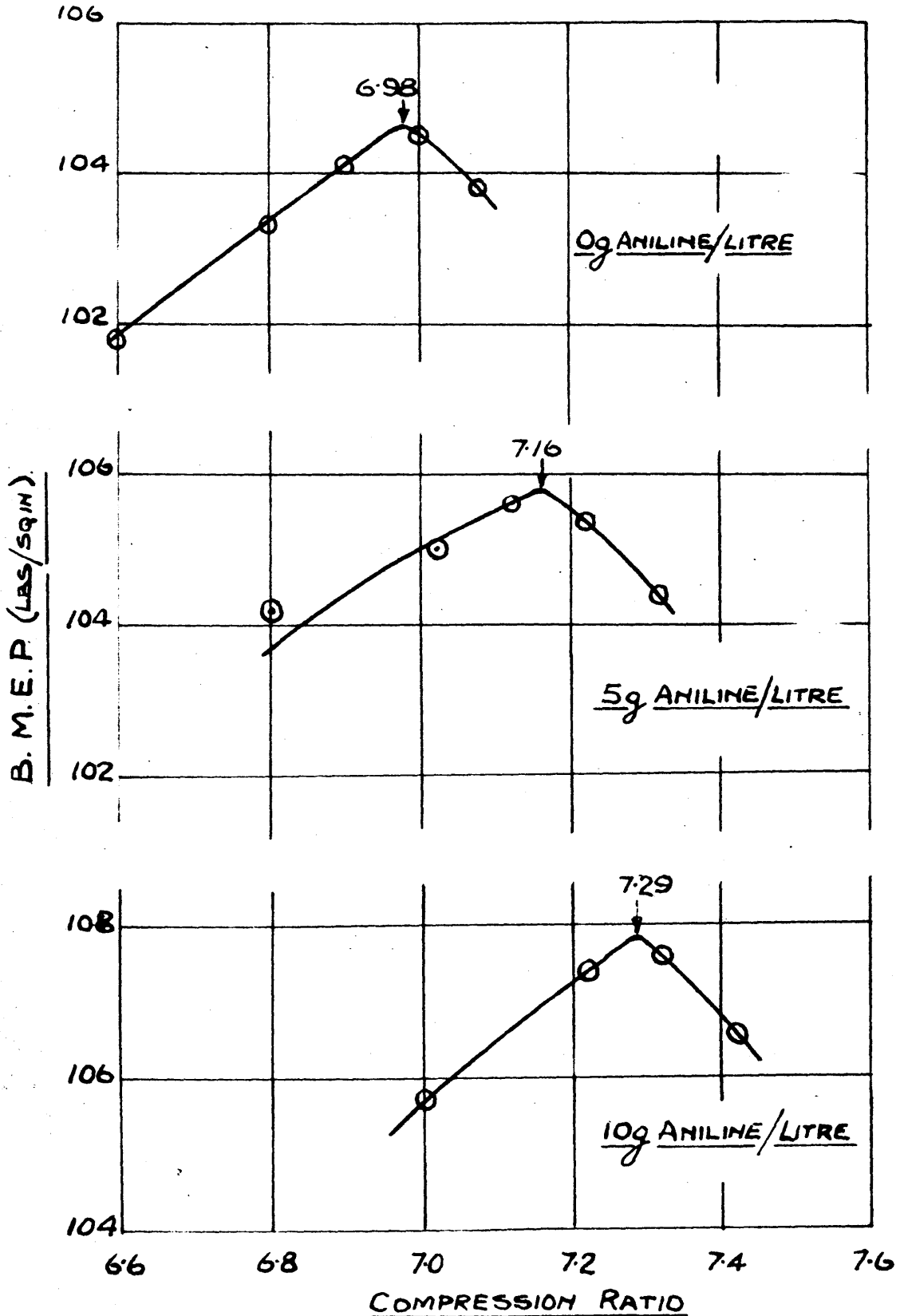
B.M.E.P (LBS/SQIN)
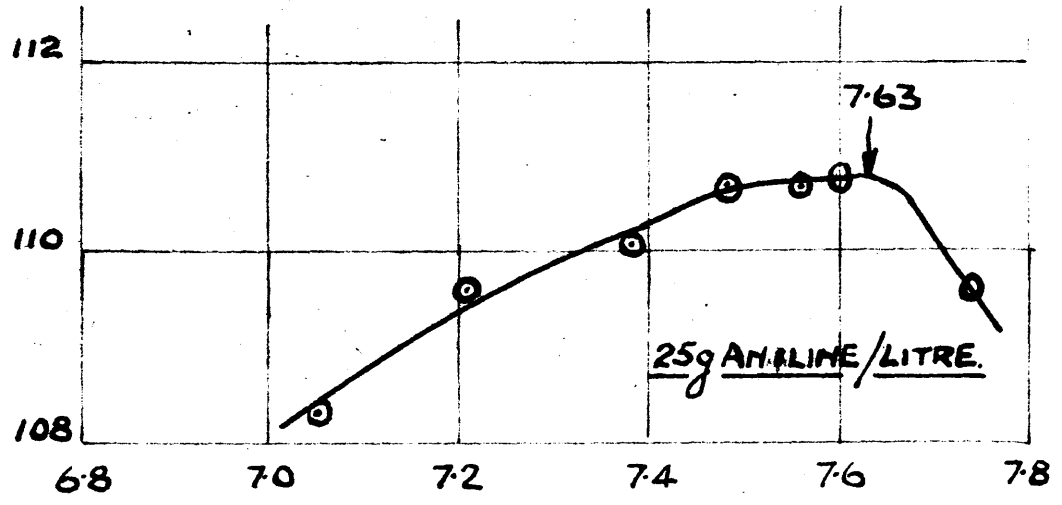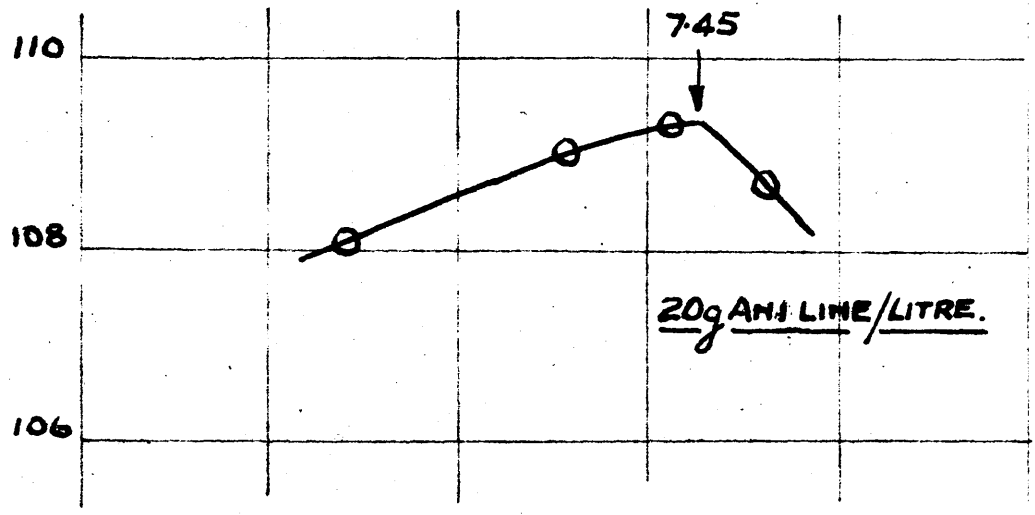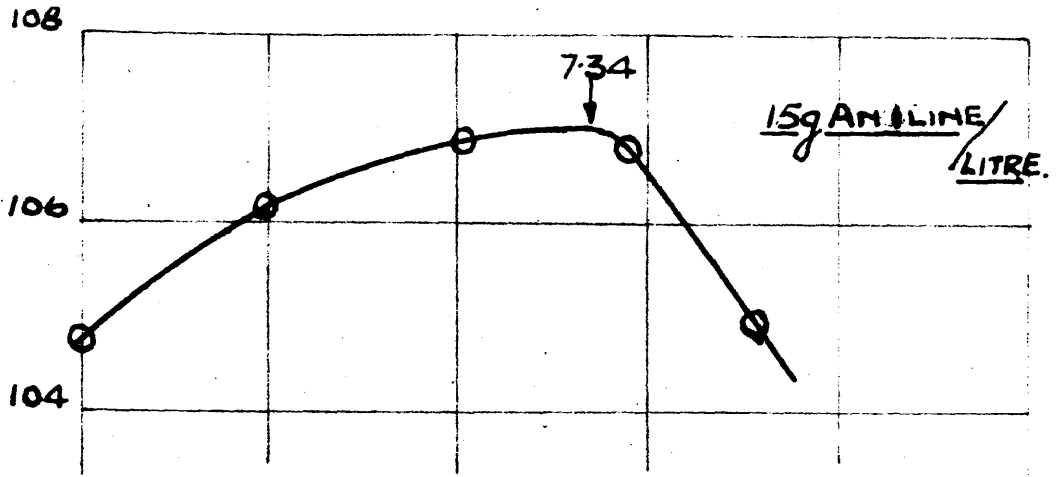
COMPRESSION RATIO

FIGURE 20
(CONTINUED)

Y-axis: B.M.E.P. (LBS/SQ.IN)

X-axis: COMPRESSION RATIO.

30g ANALINE/LITRE — 7.92

40g ANALINE/LITRE — 8.00
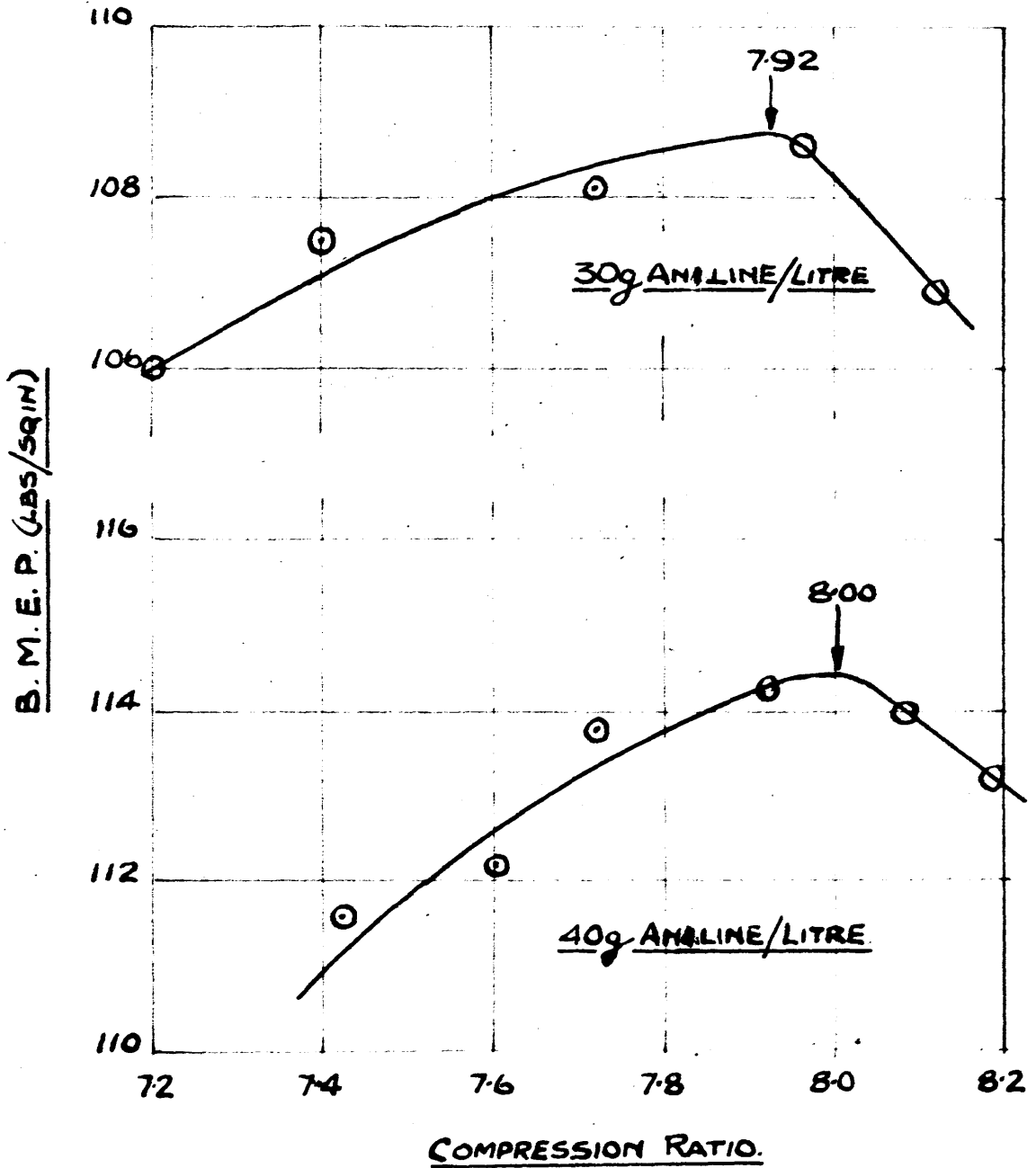
a pro-knock compound.   The hexacarbonyl appeared to develop
its maximum pro-knock effect at a concentration remarkably
low even in the field of organometallic petroleum additives.
The results of the H.U.C.R. tests are given in Figure 22, and
a graph of"H.U.C.R. against Concentration of Chromium
Hexacarbonyl" is shown in Figure 23.

Figure 23 shows that at concentrations of 0.5 g./l.
and over the hexacarbonyl has lowered the H.U.C.R. of the petrol
by 0.56.   A concentration of chromium hexacarbonyl as low as
0.02 g./l. lowers the H.U.C.R. to almost the same extent (0.48).
At very low concentrations the pro-knock effect is surprisingly
great.   This is seen when a comparison is made with the anti-
knock potency of lead tetraethyl.   Ricardo and Glyde[56] have
published a graph showing the effect of varying proportions
of ethyl fluid on the H.U.C.R. of a typical gasoline.   This
graph is reproduced in Figure 24 with the units converted to
metric and the dope concentration expressed as lead tetraethyl
instead of ethyl fluid.   The graph shows that to raise the
H.U.C.R. by 0.48 would require a concentration of 0.7 g./l.
lead tetraethyl.   This compares with 0.02 g./l. chromium
hexacarbonyl required to give a similar lowering of H.U.C.R.
in Pool Petrol A.   It must be stated that neither were the two
base fuels the same nor were the test engines identical.
However, the effectiveness of an anti-knock compound does not
vary to any large extent in different engines[57] and the fuel
used by Ricardo & Glyde (Texas gasoline) was not unduly different
as regards knocking characteristics from that employed by the

FIGURE 22

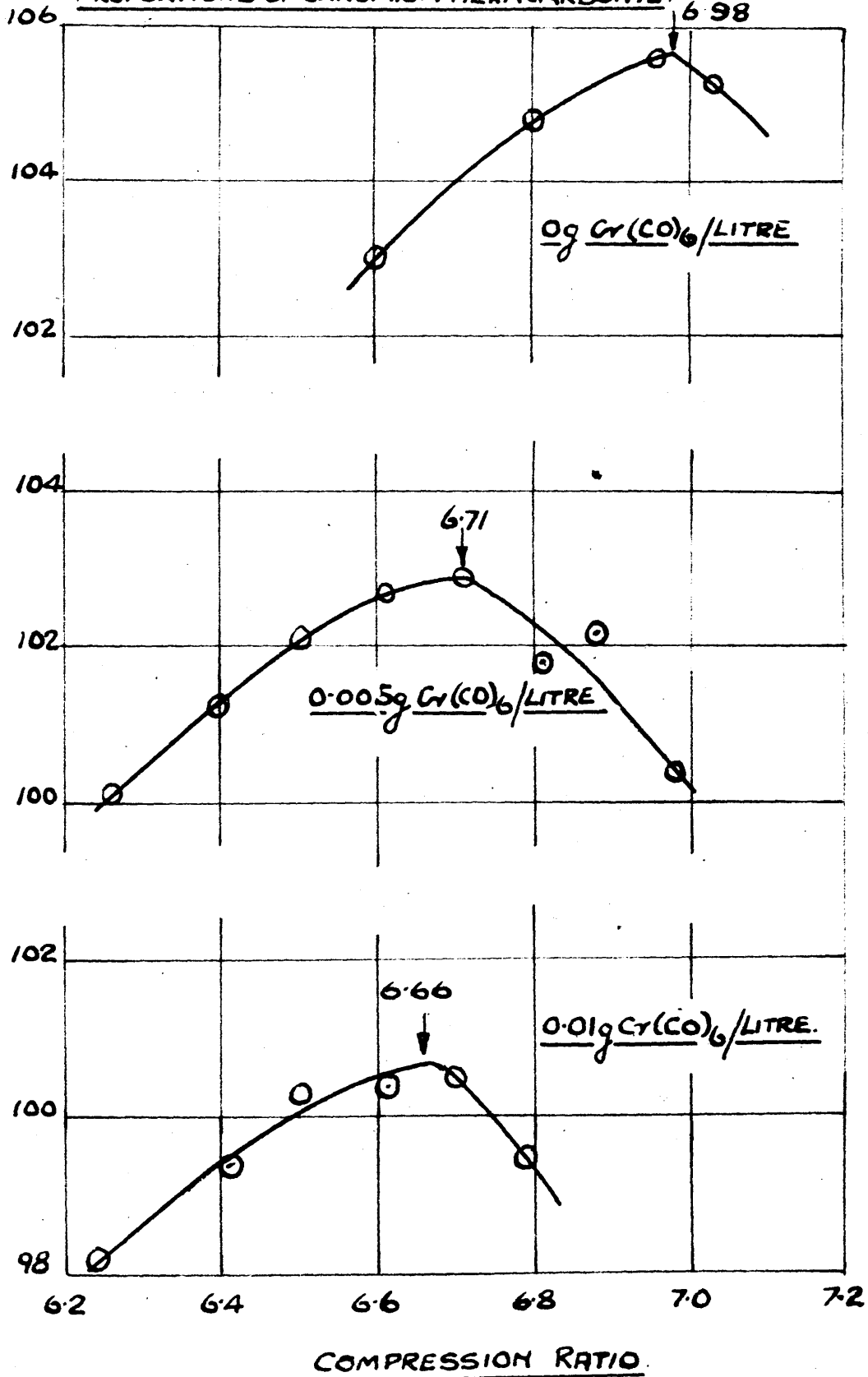## THE H.U.C.R. OF POOL PETROL (A) CONTAINING VARYING PROPORTIONS OF CHROMIUM HEXACARBONYL

6·98

0g Cr(CO)₆/LITRE

6·71

0·005g Cr(CO)₆/LITRE

6·66

0·01g Cr(CO)₆/LITRE.

B.M.E.P. (LBS/SQ IN)

COMPRESSION RATIO.

FIGURE 22
(CONTINUED)

COMPRESSION RATIO

FIGURE 22
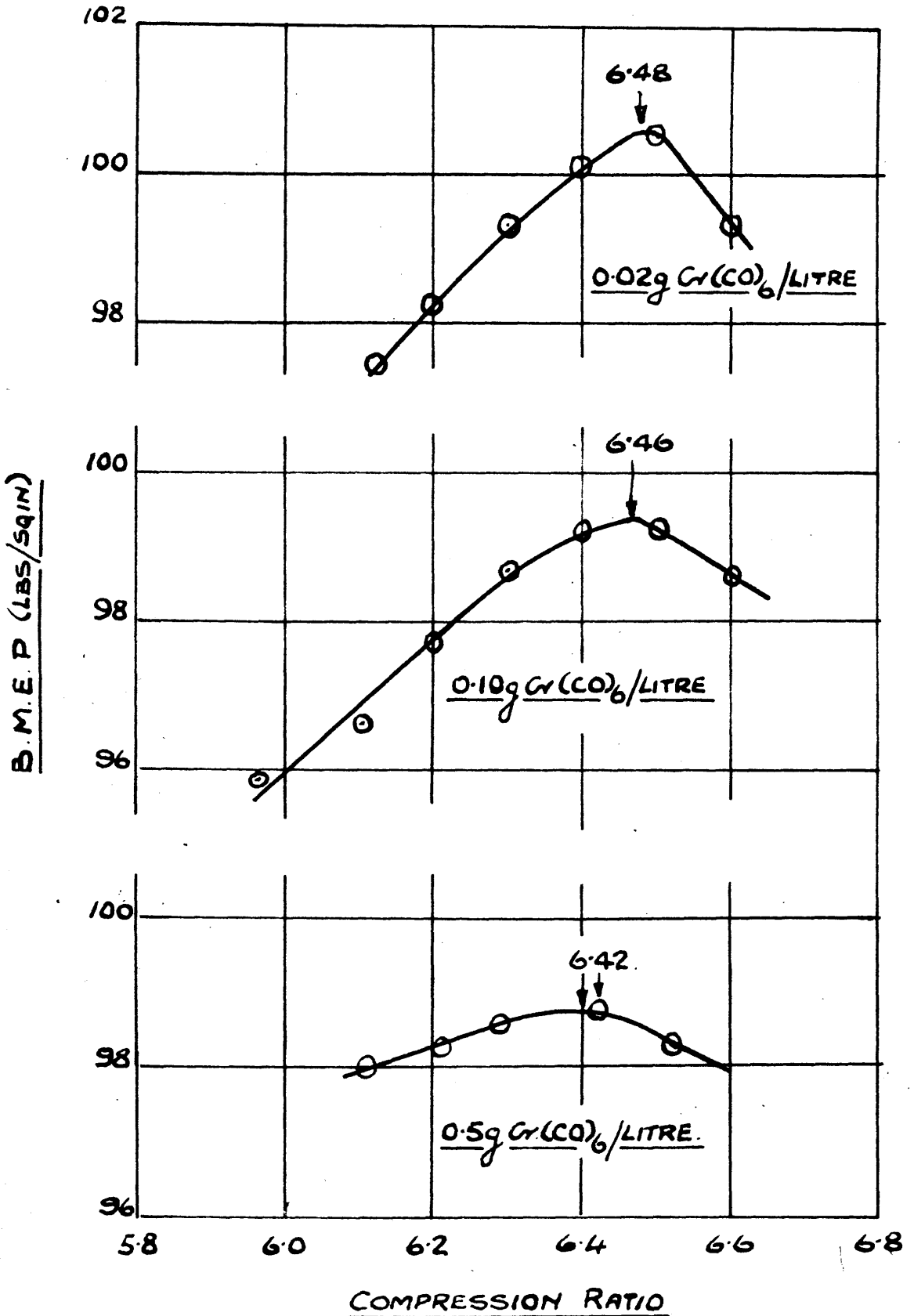## (CONTINUED)

1·0g Cr(CO)₆/LITRE

3·0g Cr(CO)₆/LITRE

0g Cr(CO)₆/LITRE

B.M.E.P. (LBS/SQIN)
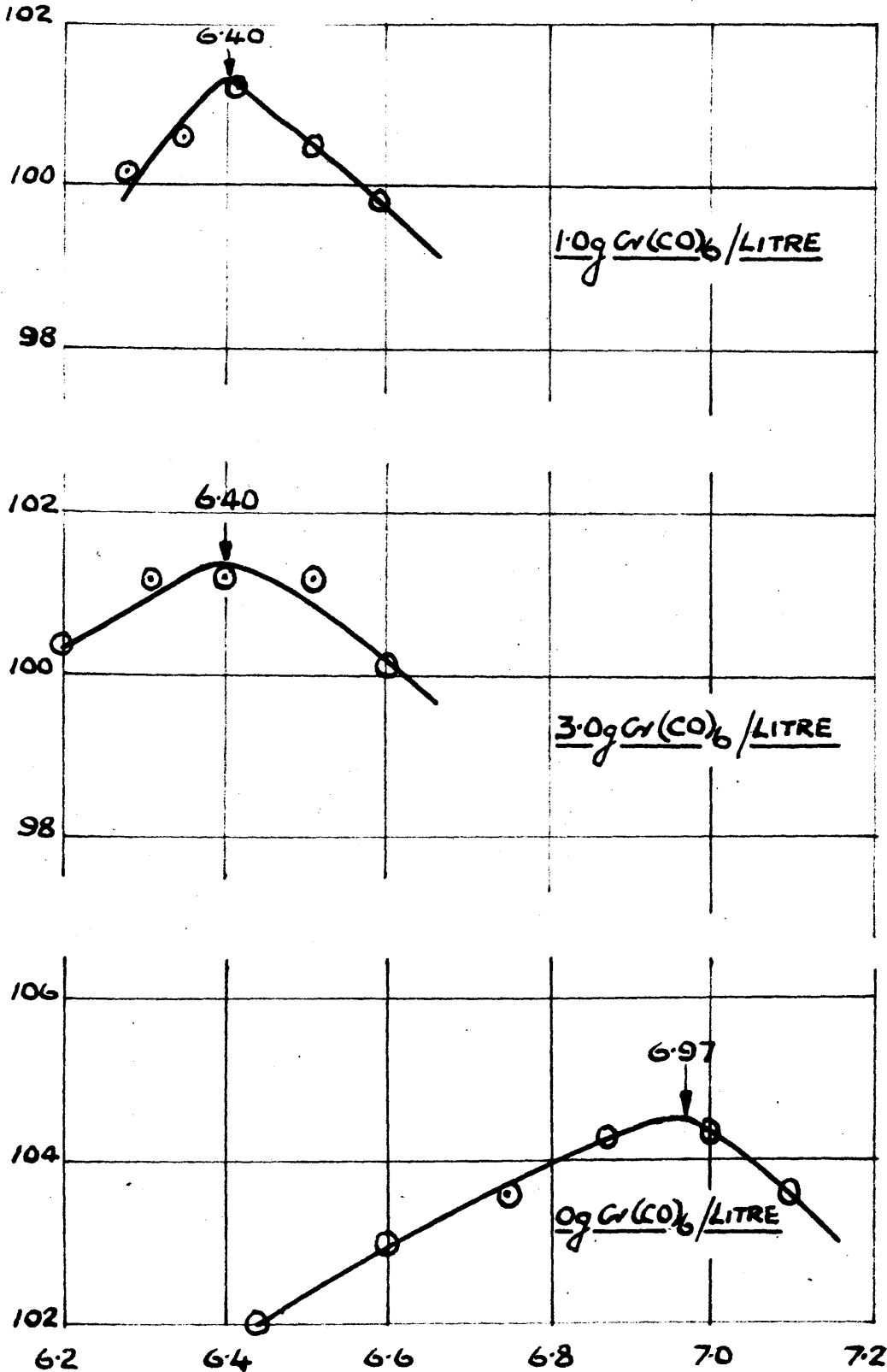
COMPRESSION RATIO

FIGURE 23

THE EFFECT OF CHROMIUM HEXACARBONYL ON THE
H.U.C.R OF POOL PETROL (A)

CONCENTRATION OF $Cr(CO)_6$ (GRAMS/LITRE)
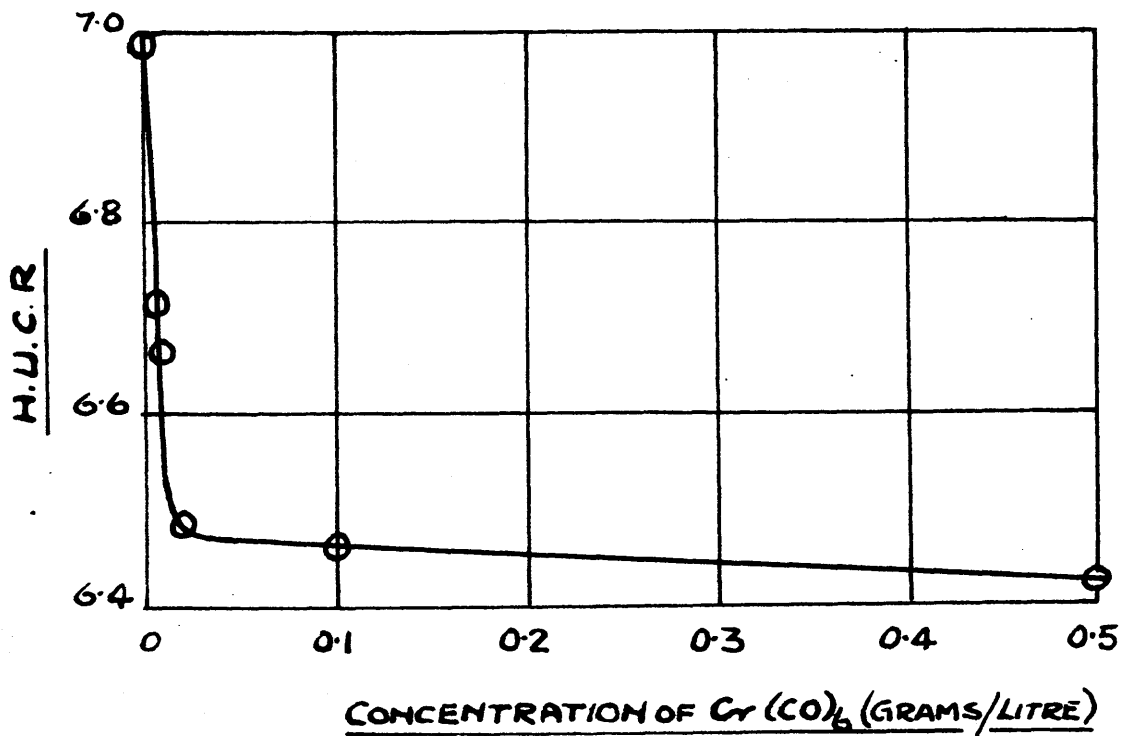
FIGURE 24

THE EFFECT OF LEAD TETRAETHYL ON THE
H.U.C.R OF PETROL

CONCENTRATION OF $Pb(Et)_4$ (GRAMS/LITRE)
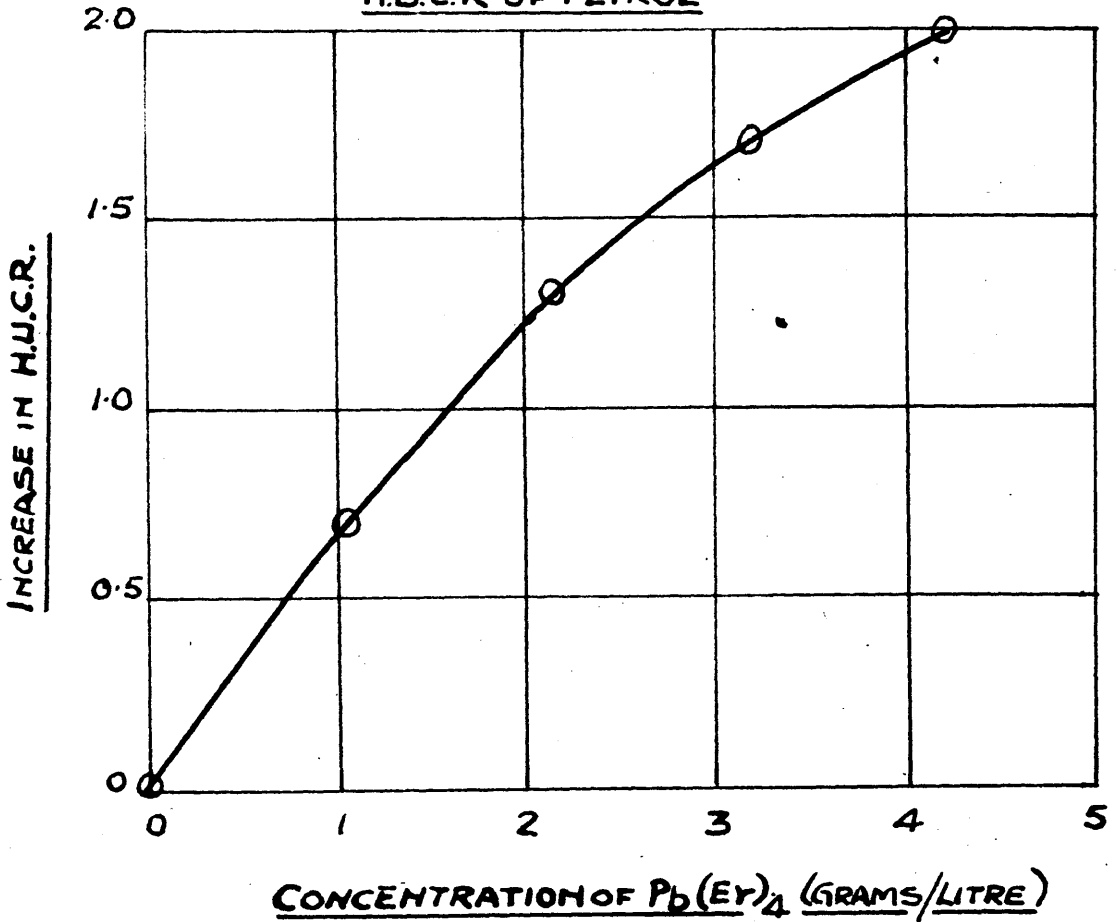
author (Pool Petrol A).   The octane numbers of the two
fuels were approximately 70 and 75 respectively as calculated
from data supplied by Ricardo & Glyde[58] for inter-relating
H.U.C.R. and octane number.   At low concentrations, therefore,
chromium hexacarbonyl is approximately 35 times as potent as
lead tetraethyl but in the reverse direction.   At concentrations
above 0.02 g./l. the relative effect of the hexacarbonyl is
less striking because it has almost reached the concentration
corresponding to maximum pro-knock effect.

Since the efficacy of the commoner ignition promoters
or pro-knock compounds is of the same order as that of lead
tetraethyl though in the opposite direction[59] it is evident
that the pro-knock activity of chromium hexacarbonyl at low
concentrations (0.02 g./l.) is considerably greater than that
of other pro-knock agents.

The behavior of chromium hexacarbonyl in spark-ignition
engine fuels appears to be highly anomalous in that, although
it raises the S.I.T. of n-heptane considerably it has a pro-
knock effect when Pool Petrol A is tested in a variable-
compression engine.

3) The Effects of Chromium Hexacarbonyl and Aniline on the
    S.I.T. of Pool Petrol A.

In order to establish whether the anomaly was due
solely to some peculiarity in the fuel it was decided to carry
out a series of S.I.T. tests on Pool Petrol A containing
varying proportions of aniline and chromium hexacarbonyl.

If the pro-knock effect were due to some characteristic of
the fuel it would be expected that the hexacarbonyl would
exhibit a pro-detonant effect during S.I.T. tests: i.e. it
would depress the S.I.T. of Pool Petrol A.

The results of the tests are shown in Figures 25 and
26.   Figure 25 shows that the effect of aniline is to raise
the S.I.T. of the fuel.   Since aniline is an established anti-
knock agent this is the expected result.   All anti-knock
agents so far investigated have, as far as the author is aware,
raised the S.I.T. of hydrocarbon fuels.   Figure 26 shows that
the presence of small proportions of chromium hexacarbonyl
raises the S.I.T. of Pool Petrol A to a considerable extent.
A comparison of Figures 25 and 26 shows that chromium
hexacarbonyl is approximately 40 times as effective as aniline
(on a weight basis) in raising the S.I.T. of the petrol.   The
S.I.T. tests thus confirm that chromium hexacarbonyl is
exhibiting an anti-detonant effect although engine tests on
the same fuel have already established that it exhibits a pro-
knock or pro-detonant effect.

4)   The Effects of Chromium Hexacarbonyl on the S.I.T. and
     H.U.C.R. of Refined Straight Run Spirit.

In an attempt to confirm the existence of the
anomaly referred to in the last paragraph it was decided to
test the effect of chromium hexacarbonyl on the S.I.T. and
H.U.C.R. of a different base fuel.   "Refined Straight Run
Spirit" was obtained from Messrs. Anglo-Iranian Oil Co.Ltd.

FIGURE 25

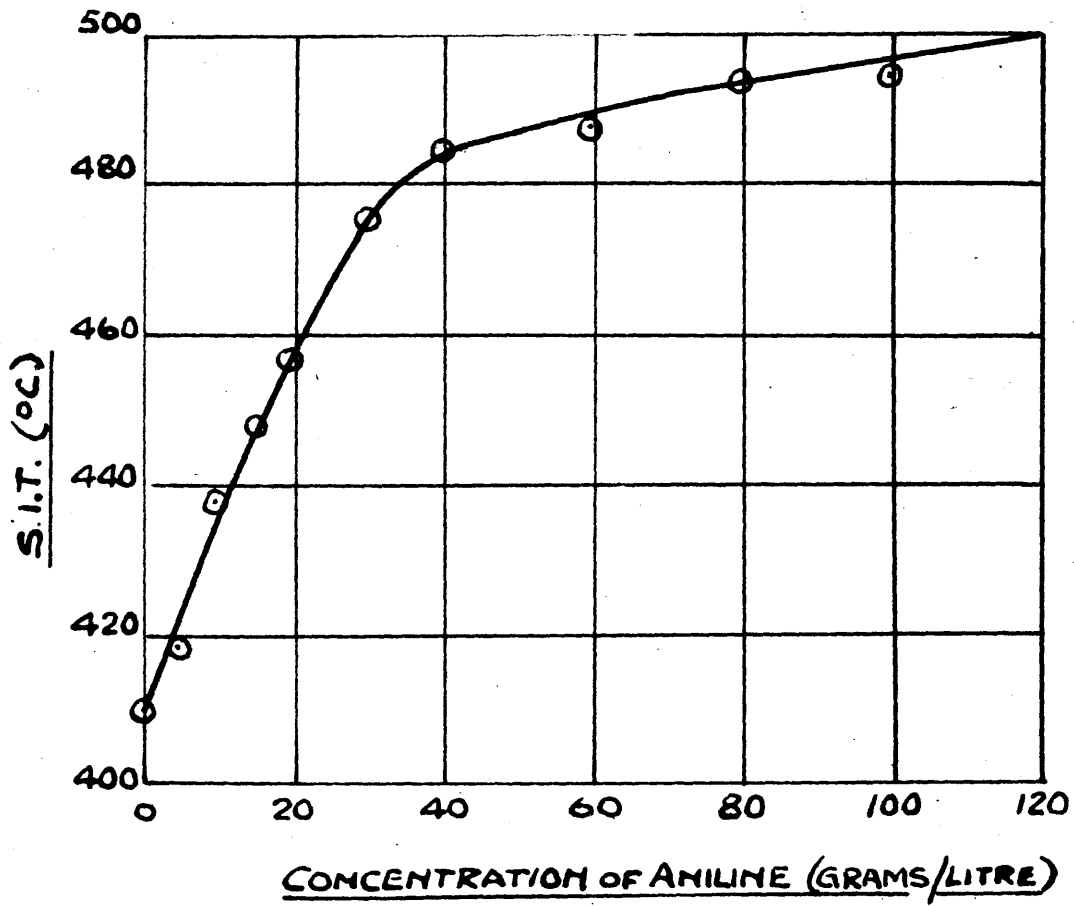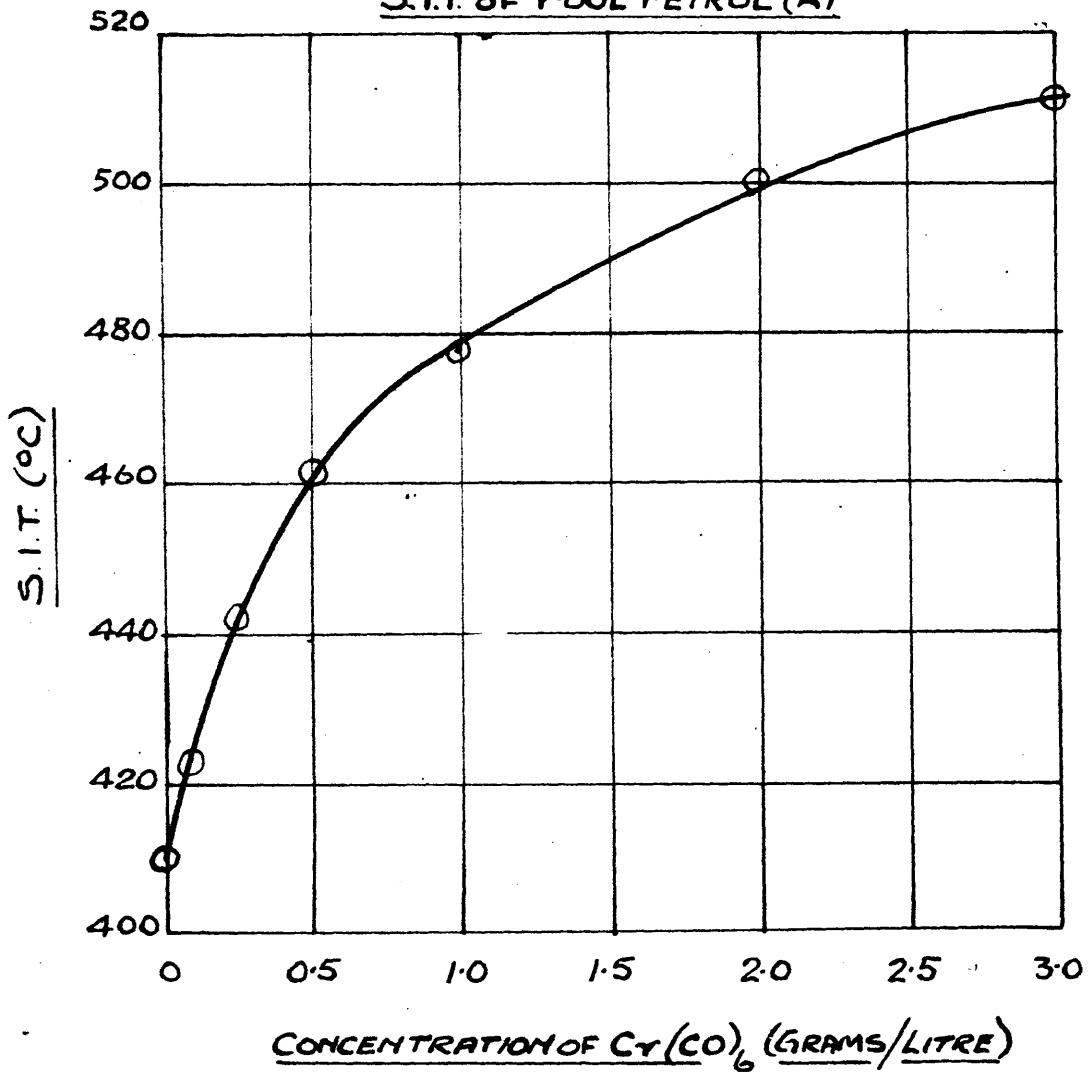## THE EFFECT OF ANILINE ON THE S.I.T. OF POOL PETROL (A)

FIGURE 26

THE EFFECT OF CHROMIUM HEXACARBONYL ON THE
S.I.T. OF POOL PETROL (A)

and was stated to contain no petroleum additives and to have an octane number of 59.5 (See Appendix II).

The effect of varying concentrations of chromium hexacarbonyl on the S.I.T. of Refined Straight Run Spirit is shown in Figure 27. The graph is similar in form to that obtained when using n-heptane as the base fuel (Figure 18) and shows that chromium hexacarbonyl is exhibiting a marked anti-detonant effect at concentrations of 1 g./l. and over.

The effect of 0.2 g./l. chromium hexacarbonyl on the H.U.C.R. of Refined Straight Run Spirit is shown in Figure 28. The presence of 0.2 g./l. chromium hexacarbonyl alters the H.U.C.R. of Refined Straight Run Spirit from 6.10 to 5.88, a decrease of 0.22. The effect of chromium hexacarbonyl is less marked than in Pool Petrol A (Decrease in H.U.C.R. of Pool Petrol A caused by 0.2 g./l. $Cr(CO)_6$ = 0.53). The anomalous behavior of chromium hexacarbonyl as a fuel additive is thus confirmed.

5) The Effects of Chromium Hexacarbonyl on the S.I.T. and H.U.C.R. of iso-Octane.

In further confirmation of the apparently contradictory anti-detonant and pro-knock activity of chromium hexacarbonyl it was decided to determine the effect of the compound on the S.I.T. and H.U.C.R. of iso-octane. One of the objections to S.I.T. tests as indications of the probable behavior of a fuel in an engine is that the temperature is much lower than would normally be experienced inside an engine combustion chamber.

FIGURE 27

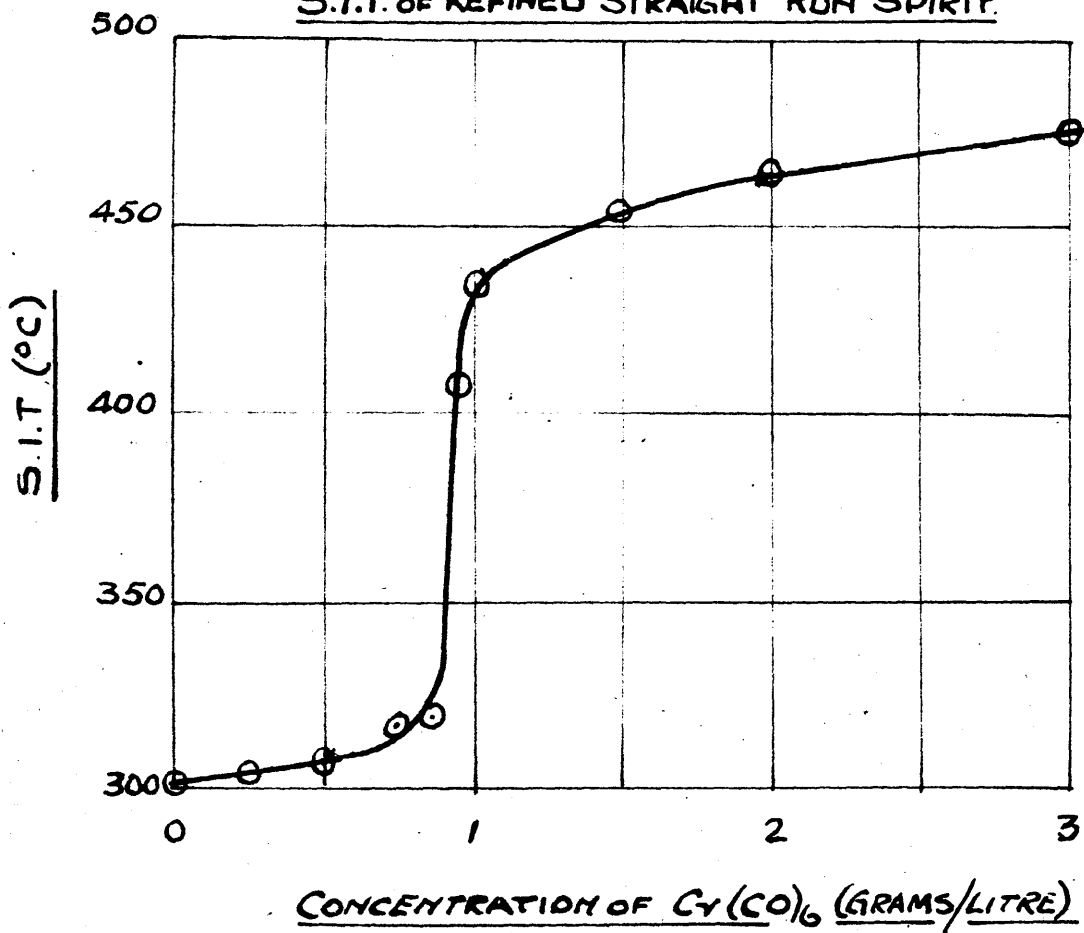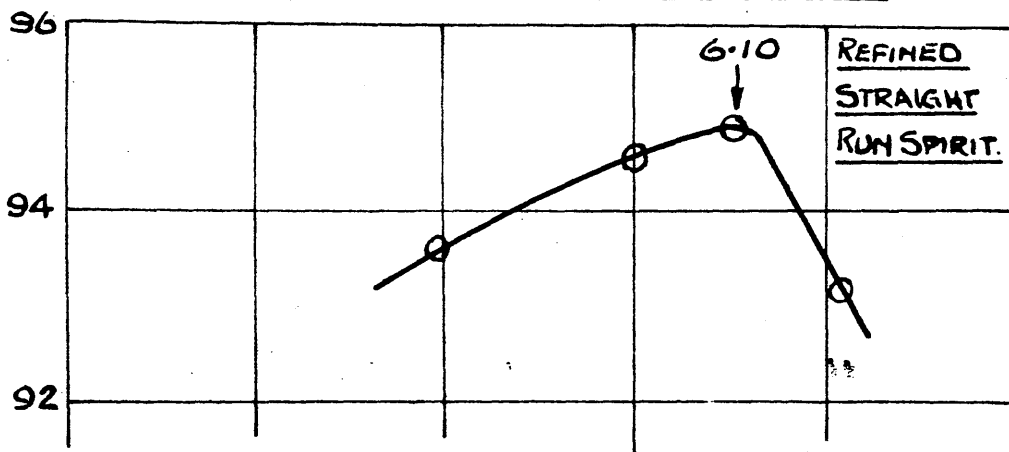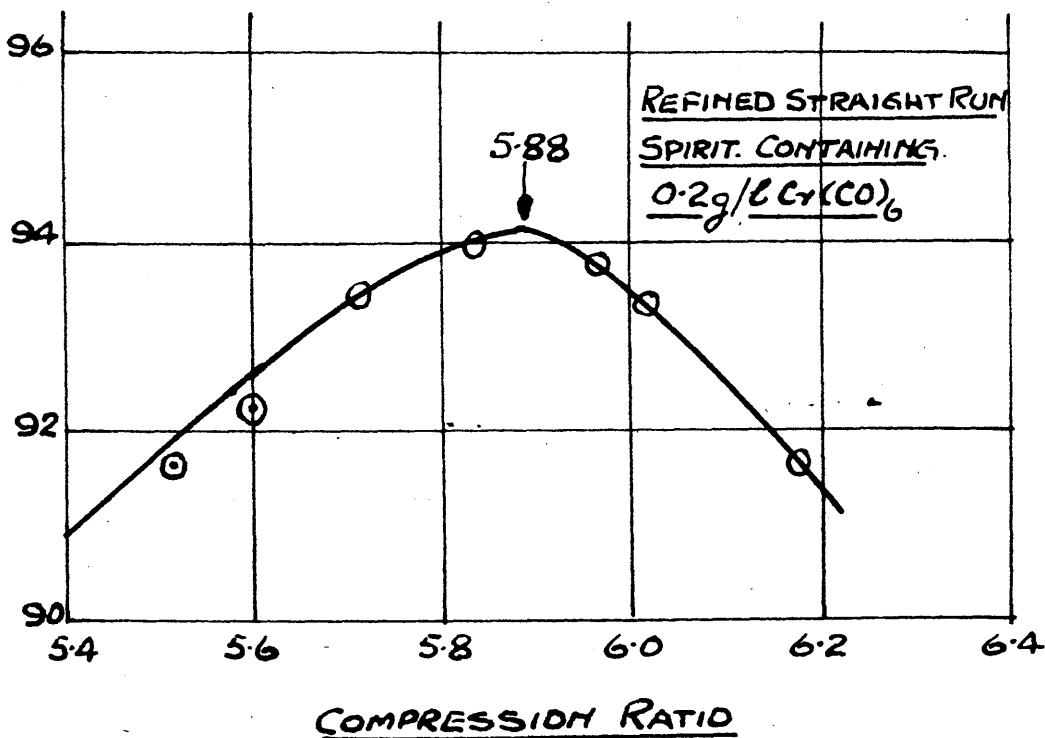THE EFFECT OF CHROMIUM HEXACARBONYL ON THE S.I.T. OF REFINED STRAIGHT RUN SPIRIT.

FIGURE 28

THE EFFECT OF 0.2 g/ℓ CHROMIUM HEXACARBONYL ON
THE H.U.C.R. OF REFINED STRAIGHT RUN SPIRIT.

Since the S.I.T. of undoped iso-octane is considerably
higher than those of Pool Petrol or Refined Straight Run
Spirit the effect of chromium hexacarbonyl on the S.I.T. at
this higher temperature might be more likely to correspond
to engine conditions.

The effect of chromium hexacarbonyl on the S.I.T.
of iso-octane is shown in Figure 29.   The graph is similar
in form to that obtained when using Pool Petrol A as the
base fuel (Figure 26) and shows that chromium hexacarbonyl
has a definite antidetonant effect, reaching its maximum at
a concentration of 1 g./l.   Further increase in the
concentration appears to have little effect on the S.I.T.
The magnitude of the rise in S.I.T. is less than was noted for
the fuels tested previously.   Thus with n-heptane, Refined
Straight Run Spirit, and Pool Petrol rises in S.I.T. of 180,
170, and 100 centigrade degrees respectively were obtained
while with iso-octane the rise was only 50 centigrade degrees.

The effect of 0.2 g./l. chromium hexacarbonyl on
the H.U.C.R. of iso-octane is shown in Figure 30.   The presence
of 0.2 g./l. chromium hexacarbonyl alters the H.U.C.R. from
10.5 to 10.2, a decrease of 0.3.   The pro-knock effect
observed with Pool Petrol and Refined Straight Run Spirit is
therefore still evident and the anomalous S.I.T. behavior is
still to be explained.

6)   The Aniline Coefficient of Chromium Hexacarbonyl.

One method by which the relative efficacy of anti-

FIGURE 29

THE EFFECT OF *CHROMIUM HEXACARBONYL* ON THE
S.I.T. OF ISO-OCTANE.
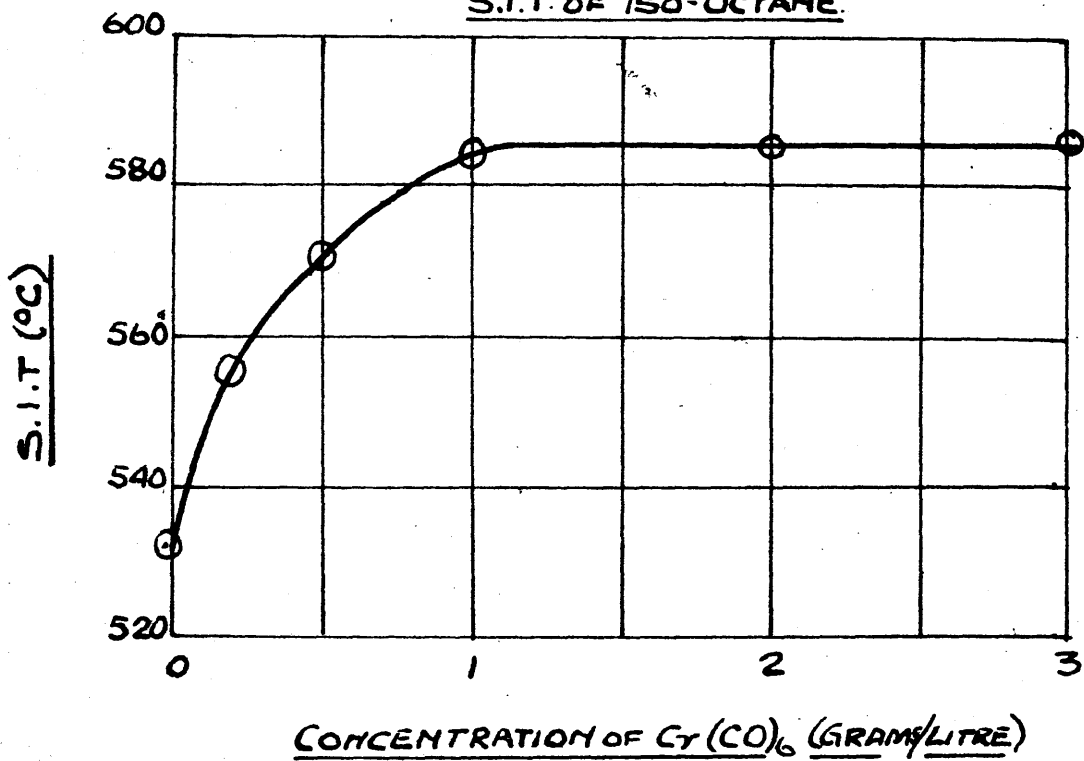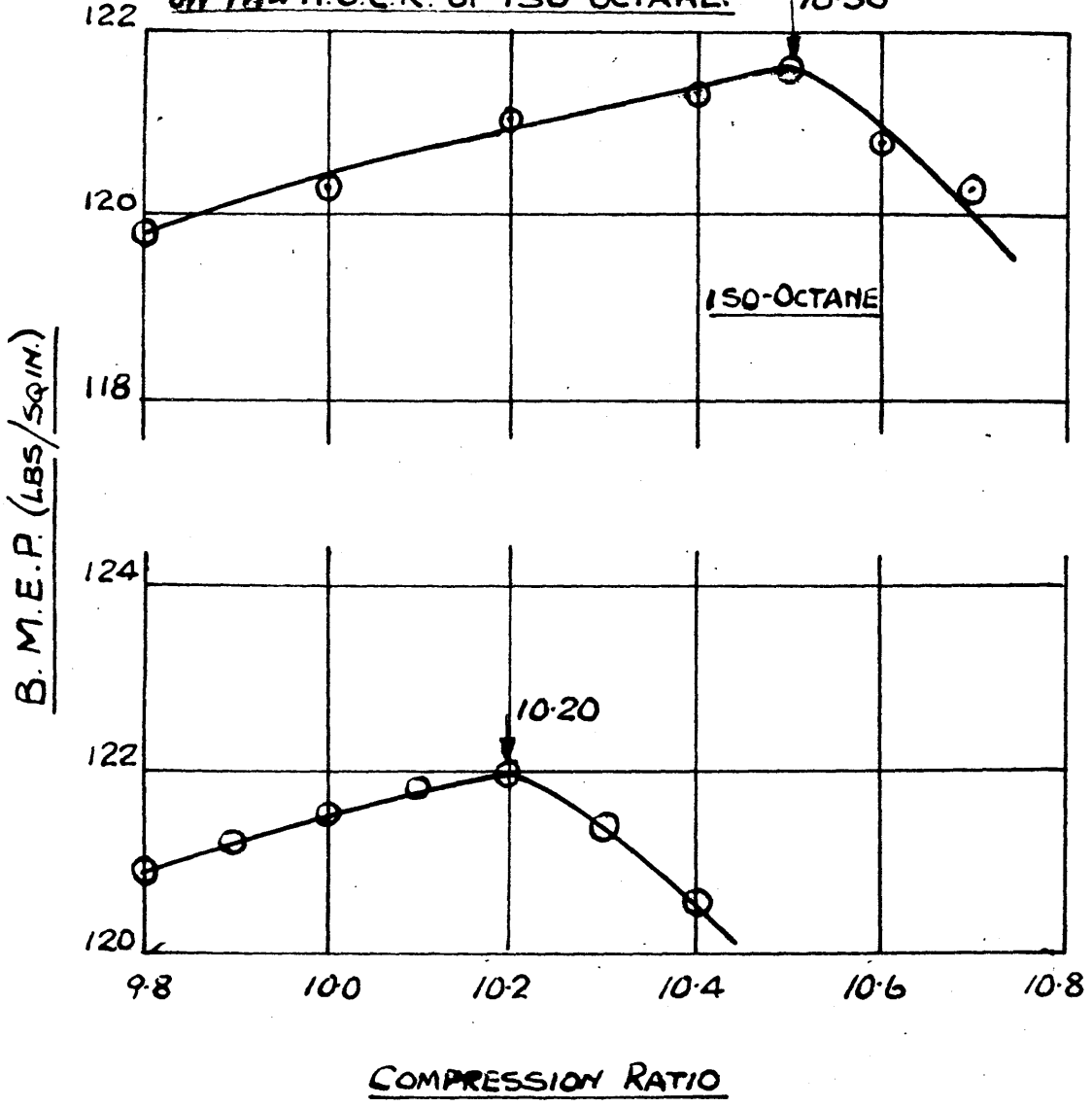

CONCENTRATION OF $Cr(CO)_6$ (GRAMS/LITRE)

FIGURE 30

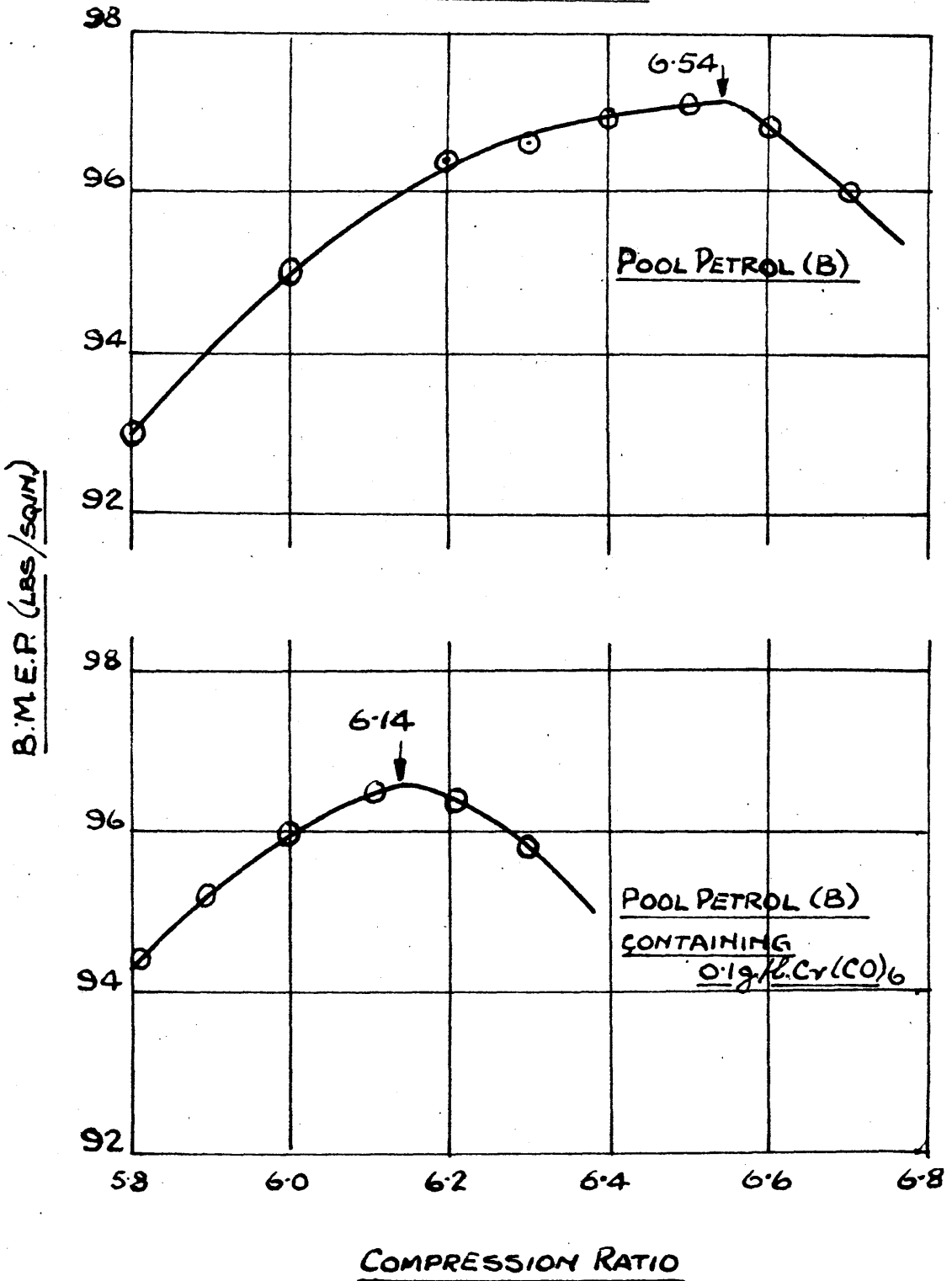THE EFFECT OF 0.2g/ℓ CHROMIUM HEXACABONYL ON THE H.U.C.R. OF ISO-OCTANE.

knock compounds can be studied is by comparison of their aniline coefficients[60]. The aniline coefficient of an anti-knock agent may be defined as the reciprocal of the number of moles of the substance giving the same effect as one mole of aniline. For pro-knock compounds the aniline coefficient is negative and may be defined as the reciprocal of the number of moles of the substance required to counteract the effect of one mole of aniline. Several workers have expressed the efficacy of anti-knock agents in terms of aniline coefficients and there appears to be reasonably good correlation between the results obtained by different workers. To obtain comparative results it appears to be necessary to use aniline concentrations no greater than 30 g./1.

The method of determining the aniline coefficient of chromium hexacarbonyl was to dope a supply of Pool Petrol with chromium hexacarbonyl of known concentration, and to determine the effect on the H.U.C.R. of adding varying concentrations of aniline to the doped fuel. By graphing the effect of varying concentrations of aniline on the doped fuel it is possible to determine the concentration of aniline which would have been required to bring the H.U.C.R. to the same value as that of the undoped fuel. The supply of Pool Petrol A was exhausted and it was necessary to use a different base fuel. This fuel is hereafter referred to as Pool Petrol B (See Appendix II). The H.U.C.R. curves of Pool Petrol B and Pool Petrol B containing 0.1 g./1. chromium hexacarbonyl are shown in Figure 31. The

FIGURE 31.

THE EFFECT OF 0.1g/ℓ CHROMIUM HEXACARBONYL ON THE H.U.C.R. OF POOL PETROL (B)

POOL PETROL (B)

6.54

POOL PETROL (B)
CONTAINING
0.1g/ℓ.Cr(CO)₆

6.14

B.M.E.P. (LBS/SQ.IN)

COMPRESSION RATIO

effect of chromium hexacarbonyl on the H.U.C.R. of Pool

Petrol B is similar to but slightly smaller than its effect

on Pool Petrol A. (See Figure 23). The amount of aniline

likely to be required to counteract the effect of the chromium

hexacarbonyl was estimated from Figures 21 and 23. From

Figure 23 it was learned that 0.1 g./l. of chromium hexacarbonyl

reduced the H.U.C.R. of Pool Petrol A by 0.52, while from

Figure 21 it was learned that the concentration of aniline

required to raise the H.U.C.R. of Pool Petrol A by 0.52 was

approximately 20 g./l. The required concentration of aniline

was therefore estimated as being in the neighbourhood of

20 g./l. and samples of Pool Petrol B already containing 0.1

g./l. chromium hexacarbonyl were doped with 15,25, and 40 g./l.

of aniline respectively. The H.U.C.R.s of these solutions

were then determined, the results being shown in Figure 32.

The effect of aniline on the H.U.C.R. of Pool Petrol B

containing 0.1 g./l. chromium hexacarbonyl is shown in Figure

33. From Figure 33 it is possible to tell the concentration

of aniline required to raise the H.U.C.R. of the chromium

hexacarbonyl doped fuel to the value for the undoped fuel

(6.54, v. Figure 31). The concentration of aniline required

to counteract the effect of 0.1 g./l. chromium hexacarbonyl

is found to be 15.0 g./l.

If the aniline coefficient is independent of

concentration a variation in the concentration of hexacarbonyl

would require a proportional variation in the concentration of

FIGURE 32

THE EFFECT OF ANILINE ON THE H.U.C.R. OF POOL PETROL (B) CONTAINING 0.1g/ℓ CHROMIUM HEXACARBONYL

15g. ANILINE/LITRE.

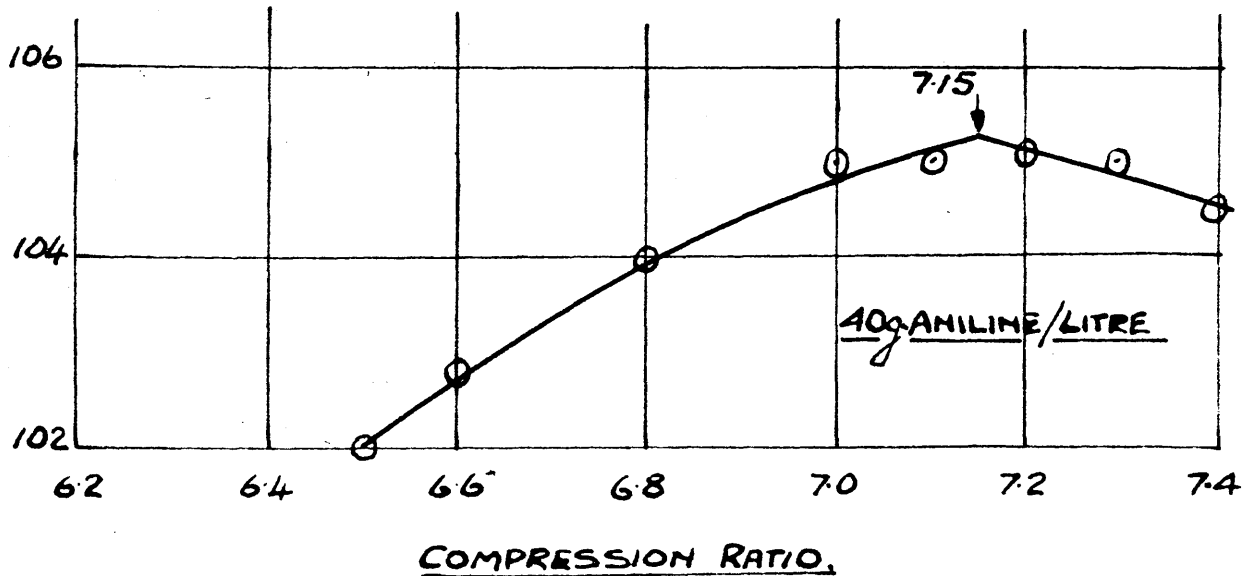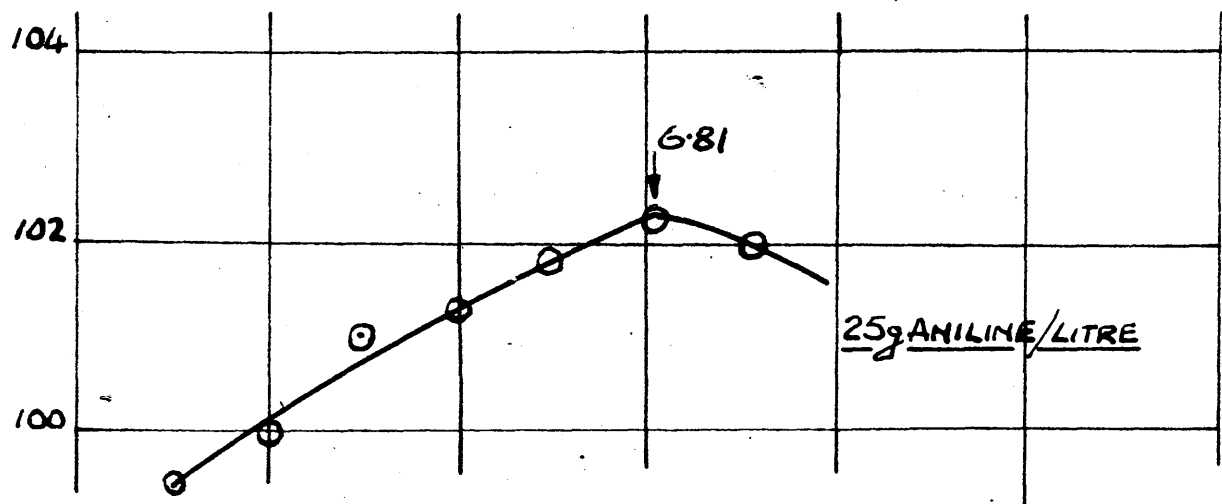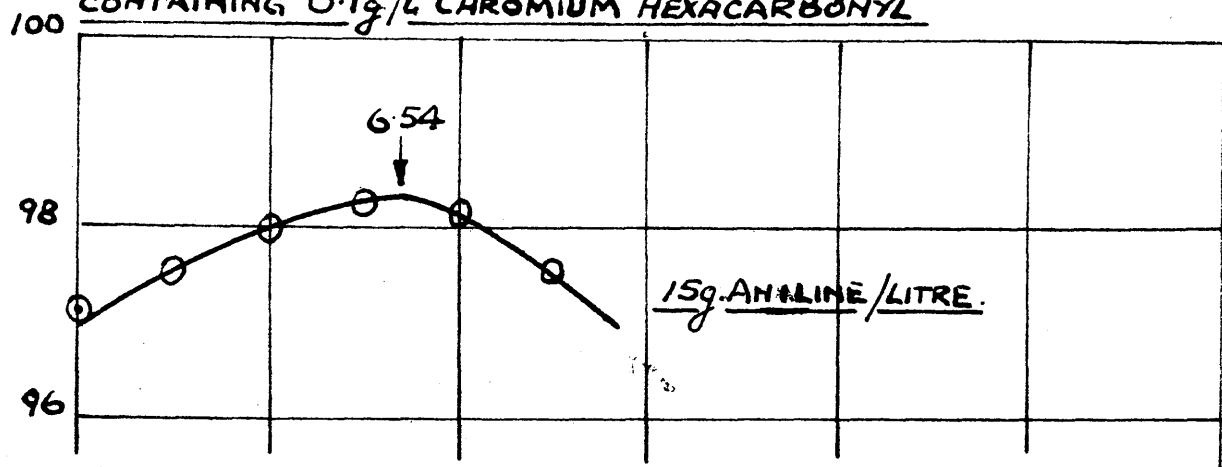25g ANILINE/LITRE

40g ANILINE/LITRE

B.M.E.P. (LBS/SQIN.)

COMPRESSION RATIO.

FIGURE 33

THE EFFECT OF ANILINE ON THE H.U.CR. OF POOL PETROL (B)
CONTAINING 0·1g/ℓ CHROMIUM HEXACARBONYL
DATA FROM FIGURES 31 AND 32.

H.U.C.R.
OF UNDOPED
POOL PETROL (B)

H.U.C.R.

CONCENTRATION OF ANILINE (GRAMS/LITRE)
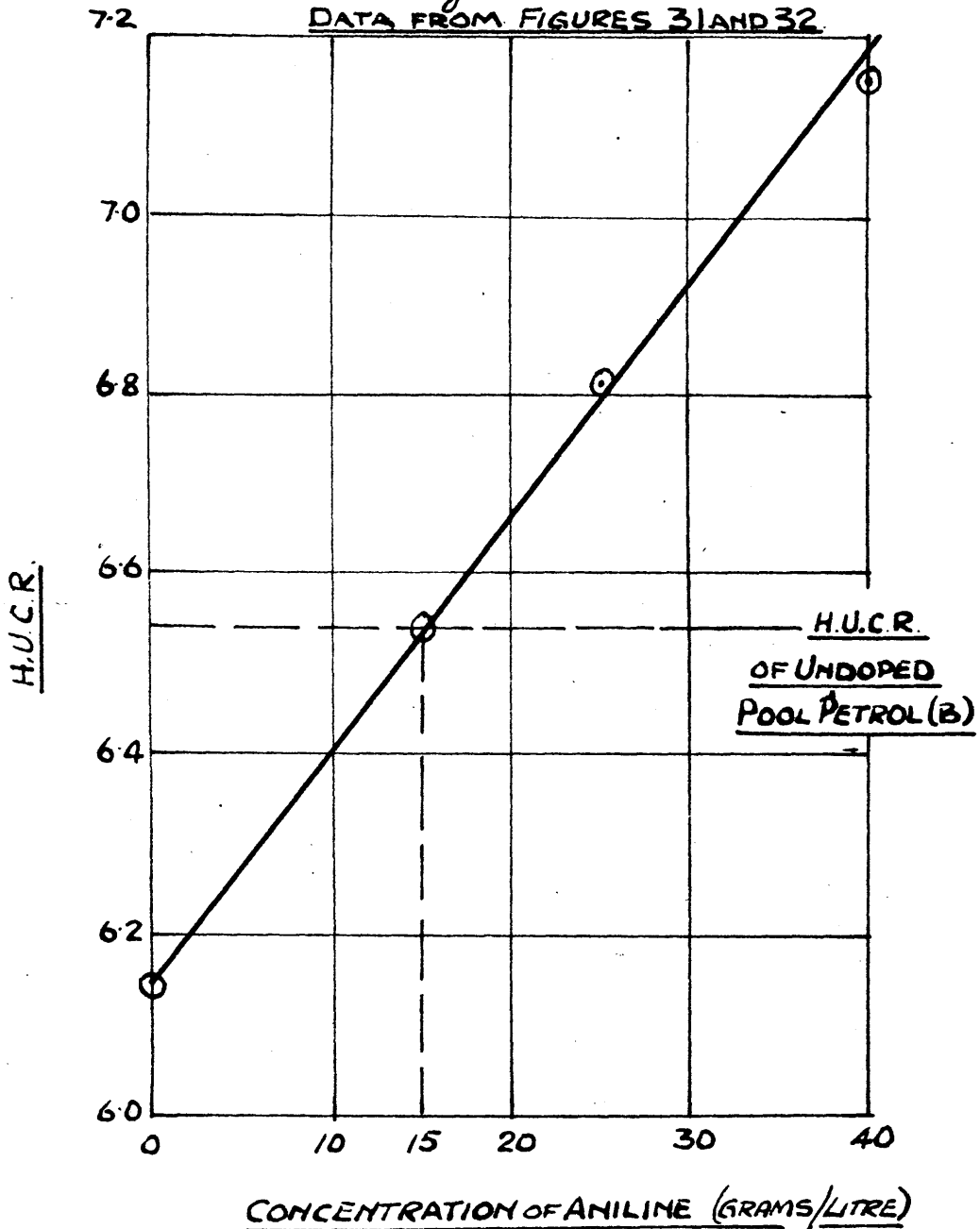
aniline to bring the H.U.C.R. to the value for undoped fuel.
This was verified by using concentrations one fifth of those
previously employed : i.e. 0.02 g./l. chromium hexacarbonyl and
3 g./l. aniline.   The results are shown in Figure 34.   Figure
34 shows that 3.0 g. of aniline are required to counteract the
effect of 0.02 g. chromium hexacarbonyl.

Calculation of Aniline Coefficient.

15 g. Aniline is counteracted by 0.1 g. $Cr(CO)_6$

93 g. Aniline (1 mole)   "   "   0.00282 moles $Cr(CO)_6$

$$\text{Aniline Coefficient of } Cr(CO)_6 = -\frac{1}{0.00282}$$

$$= -350$$

A calculation based on 3 g. aniline counteracting 0.02 g.
chromium hexacarbonyl would give the same result.   The values
of aniline coefficients of some common anti-knock compounds as
quoted by Calingaert[60] are shown below for purposes of comparison.

Benzene   0.085

Aniline   1.000

Tin Tetraethyl 4.0

Nickel carbonyl 35

Iron carbonyl   50

Lead tetraethyl 118

The value of - 350 shows that at low concentrations
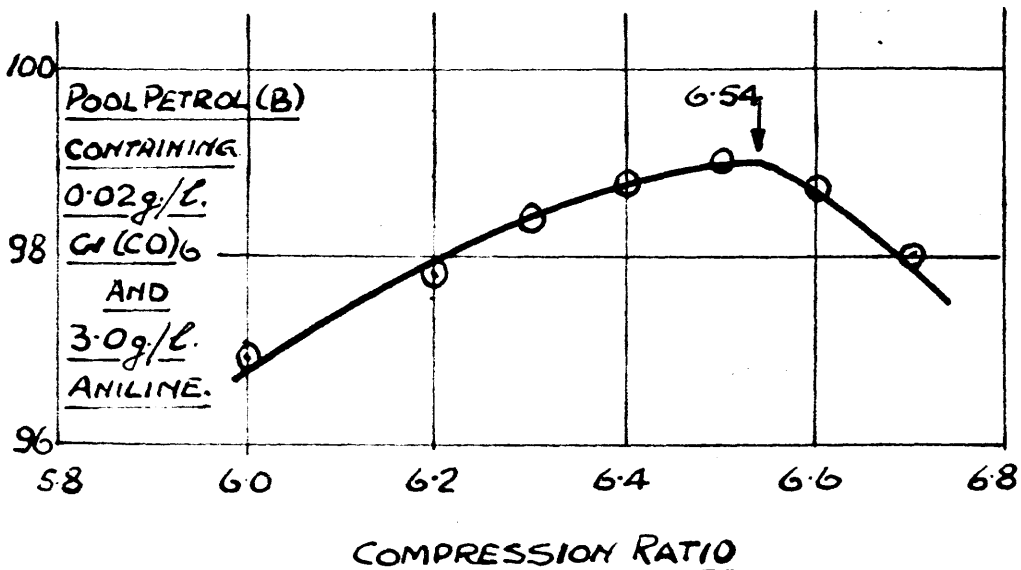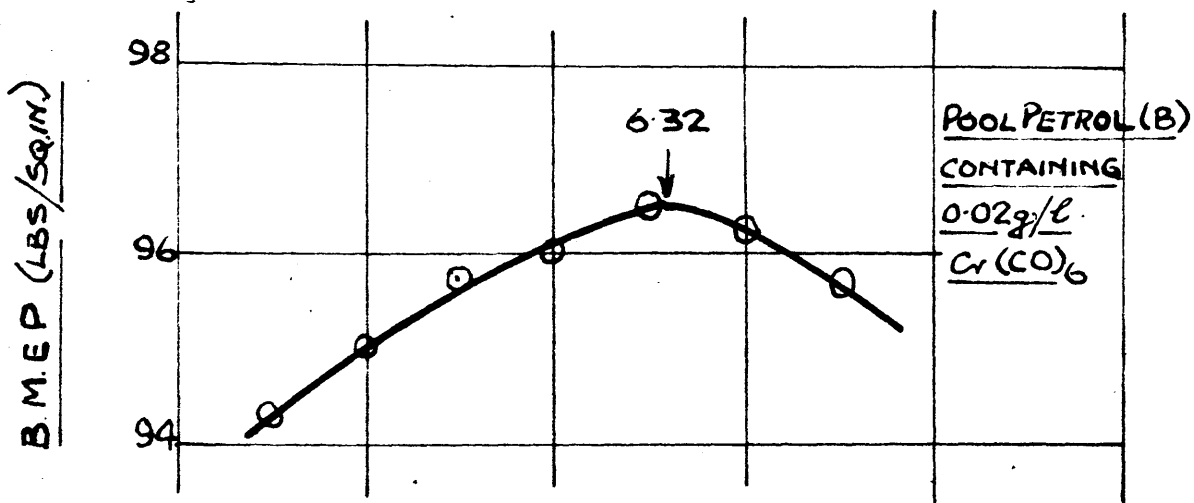the pro-knock potency of chromium hexacarbonyl is very high.

7) The Relationship between H.U.C.R. and Octane Number.

It has already been stated (p. 8) that there is a
relationship between H.U.C.R. and octane number.   In order that

FIGURE 34
VERIFICATION OF THE ANILINE COEFFICIENT OF CHROMIUM HEXACARBONYL

POOL PETROL (B)

6.54

POOL PETROL (B)
CONTAINING
0.02g/l.
Cr (CO)$_6$

6.32

POOL PETROL (B)
CONTAINING
0.02g/l.
Cr (CO)$_6$
AND
3.0g/l.
ANILINE.

6.54

B.M.E P (LBS/SQ.IN.)
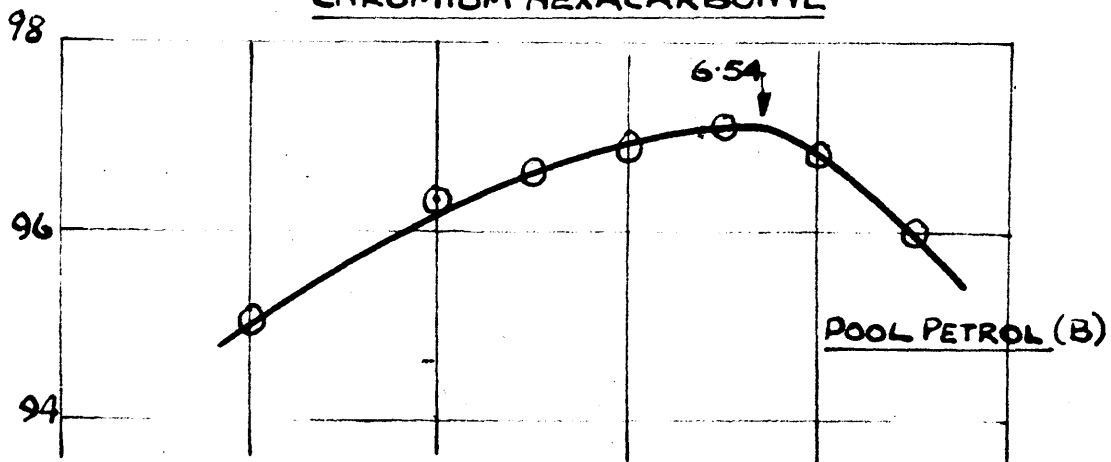
COMPRESSION RATIO

the results obtained previously may be expressed, if desired,
in terms of octane number it was decided to determine the
H.U.C.R.s of a number of fuels of known octane number in the
Ricardo E6/S Variable Compression Engine and to plot the
relationship between octane number and H.U.C.R. The fuels
used were Refined Straight Run Spirit which was known to have
an octane number of 59.5 and various blends of iso-octane and
n-heptane whose octane numbers were known from their composition.
The H.U.C.R. curves are shown in Figure 35 and the relationship
between H.U.C.R. and octane number is shown in Figure 36.
Also shown in Figure 36 is a similar curve obtained by Ricardo
and Glyde in a Ricardo E6 Engine[58]. This curve is not
identical with the one obtained by the author but is in
reasonable agreement with it.

From Figures 23 and 36 it is possible to express the
effect of chromium hexacarbonyl on the octane number of Pool
Petrol (A). This is shown in Figure 37. The maximum decrease
in octane number is given by all concentrations of hexacarbonyl
greater than 0.5 g./l. and is 5.3 octane numbers. The presence
of 0.02 g./l. chromium hexacarbonyl is sufficient to cause a
decrease of 4.6 octane numbers in the knock rating of the fuel.

C. The Effect of Chromium Hexacarbonyl on Compression-Ignition
Engine Fuels.

Combustion in the Diesel engine has been briefly
discussed in the introduction (pp.1&2).

1) Deductions from the Behaviour of Chromium Hexacarbonyl in
Spark-Ignition Engine Fuels.

FIGURE 35

THE H.U.C.R. CURVES OF FUELS OF VARYING OCTANE NUMBER

Chart 1 — REFINED STRAIGHT RUN SPIRIT OCTANE NUMBER 59.5
- Y-axis: B.M.E.P (LBS/SQ.IN.), 92 to 96
- Peak annotated 6·10
- X-axis: COMPRESSION RATIO, 5·6 to 6·4

Chart 2 — 70% ISO OCTANE 30% n-HEPTANE OCTANE NUMBER 70·0
- Y-axis: B.M.E.P (LBS/SQ.IN.), 106 to 110
- Peak annotated 7·45
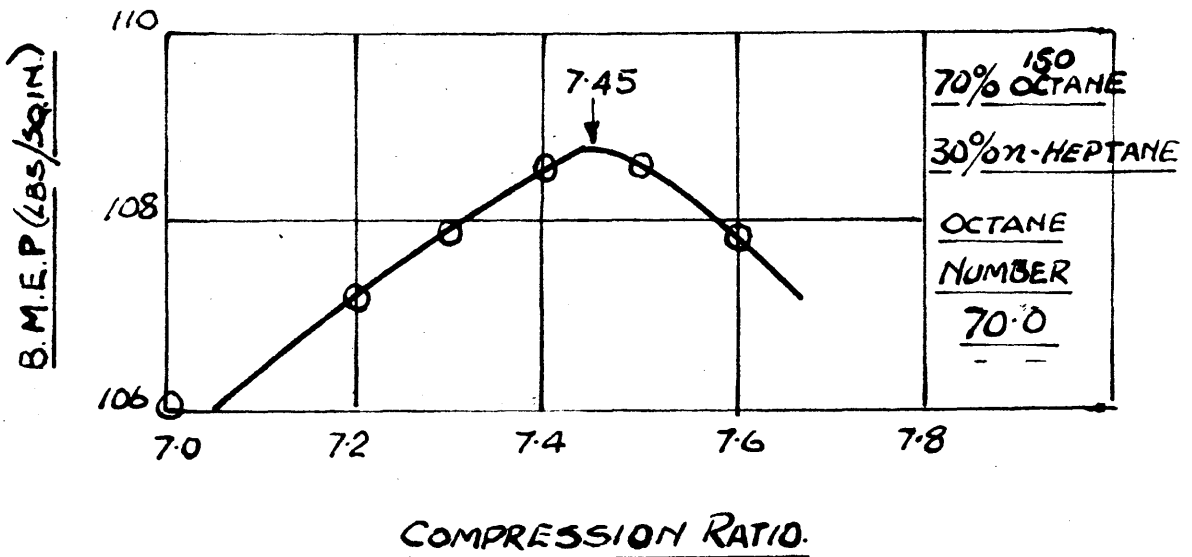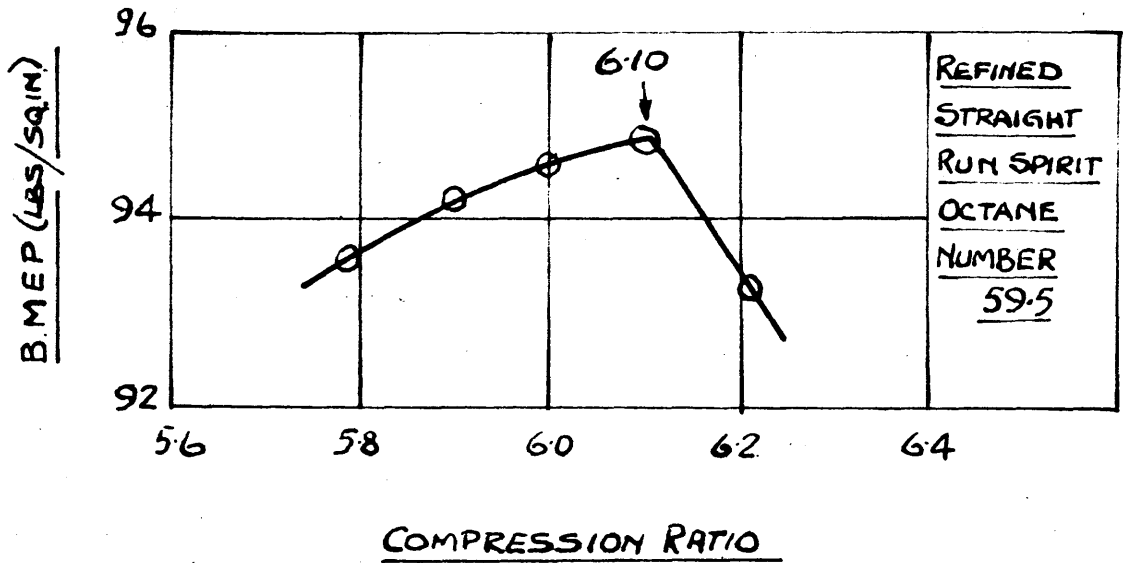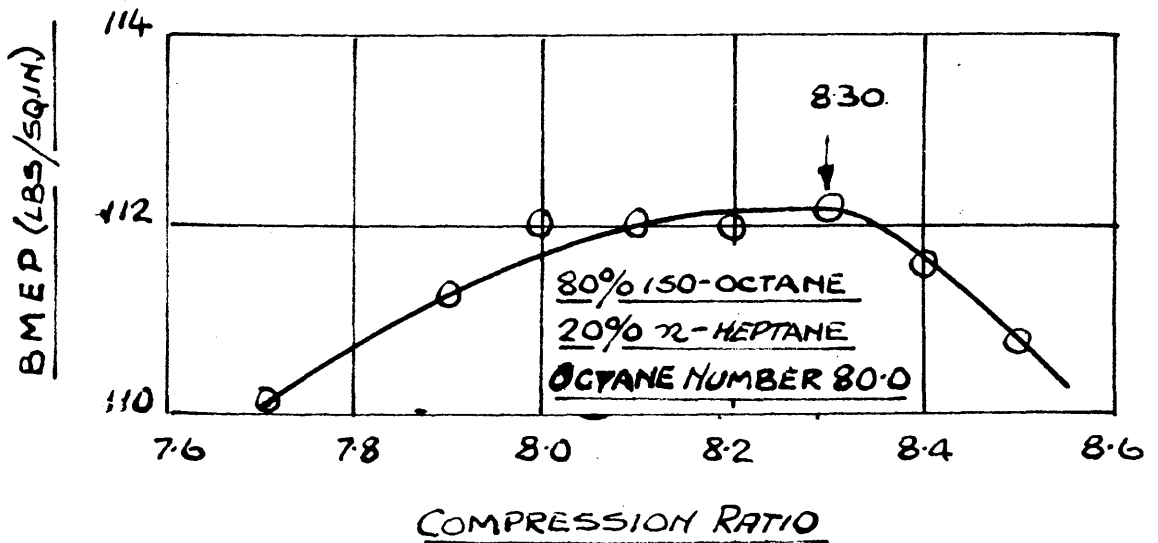- X-axis: COMPRESSION RATIO, 7·0 to 7·8

FIGURE 35
(CONTINUED)
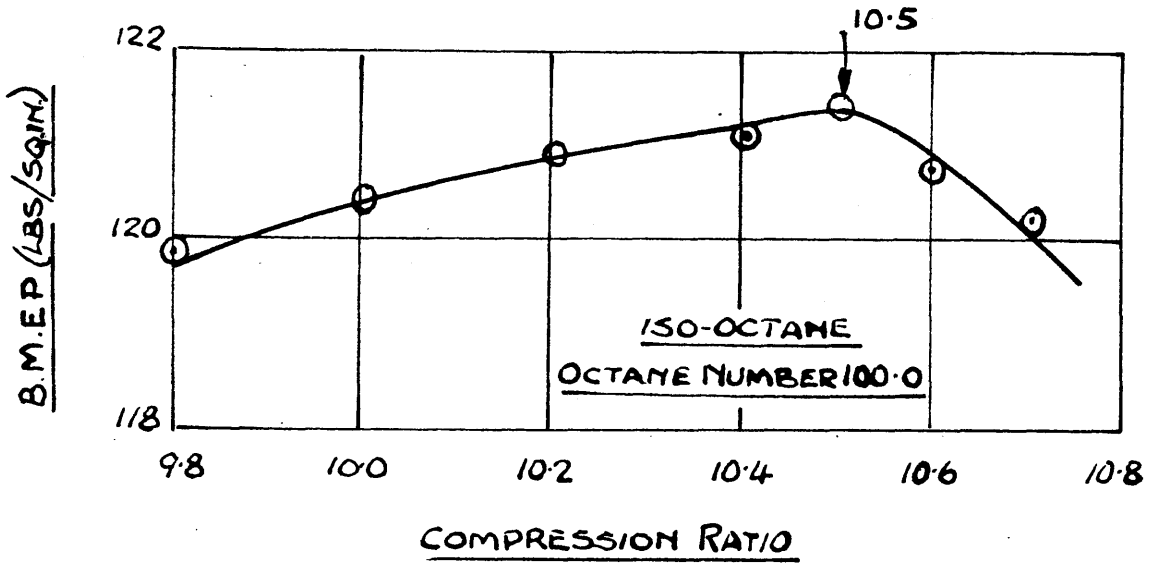
FIGURE 36

THE RELATIONSHIP BETWEEN H.U.C.R. AND OCTANE NUMBER

OCTANE NUMBER

FIGURE 37

THE EFFECT OF CHROMIUM HEXACARBONYL ON THE OCTANE NUMBER
OF POOL PETROL (A)
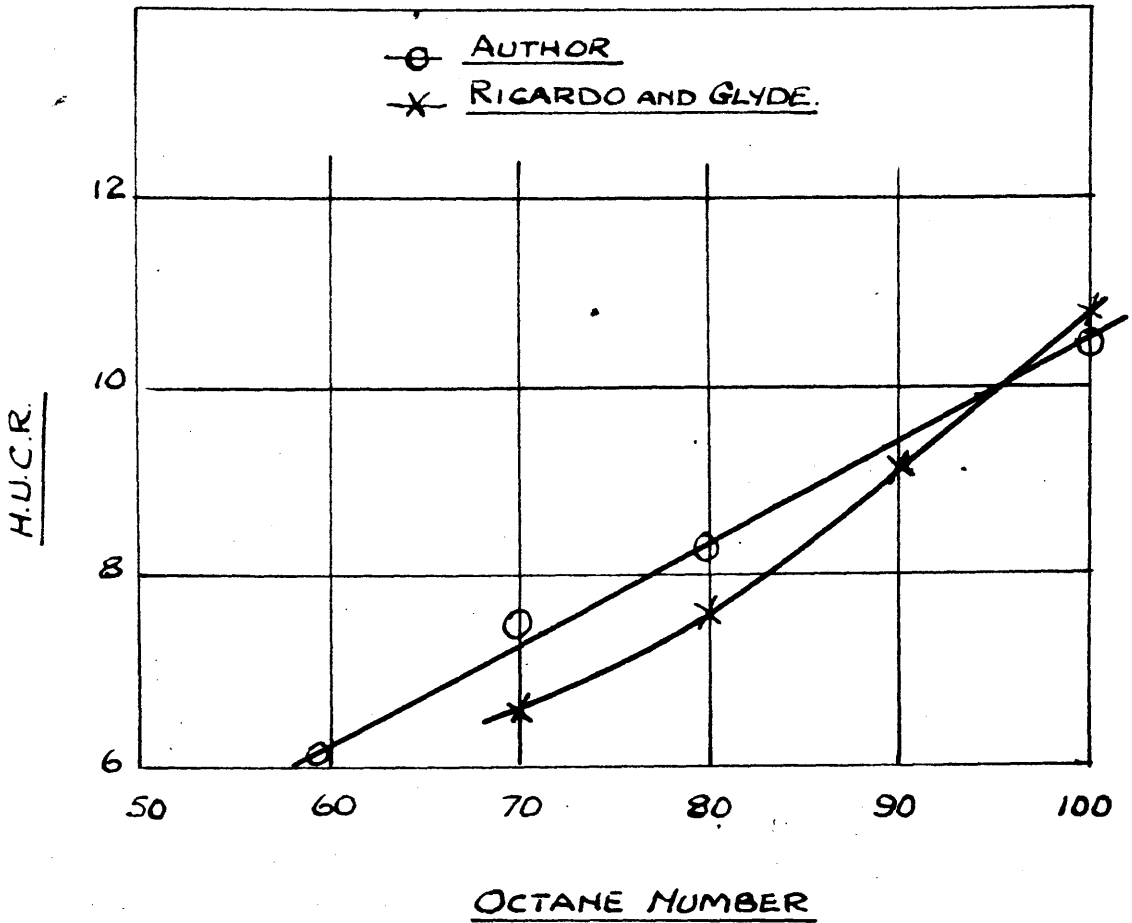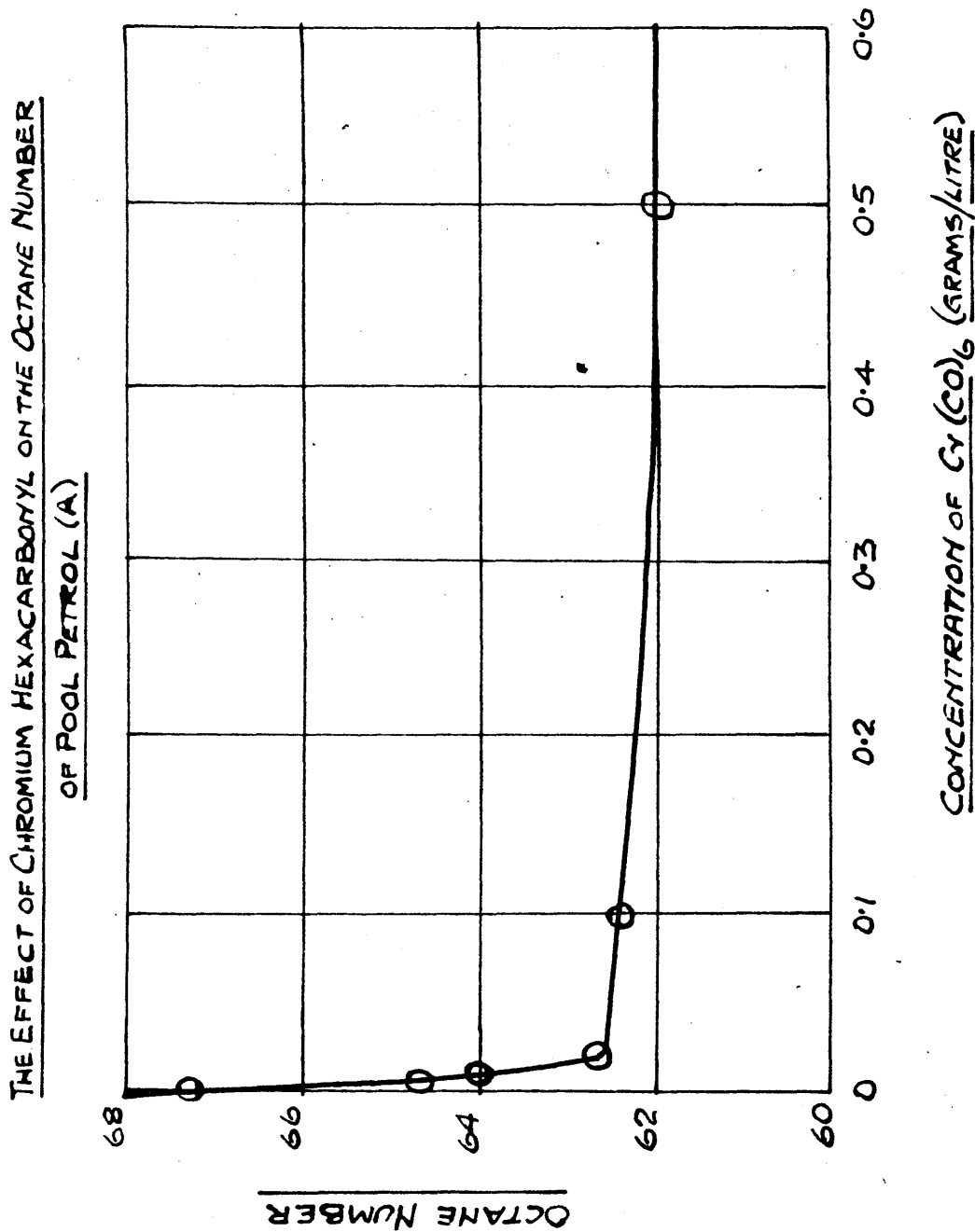

OCTANE NUMBER

CONCENTRATION OF $Cr(CO)_6$ (GRAMS/LITRE)

In 1948 Ogilvie, Davis, Thomson, Grummit, & Winkler[61] studied the pro-knock activity of a large number of substances and came to the conclusion that they were of two main types: (I) those which counteract the effect of organometallic anti-knock compounds present, and (II) those which in addition have an effect on the base stock. Compounds of the first type showed greatest effect in fuels already heavily doped with lead tetraethyl. They were similarly effective in counteracting the effect of iron carbonyl but had no effect on aniline. Compounds of the second type effectively counter-acted aniline and, when added to Diesel fuels showed a marked improvement in the ignition properties of the fuel. It has already been established (pp. 90 & 91) that chromium hexacarbonyl acted as a pro-knock compound in Refined Straight Run Spirit and iso-octane, neither of which fuels contained any anti-knock additives. This indicates that chromium hexacarbonyl is having an effect on the base fuel and so comes under the second type of pro-knock compound in the classification of Ogilvie et al. This is confirmed by the fact that chromium hexacarbonyl counteracts the anti-knock effect of aniline. Ogilvie et al., however, found that compounds of the second type were effective ignition promoters for Diesel fuels so it seems probable that chromium hexacarbonyl would be useful in this respect.

The ignition quality of a Diesel fuel is usually expressed in terms of its cetane number, just as octane numbers are used to designate the anti-knock properties of gasoline.

The cetane number of a fuel is determined by finding the composition of the mixture of cetane and α-methylnaphthalene which exactly matches the ignition lag given by the fuel. The percentage of cetane in the mixture is the cetane number of the fuel. Cetene was originally used in place of cetane but the superior quality of the latter in storage led to its adoption in America as the standard fuel. The cetene scale is very similar to the cetane scale and is still used in some European countries.

There is a direct relationship between the octane and cetane number scales. A graph showing this has been published by Nygaard et al.[62] and is reproduced in Figure 38. If it is assumed that the combustion-modifying effect of chromium hexacarbonyl on Diesel fuels is similar to its effect on petrol (A similar assumption was made by Nygaard et al.[59]) it is possible to calculate from Figures 37 and 38 the approximate efficacy of chromium hexacarbonyl as an ignition promoter for Diesel fuels. The maximum improvement in ignition properties would appear to correspond to a rise of 3.2 cetane numbers. A concentration of 0.02 g./l. would be expected to give a rise of approximately 2.7 cetane numbers. Diesel fuel additives are normally required to give a higher rise in cetane number than this[63] and the use of chromium hexacarbonyl as a practical Diesel fuel additive would seem to be strictly limited. The probable cetane number improvement seems even more inadequate when it is remembered that the exact cetane

FIGURE 38

THE RELATIONSHIP BETWEEN OCTANE AND CETANE NUMBERS

REPRODUCED FROM J. INST. PETROL, 1941- **27** - 354
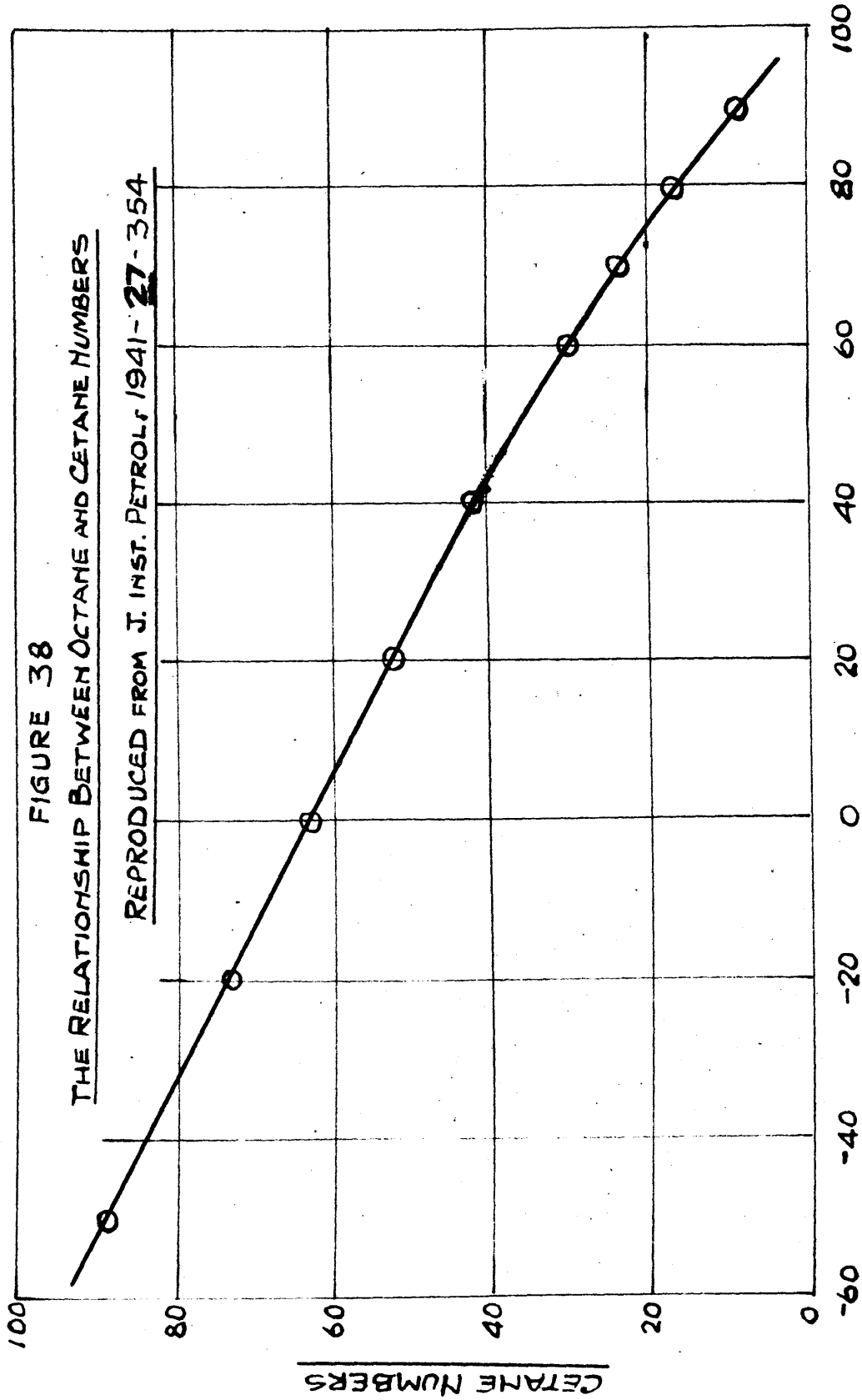
OCTANE NUMBERS.

CETANE NUMBERS

number of a fuel is not so critical from a practical point
of view as the exact octane number of a gasoline[64].

Such calculations as the above, based as they are
on the behavior of chromium hexacarbonyl in spark-ignition
engine fuels cannot be taken as a wholly reliable indication
of the behavior of the compound in Diesel fuels. It was
accordingly decided to determine the effect of chromium
hexacarbonyl on a Diesel fuel by performing a series of tests
in a suitable compression-ignition engine.

2) Method of Testing the Ignition Properties of Diesel Fuels.

The standard A.S.T.M. method for determining cetane
numbers[65] involves the use of the C.F.R. Diesel engine. This
was not available to the author and the engine used was the
Compression-Ignition Version of the Ricardo E6/S Variable
Compression Engine. The author had not access to any of the
complicated electronic methods of recording ignition delay such
as that devised recently by Hulf, Rubach & Withers[66]. The
Ricardo E6 Engine was however fitted with a "Dobbie McInnes
'Farnboro' Electric Indicator" which recorded the pressure in
the combustion chamber at all points in the cycle. Most of
the modern text books on Engine Testing contain a description
of this indicator[67].

The duration of the ignition-lag was determined
empirically from study of the indicator cards. The indicator
cards obtained from the Farnboro Indicator are on black paper
and a series of small holes indicate the position of the curve.

The final indicator diagram is traced from the card.
Figure 39 shows a half size representation of an indicator
diagram obtained from a Ricardo E6 Engine with injection 39°
before "Top Dead Centre" (T.D.C.) and compression ratio 20.0.
A diagram obtained when motoring the engine is shown in the
same figure.   The "motoring cycle diagram" is symmetrical
about the top dead centre line and this enables the exact
position of the top dead centre to be found.   In determining
the position of T.D.C. for the working cycle it is necessary
to move a tracing of the curve over the motoring cycle diagram
until the initial portions of the curves coincide.   Top dead
centre is then the same for both curves and the T.D.C. of the
working cycle can be obtained from that of the motoring cycle.

The ignition-lag or delay period may be defined as
the time which elapses between the commencement of injection
and the start of rapid combustion[68].   The ignition-lag is
frequently expressed in "degrees of crank angle" and provided
the speed of the engine is maintained constant throughout the
tests this is directly proportional to time.   It is not easy
to measure the delay period accurately from an indicator
diagram and a number of assumptions have to be made when so
doing.

(a)   The exact point at which injection commences
is not known unless special instruments have been fitted for
this purpose.   Even when it is possible (as here) to set the
injection pump to operate at any desired crank angle (say 39°

FIGURE 39

WORKING AND MOTORING INDICATOR DIAGRAMS ON THE RICARDO E6.
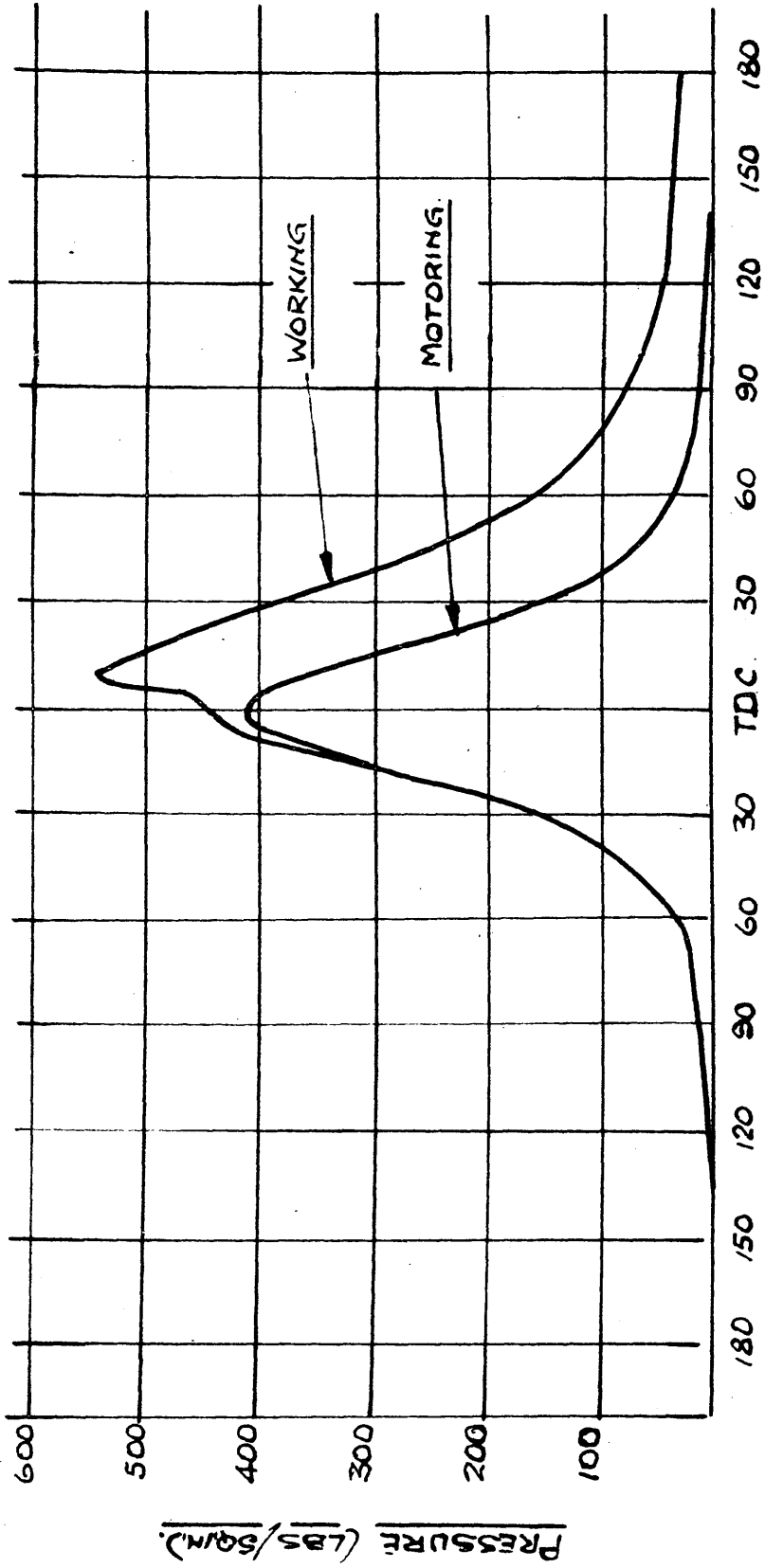
before T.D.C.), the angle refers to the operation of the
pump rather than to the entry of the fuel into the combustion
chamber.   In order to surmount this difficulty it was decided
to select suitable injection timing and engine speed and
maintain these constant throughout the experiments.   It is
assumed that under these conditions the actual commencement of
injection will remain constant relative to T.D.C. and ignition-
lags may be compared (though not determined absolutely) by
measuring the crank angle between T.D.C. and the start of
rapid combustion.   The above assumption will only be valid
if the stroke of the injection pump remains reasonably constant
throughout the tests.   The pump was set to give a "just
visible exhaust" and very little variation in setting was
required to maintain this condition throughout the tests.
This is confirmed by the relative constancy of the power
readings, the difference between the highest and lowest being
only 8% despite the effect of different fuels.

        (b) Unless the engine is provided with special
equipment it is difficult to determine the exact point at which
ignition occurs.   It is, for example, possible to tell from
Figure 39 that ignition occurs somewhere between two and five
degrees after T.D.C.   This, however, is not sufficiently
accurate and it is necessary to fix a standard method of
determining the start of rapid combustion and to adhere to
that method throughout the tests.   The exact method employed
is illustrated in Figure 40 which reproduces part of an

FIGURE 40

METHOD of DETERMINING. POINT of IGNITION FROM. FARNBORO INDICATOR DIAGRAM.
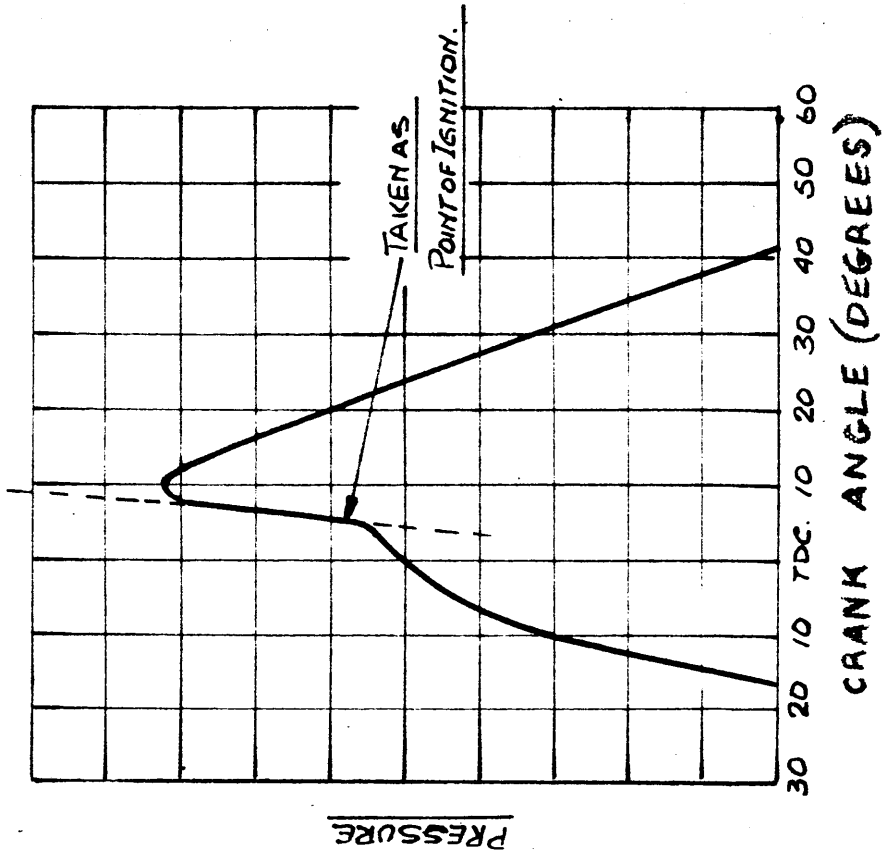
indicator diagram at full size. The rapid rise of pressure
which occurs almost at the top of the curve always approximates
closely to a straight line on the indicator diagrams. A
collinear straight line is drawn (shown dotted in Figure 40)
and the point where the indicator curve leaves this line is
taken as the point of ignition or start of rapid combustion.
The actual ignition may occur slightly earlier in the cycle
but it is assumed that the difference between the true point
of ignition and the one determined by this method will remain
constant in all the tests. In view of the similarity in the
form of all the indicator diagrams obtained this seems highly
probable.

On account of the two factors described above the
ignition-lags referred to hereafter should be regarded as
relative rather than absolute.

3) Preliminary Tests on Pool Gas Oil. (See Appendix II)

The Diesel fuel used in this and all subsequent
tests was Pool Gas Oil. A five gallon sample of this fuel
was taken at the start of the tests and used as the base fuel
in all subsequent experiments. The preliminary tests were
carried out to determine what compression ratio, engine speed,
and injection timing would give the most suitable type of
indicator diagram.

(a) Compression Ratio:- The engine speed was
maintained at 1500 r.p.m., the injection pump was adjusted to
give "just visible exhaust", and the injection timing was set

at 39° before T.D.C.   Under these conditions a series of
indicator cards was obtained from the engine at different
compression ratios.   It was found that at compression ratios
above 20 the diagram did not have its characteristic shape,
being almost symmetrical about a line corresponding to a
few degrees after T.D.C.   This made it very difficult to
establish from the card exactly when ignition occurred.   It
was also found that as the compression ratio was decreased
below 20 the points on the original indicator card were more
scattered and it was difficult to trace the exact position of
the curve.   A compression ratio of 20.0 was therefore selected
and used in all subsequent tests.

(b) Engine Speed:-   The compression ratio was set
at 20.0, the injection pump stroke was adjusted to give "just
visible exhaust", and the injection timing was set to 39°
before T.D.C.   Under these conditions indicator cards were
obtained at engine speeds of 1000, 1250, 1500, 1750 and 2000
r.p.m.   As the speed increased the ignition lag (expressed
in degrees crank angle) also increased.   At 1750 and 2000 r.p.m.
however, the rate of pressure rise at the top of the curve
was more gradual and it was very difficult to tell exactly
where ignition took place.   The speed selected was 1500 r.p.m.
since this was the highest speed consistent with the production
of an indicator diagram of suitable shape.

(c) Injection Timing:-   The compression ratio was
set at 20.0, the injection pump was adjusted to give just

visible exhaust, and the engine speed was maintained at
1500 r.p.m.   The injection timing recommended by the
manufacturers of the engine was 39° before T.D.C. and this
was found to give a satisfactory indicator diagram.   Advancing
of the injection was found to reduce the ignition-lag and
retarding was found to produce a smoother curve which made
it more difficult to estimate the point of ignition.   The
timing of the injection pump selected for future tests was
therefore 39° before T.D.C.

As a result of the tests described above the
following conditions were maintained throughout all subsequent
tests:-

1) The stroke of the injection pump was adjusted till the
   exhaust was "just visible".

2) The injection pump timing was set at 39° before T.D.C.

3) The compression ratio was fixed at 20.0.

4) The engine speed was maintained at 1500 r.p.m.

4) The Effect of Amyl Nitrate on the Ignition Properties of
   Pool Gas Oil.

In order to assess the efficacy of chromium
hexacarbonyl as an ignition promoter for Diesel fuels it was
decided to establish the effect of a well known ignition
promoter on the ignition-lag obtained with Pool Gas Oil.
The ignition promoter used was amyl nitrate and this was tested
at concentrations of 5.0 and 0.5 g./l.   These two concentrations
represent the upper and lower limits normally used.   The

conditions of the tests were as described in the previous paragraph and the results are given in Table XV.

The ignition-lags recorded in Table XV were measured from the appropriate indicator diagrams by use of a graduated transparent sheet supplied by the makers of the Farnboro indicator. The top portions of the indicator diagrams for tests 3 and 5 are shown in Figure 41. These tests gave the maximum and minimum ignition-lags respectively. The other diagrams were similar in form and lay between these two extremes. It was therefore thought unnecessary to reproduce them.

The results in Table XV show that the effect of amyl nitrate on ignition-lag is readily detectable by the Ricardo E6 provided with a Farnboro Indicator. Even at the relatively low concentration of 0.5 g./l. there was a reduction in ignition lag of approximately 2°. From a graph obtained by Butterworth and quoted by Ricardo & Glyde[69] it is possible to correlate ignition delay and cetane number. Since Butterworth performed his tests on a Ricardo E6 Variable Compression Engine at 1500 r.p.m. and 19.75 compression ratio it seems justifiable to apply his results to the author's work (Performed on a Ricardo E6 at 1500 r.p.m. and 20.0 C.R.). Butterworth found that a change in ignition lag of one degree corresponded to a change in ignition rating of approximately three cetane numbers. On this basis the effect of 5.0 g./l. amyl nitrate would be to cause a rise of approximately 11 in the cetane number of Pool

Table XV.

The Effect of Amyl Nitrate on the Ignition Lag Obtained with Pool Gas Oil.

Test No.	Concn. of Amyl nitrate g./l.	Ignition-lag (Degrees crank) angle.	Average Ignition-lag. (Degrees)	Effect of Additive on Ignition-lag (Degrees)
1	Nil	5.3		
2	Nil	5.2	5.3	----
3	Nil	5.4		
4	Nil	5.1		
5	5.0	1.4	1.5	- 3.8
6	5.0	1.6		
7	0.5	3.0	3.0	- 2.3
8	0.5	3.0		

FIGURE 41.

The Effect of Amyl Nitrate on the Ignition Lag Obtained with Pool Gas Oil.
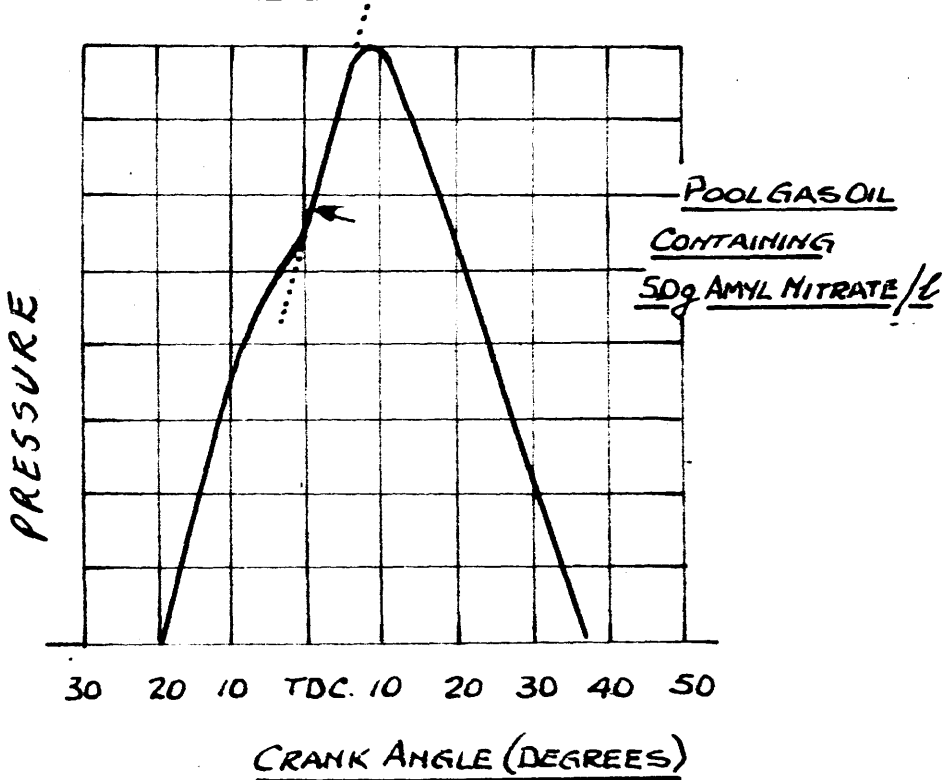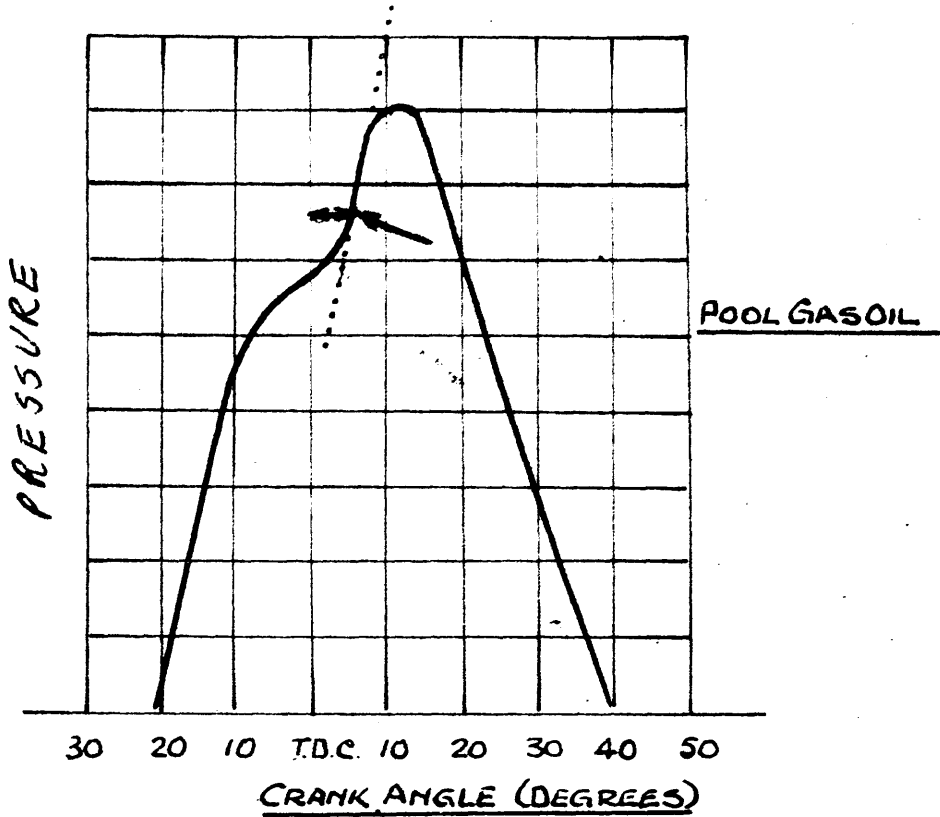
Gas Oil while 0.5 g./l. of the compound would cause a rise of approximately 7 cetane numbers.   This result is in reasonable agreement with one quoted by Nygaard et al.[70] in which 5.0 g./l. amyl nitrate was stated to cause a rise of 8.9 in the cetane number of a straight run Diesel fuel.   This confirms that the results obtained by the author from the Ricardo E6 are of the same order as those obtained by other workers.

5)   The Effect of Chromium Hexacarbonyl on the Ignition Properties of Pool Gas Oil.

Samples of Pool Gas Oil containing 0.5, 0.2, and 0.05 g./l. chromium hexacarbonyl were tested in the Ricardo E6 and their ignition-lags determined under the same conditions as those used for previous tests.   The results are shown in Table XVI.

The indicator diagrams had approximately the same form as those obtained with undoped Pool Gas Oil (v. Figure 41) and are not reproduced.   The results in Table XVI show that chromium hexacarbonyl has only a very slight effect on the ignition properties of Pool Gas Oil.   Increase in concentration does not appear to increase the effect: this is similar to the behaviour of the compound in gasoline, where increases in concentration over 0.02 g./l. had very little effect on the knocking properties of the fuel.   Chromium hexacarbonyl appears to decrease the ignition-lag by approximately 1° crank angle, which is equivalent to an increase of approximately 3 cetane

Table XVI.

The Effect of Chromium Hexacarbonyl on the Ignition-lag

Obtained with Pool Gas Oil.

Test No.	Concn. of $Cr(CO)_6$ (g./l.)	Ignition-lag (degrees crank angle)	Average Ignition-lag. (degrees crank angle).	Effect of additive on ignition-lag (degrees crank angle)
9	Nil	5.3	5.2	---
10	Nil	5.1		
11	0.5	4.6	4.5	- 0.7
12	0.5	4.4		
13	0.2	4.4	4.3	- 0.9
14	0.2	4.2		
15	0.05	4.2	4.1	- 1.1
16	0.05	4.0		

numbers if it is assumed that the results obtained by
Butterworth are applicable.   This is in good agreement with
the result reported earlier.   From the behaviour of chromium
hexacarbonyl in spark-ignition engine fuels it was deduced (p.97)
that the effect of the substance on the ignition properties
of a Diesel fuel would be to cause a rise of from 2.7 to 3.2
cetane numbers.

Chromium hexacarbonyl thus compares unfavourably
with amyl nitrate as an ignition promoter.   The maximum effect
of the substance is to cause a rise of approximately three in
the cetane number of a fuel.   This effect can, however, be
produced by very low concentrations of the compound.

D.   The Effect of Chromium Hexacarbonyl on an Aromatic Fuel.

Aromatic fuels such as benzene possess excellent
anti-knock properties in a spark-ignition engine.   The
compression ratio at which they may be used is limited not by
detonation but by pre-ignition.   The phenomenon of pre-ignition
is quite distinct from that of detonation or knock.   It
consists of the premature ignition of the charge by some hot
spot in the combustion chamber before the passing of the spark.
The hot spot is frequently at or near the plug.   The charge
burns at a normal rate after pre-ignition, there being no
sudden increase in the rate of combustion as experienced after
detonation or knock.   If pre-ignition is occurring only
slightly earlier in the cycle than normal ignition it is
possible to switch off the ignition and the engine will
continue to run normally.   Usually, however, pre-ignition

occurs so early in the cycle that an appreciable proportion
of the charge has been burned before the piston reaches
T.D.C. and there is consequently a considerable fall in engine
efficiency.

It was decided to test the effect of chromium
hexacarbonyl on the S.I.T. and H.U.C.R. of benzene.

1) The Effect of Chromium Hexacarbonyl on the S.I.T. of Benzene.

The effect of varying concentrations of chromium
hexacarbonyl on the S.I.T. of benzene is shown in Figure 42.
The presence of chromium hexacarbonyl in benzene causes a
considerable lowering of the S.I.T.   This is the opposite
effect to that observed with all fuels previously tested but
it is consistent with the pro-knock properties of the hexacarbonyl
in engine tests.   The S.I.T. of undoped benzene is unusually
high (665°C) and the fact that the tests on benzene were being
carried out at a higher temperature level might explain the
reversal of the S.I.T. effect.   This would imply that chromium
hexacarbonyl had an anti-detonant effect at relatively low
temperatures and a pro-detonant effect at higher temperatures.
Since higher temperatures would be more likely to prevail in an
engine combustion chamber this would explain the pro-knock
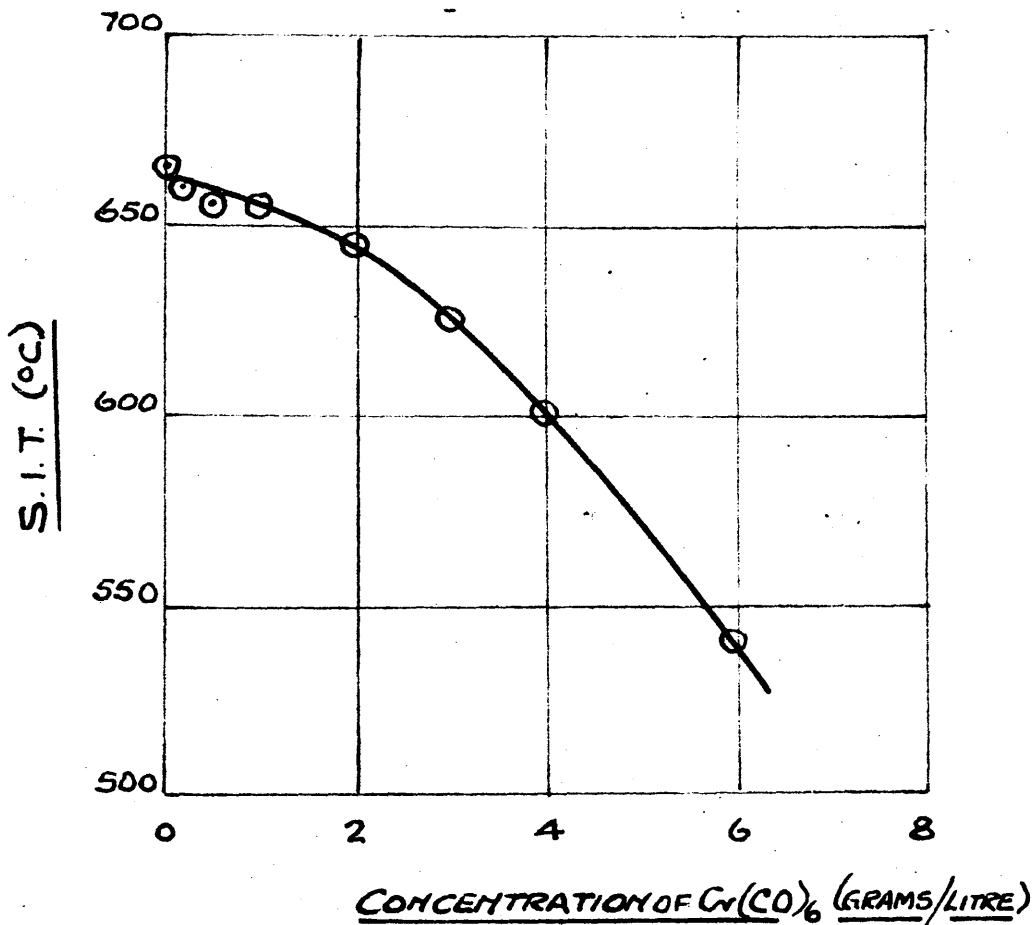effect observed under engine conditions.

2) The Effect of Chromium Hexacarbonyl on the H.U.C.R. of Benzene.

Two H.U.C.R. curves of "Analar" benzene are shown in
Figure 43.   During the tests on benzene the cooling water
temperature was maintained at 110°F.   The experiment was

FIGURE 42

THE EFFECT OF CHROMIUM HEXACARBONYL
ONTHE S.I.T. OF BENZENE.

duplicated because of the irregular behaviour of the benzene
at high compression ratios. The curves in Figure 43 do not
have the smooth form usually associated with H.U.C.R. curves.
At compression ratios above 14 the power developed by the
engine varied considerably without any apparent reason and this
was assumed to be due to pre-ignition. This was confirmed by
switching off the spark-ignition. At compression ratios between
14.5 and 15 the engine continued to run without spark-ignition
thus proving that pre-ignition was taking place. At compression
ratios over 15 the engine ran very unsteadily without spark-
ignition and quickly lost power. This was taken to mean that
pre-ignition was occurring so early in the cycle that smooth
running was no longer possible.

The H.U.C.R. curve of benzene containing 0.2 g./l.
chromium hexacarbonyl is shown in Figure 44. The doped benzene
gave a smooth curve without the irregularities obtained when
using the undoped fuel. The engine behaved in a more normal
way, there being no sudden fluctuations of power at even the
highest compression ratios. After each power reading the spark-
ignition was switched off for a few seconds and in every case
the power fell off steadily and rapidly, indicating that little
or no pre-ignition was taking place. It has thus been
established that the presence of a relatively small concentration
of chromium hexacarbonyl in benzene effectively inhibits
pre-ignition of the fuel and raises the H.U.C.R. of the fuel
from about 14.5 (with pre-ignition) to 15.6.

FIGURE 44

THE H.U.C.R. OF BENZENE CONTAINING 0.2g/ℓ.
CHROMIUM HEXACARBONYL
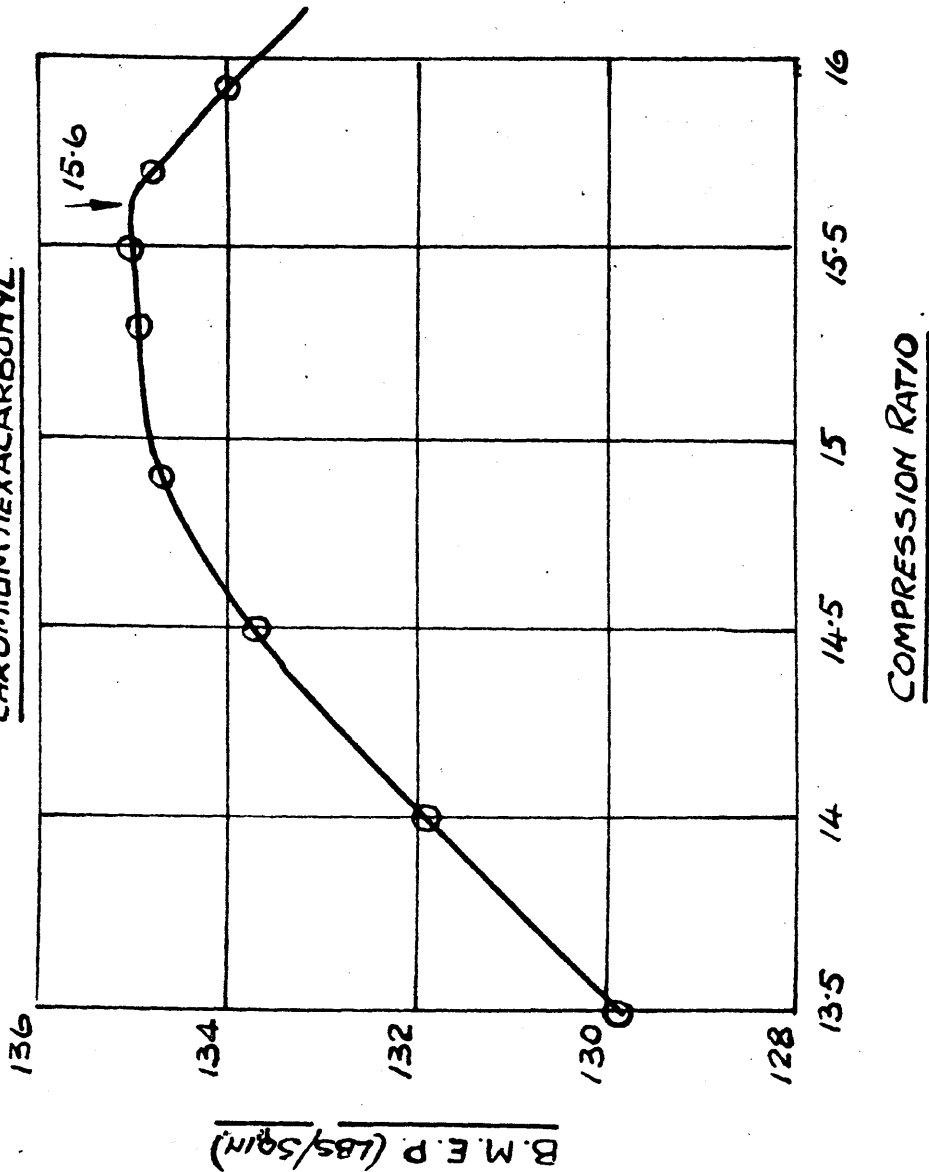
COMPRESSION RATIO

The H.U.C.R. of benzene was first determined by Ricardo who, in 1923,[71] obtained a value of 6.9 in a Ricardo E35 Variable Compression Engine.   Ricardo stated that this relatively low value was due to pre-ignition rather than the onset of knock.   In recent years improved sparking plug design has delayed the onset of pre-ignition and recently Downs & Pigneguy[72] reported a value of 14.64 for the H.U.C.R. of benzene.

As far as the author is aware the H.U.C.R. value of 15.6 is higher than that obtained by any previous worker for benzene or indeed any other fuel except acetone.   This improvement in H.U.C.R. has been abhieved despite the fact that chromium hexacarbonyl has already been proved to be a pro-knock agent and it can only be assumed that the hexacarbonyl is acting as a pre-ignition inhibitor.   If pre-ignition could be inhibited without the use of a pro-knock agent it is probable that the H.U.C.R. of benzene would be approximately 16.0.   This is based on the assumption that the pro-knock effect of chromium hexacarbonyl in benzene would be approximately similar to its effect in other fuels.

E. Discussion of the Results of Section lll.

The results of Section lll may be briefly summarised as follows:-

Chromium hexacarbonyl raises the S.I.T. of Pool Petrol, Refined Straight Run Spirit, n-heptane and iso-octane and lowers the S.I.T. of benzene.

Chromium hexacarbonyl lowers the H.U.C.R. of Pool Petrol, Refined Straight Run Spirit, and iso-octane and raises the H.U.C.R. of benzene.

The effect of chromium hexacarbonyl on S.I.T.s is that of a typical anti-knock compound. The maximum S.I.T. effect is obtained at concentrations of 1 g./l. or over in each case. The effect of chromium hexacarbonyl on the H.U.C.R. of spark-ignition engine fuels is rather unusual. A surprisingly low concentration of the compound (0.02 g./l.) gives an appreciable pro-knock effect but a further increase in concentration has little or no additional effect. This behaviour is different from that of established pro-knocks such as amyl nitrate which require a concentration of at least 0.2 g./l. before they produce any detectable effect : as the concentration of these pro-knock agents increases the pro-knock effect also increases and this effect continues for concentrations as high as 50 g./l. These differences between chromium hexacarbonyl and the well known ignition promoters suggest that the mode of action of the hexacarbonyl is different from that of other pro-knocks.

Any theory of the mode of action of chromium hexacarbonyl as a fuel additive must explain the following apparently anomalous facts:-

1) Chromium hexacarbonyl raises the S.I.T. of an average hydrocarbon fuel but in engine tests it is found to lower the H.U.C.R.

2) Chromium hexacarbonyl raises the S.I.T. of Pool Petrol,

n-heptane, iso-octane, and Refined Straight Run Spirit
but lowers the S.I.T. of benzene.

3) In contrast to its behavior in other fuels the effect of
chromium hexacarbonyl is to raise the H.U.C.R. of benzene.

There is a simple and reasonable explanation of
Fact 3.   It has been established that the effect of chromium
hexacarbonyl in benzene is to inhibit or delay pre-ignition.
Although the hexacarbonyl raises the H.U.C.R. of benzene it is
not exerting a true anti-knock effect.   The mode of action
of the hexacarbonyl in inhibiting pre-ignition is of interest.
In Section V of this thesis there is a description of the
effect on engine deposits of the presence of chromium
hexacarbonyl in a fuel.   After running an engine for some time
with a fuel containing a fairly high concentration of chromium
hexacarbonyl deposits of green chromium sesquioxide were
observed around the exhaust valve and sparking plug.   These
are the very points at which pre-ignition normally takes place[73]
(   ) and it seems likely that the deposit is either hindering
the development of hot spots or preventing them from pre-
igniting the charge.

The other two facts referred to on page 110 are not
so easily explained, and any explanation would depend largely
on the particular theory of the cause of knock on which it was
based.   A great many theories have been advanced to explain
the phenomenon of knock.   Many of the older theories have
been discarded and until recently almost all workers on the
subject accepted the "Chain Reaction Theory" reviewed by

Egerton[18], and Beatty & Edgar[20] in 1938.   There are many
minor differences between workers regarding the details
of the theory but the basic ideas of all are similar.
In 1947, however, R.O. King[19] commenced publication of a
series of papers which postulated a completely different
theory of knock.

The two theories are completely different and in
many respects contradictory and the author has not found it
possible to postulate any one theory of the mode of action of
chromium hexacarbonyl which is in accord with both theories.
The behaviour of the compound, can, however, be accounted for on
the basis of either theory, the two explanations being
completely different.   Both explanations are, therefore, given
in turn:-

1) The Mode of Action of Chromium Hexacarbonyl as a Fuel
    Additive Based on the Chain-Reaction Theory of Knock.

A brief summary of the Chain-Reaction Theory has
already been given in the introduction to this thesis (p. 4).
Since chromium hexacarbonyl has an appreciable pro-knock
property at very low concentrations this can only be due to
some effect whereby it increases the rate of propagation of
chain reactions.   It is easy to understand how the established
ignition promoters such as amyl nitrate could have this effect
since these compounds contain chemically active oxygen[74]
which could initiate reaction chains, either directly or via the
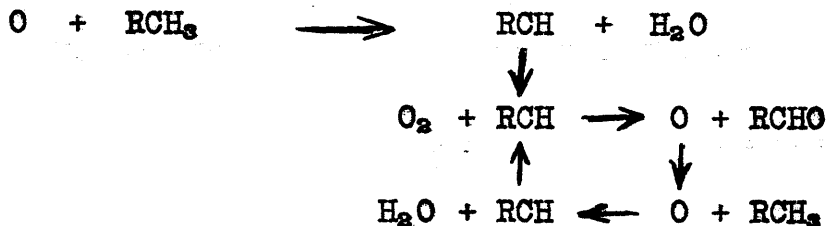formation of peroxides.   It is difficult to see how chromium

hexacarbonyl could act in this way as it does not seem
likely that oxygen could readily be evolved from the compound.

According to Egerton & Gates, and to Egerton[75] himself
metals which form organometallic compounds are capable of
forming two oxides which are in equilibrium under the conditions
of temperature and pressure normally experienced in an engine
cylinder. It is suggested that the active anti-knock agent
is formed by the decomposition of the original compound and
the formation of a metallic oxide in an especially active
finely divided form. The higher oxide of the metal could be
reduced to the lower one, thereby oxidising an intermediate
organic product which would otherwise give rise to detonation.
On next meeting an oxygen molecule the now lower metallic oxide
is reconverted to the higher form. This oxide can then
deactivate another intermediate organic product (eg. a peroxide)
and again be regenerated by contact with oxygen. This process
can continue in such a way that a single metallic oxide
molecule can deactivate a great many "chain carrier" molecules.

Chromium forms no fewer than four oxides[76], chromium
monoxide (CrO), chromium sesquioxide (Cr_2O_3), chromium trioxide
(CrO_3), and chromium peroxide (CrO_4). It is possible that
the repeated conversion of one chromium oxide into another and
back to the original might be causing the pro-knock effect of
the compound. In view of the fact that chromium hexacarbonyl
has a pro-knock and not an anti-knock effect in an engine it
would be necessary to assume that the chromium transferred

oxygen in such a way as to encourage the propagation of the
chain reaction rather than to interfere with it. The
chromium oxides could do this by themselves acting as chain
carriers. Alternatively, they might act by initiating a
chain reaction in the manner suggested by Norrish[77].

$$O + RCH_3 \longrightarrow RCH + H_2O$$
$$\downarrow$$
$$O_2 + RCH \longrightarrow O + RCHO$$
$$\uparrow \qquad \downarrow$$
$$H_2O + RCH \longleftarrow O + RCH_3$$

The active oxygen atom in Norrish's scheme could be supplied
by the reduction of one oxide of chromium to a lower one.

eg. $Cr_2O_3 \longrightarrow 2CrO + O$

The anomalous behaviour of chromium hexacarbonyl as regards
H.U.C.R. and S.I.T. tests can be explained by assuming that
the conditions in the two types of test favour equilibrium
between different pairs of chromium oxides. The equilibrium
between one pair of oxides might occur at lower temperatures
and the properties of the oxides and the conditions of the
test might be such that an anti-oxidant effect similar to that
of anti-knock compounds would be encountered. This would explain
the fact that chromium hexacarbonyl and anti-knock compounds
have similar effects on S.I.T.s. At the higher temperatures
and pressures prevailing in an engine combustion chamber the
equilibrium might be between a different pair of chromium
oxides (Only one oxide need by different). The second pair
of oxides might act in such a way as to produce a pro-knock

effect.

The fact that chromium hexacarbonyl lowers the S.I.T. of benzene although it raises the S.I.T. of other fuels would, on the basis of the above theory, be due to the higher S.I.T. of benzene causing a change in the pair of chromium oxides in equilibrium.

The unusual behaviour of chromium hexacarbonyl in engine fuels is thus attributed indirectly to the polyvalent characteristics of chromium and the fact that no other metallic compounds have been found to behave in the same way may be due to the fact that few metals are capable of existing in so many valency states.   It is of interest to note that some nitrogen compounds (e.g. amines) are anti-knock while others (e.g. nitrates and nitrites) are pro-knocks.   Nitrogen is also polyvalent.

The theory does not explain why such a low concentration (0.02 g./l.) is effective nor why further increase in concentration has little additional effect.   Anti-knock compounds and other pro-knock compounds continue to give increasing effect at concentrations a hundred times greater than 0.02 g./l.   The reason may, of course, be simply that the inherent pro-knock potency of chromium is very small but that the metal is sufficiently active to exhibit that property even at very low concentrations.

2)   The Mode of Action of Chromium Hexacarbonyl as a Fuel Additive based on King's Theory of Knock.

A brief summary of King's theory has already been

given in the introduction to this thesis (p. 5).

The series of papers being published by King has not yet dealt fully with the mode of action of pro-knock compounds, the only ones studied being those which counteract the effect of anti-knock compounds rather than those which have an effect on undoped fuel[78]. The chemical composition of chromium hexacarbonyl is, however, more akin to the metallic anti-knock compounds such as iron pentacarbonyl than to the typical pro-knock compounds such as amyl nitrate. It, therefore, seems likely that its mode of action is similar, though opposite in effect, to that of organometallic anti-knock compounds.

King maintains that organometallic anti-knock compounds act by the continusus deposition of a film of the metal of the dope on the combustion chamber surface. This film of metal catalyses the very rapid pre-flame oxidation of some of the fuel hydrocarbons direct to steam and carbon dioxide at temperatures above 500°C.

It has been shown[79] that steam considerably reduces inflammability and that, if dilution of the end gas by steam is sufficient, self ignition ahead of the flame cannot occur and combustion will be completed in the normal course without detonation. In the absence of an anti-knock agent hydrocarbons tend to oxidise first to aldehydes and carbon monoxide, neither of which possess the anti-knock properties of steam and carbon dioxide. At temperatures under about 500°C. (The exact temperature refers to n-pentane as fuel) the rapid formation

of aldehydes and carbon monoxide leads to the more rapid oxidation of the fuel than when dope is present. The effect of anti-knock compounds is therefore to retard oxidation at low temperatures and to promote it at higher temperatures.

If it is assumed that the mode of action of chromium hexacarbonyl is similar to that of anti-knock additives such as lead tetraethyl and iron pentacarbonyl the compound would act by the continuous deposition of a layer of chromium on the combustion chamber walls. Since chromium hexacarbonyl is a pro-knock it can be assumed that chromium is a negative catalyst in the oxidation of hydrocarbons direct to steam and carbon dioxide.

It is more difficult to explain the anomalous S.I.T. results on the basis of King's theory. King does not specifically mention S.I.T. determinations in his criticisms of previous work but confines his comments to the related subject of flow and bulb methods of studying the combustion of fuel vapours. The fact that anti-knock agents raise S.I.T.s and thus appear to exert an anti-oxidant effect need not conflict with King's theory since S.I.T. determinations are performed under conditions of temperature and pressure vastly different from those encountered in an engine combustion chamber.

It has, however, been found that all anti-knock compounds raise the S.I.T.s of hydrocarbon fuels and if King's conception of anti-knock action is correct his theory should

account for this. King studied the rate of oxidation of doped and undoped pentane in a special type of reaction chamber[80] designed in order to ensure that the fuel-air mixture being tested remained in the chamber for only a second or so. Figure 45 is reproduced from King's work[81]. It shows that in the lower temperature regions the effect of the anti-knock dope was to lower the rate of oxidation (i.e. anti-oxidant) while at temperatues over 500°C. the rate was increased. King has shown that the relatively high oxidation rate obtained with undoped pentane at lower temperatures (330 - 500°C.) is due to the formation of aldehydes and carbon monoxide. The part of the graph corresponding to this is referred to by King as the "aldehyde hump". King has obtained similar results with lead tetraethyl as the dope and n-hexane as the fuel thus showing the effect to be general.

Since S.I.T. determinations are usually performed at temperatures under 500°C., this will correspond to the aldehyde hump and the anti-knock compounds will exert an anti-oxidant effect. This is consistent with the effect of anti-knock compounds on S.I.T.s. The temperature of 500°C. refers to n̄-pentane, and it must not be assumed that the reversal of effect observed by King takes place at this temperature for every fuel.
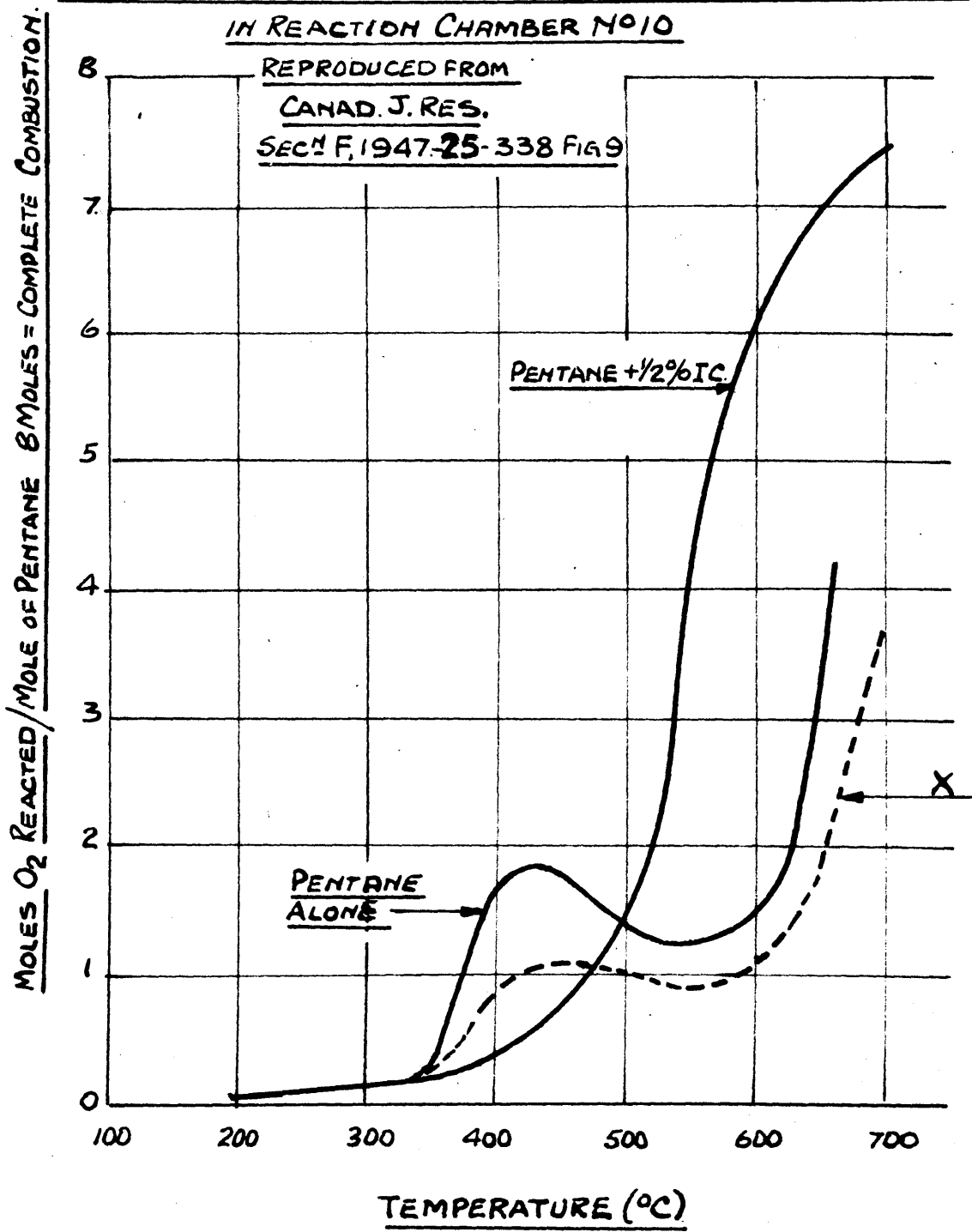
If the effect of chromium hexacarbonyl were that of a negative catalyst exactly opposite in character to iron pentacarbonyl it would be expected that the compound would increase the aldehyde hump and therefore lower the S.I.T. of

a fuel. Chromium hexacarbonyl, however, raises the S.I.T. of many fuels. It is possible that chromium hexacarbonyl is a negative catalyst over the entire temperature range. This would imply that it reduced the aldehyde hump and also reduced the rate of direct oxidation to steam and carbon dioxide which occurs at higher temperatures. The approximate position of the curve for pentane doped with chromium hexacarbonyl would then be as shown by curve X in Figure 45. (This curve is, of course, inserted by the author and is not reproduced from King's work). The reduction of the rate of oxidation at lower temperatures would explain the raising of S.I.T.s. caused by the hexacarbonyl and the reduction of the oxidation rate at higher temperatures would account for the pro-knock effect since on King's theory anti-knock agents operate by promoting oxidation at high temperatures.

The theory just described could account for the low concentration of chromium hexacarbonyl necessary to produce maximum pro-knock effect. Presumably a concentration of 0.02 g./l. was sufficient to give an almost overall thin film of metallic chromium on the combustion chamber walls of the Ricardo E6, and subsequent raising of the concentration would merely increase the thickness of the film rather than its active surface area. The low concentration of chromium necessary to produce the film would imply that chromium was more efficient in film formation than metals like iron or lead. In view of the use of chromium for plating this is not improbable. The relatively slight nature of the maximum

FIGURE 45

THE EFFECT OF IRON CARBONYL ON THE OXIDATION OF PENTANE IN REACTION CHAMBER No 10

REPRODUCED FROM
CANAD. J. RES.
SEC^n F, 1947. 25. 338 FIG 9

PENTANE + 1/2% IC.

PENTANE ALONE

X

MOLES O₂ REACTED/MOLE OF PENTANE   8 MOLES = COMPLETE COMBUSTION

TEMPERATURE (°C)

pro-knock effect is presumably due to the relatively small inherent catalytic property of the metal in this reaction.

The theory does not account for the effect of chromium hexacarbonyl on the S.I.T. of benzene. If the hexacarbonyl is exerting an anti-oxidant effect at all temperatures it would be expected to raise the S.I.T. of benzene. It is, of course, possible that under the high temperature of the benzene S.I.T. tests the chromium hexacarbonyl is itself decomposing explosively thus igniting the benzene. In view of the fact that chromium hexacarbonyl alone explodes spontaneously at 210°C. in presence of air the above explanation is by no means impossible. It is noteworthy that a concentration as high as 6 g./l. chromium hexacarbonyl was used in the benzene S.I.T. tests.

It is thus possible to account for the behaviour of the hexacarbonyl on the basis of either the Chain-Reaction Theory of Knock or the more recent theory of R.O. King. The chain-reaction theory provides no explanation of the low concentration of chromium hexacarbonyl required for maximum pro-knock effect but King's theory is less convincing in the explanation of S.I.T. behavior.

Conclusions - Section 111.

1) Chromium hexacarbonyl raises the S.I.T. of most hydrocarbon fuels thus exhibiting an anti-oxidant effect.

2) Chromium hexacarbonyl lowers the H.U.C.R. of most hydrocarbon fuels thus exhibiting a pro-knock effect. The concentration of hexacarbonyl required to produce the pro-

knock effect is surprisingly small compared with that
required by other petroleum additives to produce comparable
effects.   A concentration of 0.02 g./l. is sufficient to
produce almost the maximum pro-knock effect and further
increases in concentration cause very little alteration in
the magnitude of the effect.   The maximum pro-knock effect
is not very great, being equivalent to a reduction of 0.5
in the H.U.C.R. of Pool Petrol. (This is equivalent to a
decrease of 5 octane numbers in the knock rating of the fuel.).

    At low concentrations the value of the aniline
coefficient of chromium hexacarbonyl is - 350. i.e. It requires
350 moles of aniline to counteract the effect of 1 mole of
chromium hexacarbonyl.

    3)   As would be expected from its behaviour in spark-
ignition engine fuels chromium hexacarbonyl acts as an
ignition promoter when added to Diesel fuels.   It raises the
cetane number of Pool Gas Oil by approximately 3.   This effect
is achieved at very low concentrations of the hexacarbonyl
and increase in concentration does not appreciably alter the
magnitude of the effect.   The use of the compound as an
ignition promoter is therefore limited to fuels in which a very
small increase in cetane number is required.

    4)   In contrast to its behavior in other hydrocarbons
chromium hexacarbonyl lowers the S.I.T. of benzene.

    5)   Chromium hexacarbonyl inhibits the pre-ignition
normally encountered when benzene is used as a spark-ignition

engine fuel at high compression ratios.   The H.U.C.R. of benzene is raised by more than 1.0 units to the remarkably high value of 15.6.

6)   The anomalous anti and pro-oxidant effects of chromium hexacarbonyl in S.I.T. and H.U.C.R. tests respectively can be explained on the basis of either the classical chain-reaction theory or the more recent theory propounded by R.O. King.   On the chain-reaction theory the unusual behaviour could be due to the polyvalent character of chromium and on King's theory the explanation could be the existence of a negative catalytic effect caused by a film of chromium metal. Details are given in Section 111, Sub-Section E.

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COMPOUNDS OF CHROMIUM OTHER THAN CHROMIUM HEXACARB...

As the title of this thesis implies it was not
originally intended to confine the work to a study of ... ...
hexacarbonyl. It was originally hoped that organo-chr... ...
compound generally could be studied. ... ... of th...
various literature, however, revealed that organometall...
compound of chromium were too unstable to be used as ... ...
additives.

The reasons for selecting chromium hexacarbo... ...
subsequent testing have already been outlined in the ... ...
to tell these (SECTION IV) other stable compound...
containing a direct carbon-to-carbon linkage which a...
mentioned in the literature are compounds such as dit...
cyclopentadienyl tripyridine which are really derivatives of
hexacarbonyl. In view of the fact that use of the...
compounds would involve the preparation of chromium he...
as an intermediate with the consequent lowering of th...
yield, it was decided to perform the reduction tests on
hexacarbonyl itself. Almost every article on the subje...
organo-metallic petroleum additives say... ... the pro... ...
... effect of these compounds is dependent upon the m...
atom rather than the radicle to which it is attached an...

SECTION IV.

COMPOUNDS OF CHROMIUM OTHER THAN CHROMIUM HEXACARBONYL.

As the title of this thesis implies it was not originally intended to confine the work to a study of chromium hexacarbonyl. It was originally hoped that organo-chromium compounds generally could be studied. A review of the relevant literature, however, revealed that organometallic compounds of chromium were too unstable to be used as petroleum additives.

The reasons for selecting chromium hexacarbonyl for subsequent testing have already been outlined in the introduction to this thesis (p.14). The only other stable compounds containing a direct chromium-to-carbon linkage which are mentioned in the literature are compounds such as chromium tricarbonyl tripyridine which are really derivatives of chromium hexacarbonyl. In view of the fact that the use of these compounds would involve the preparation of chromium hexacarbonyl as an intermediate with the consequent lowering of the final yield, it was decided to perform the combustion tests on the hexacarbonyl itself. Almost every worker on the subject of organometallic petroleum additives agrees that the pro or anti-knock effect of these compounds is dependent upon the metallic atom rather than the radicle to which it is attached and it seemed pointless to prepare complicated derivatives of chromium hexacarbonyl when the compound itself was likely to exhibit similar properties as a fuel additive.

This section is perhaps a convenient point for explaining the reason for the exact title of the thesis. There are two reasons for the use of the phrase "compounds containing a direct chromium-carbon linkage" rather than "organo-chromium compounds". Firstly, metallic carbonyls are not always regarded as true organic compounds although they contain carbon, and secondly, the title excludes from the scope of the work chromium salts of organic acids. This type of compound has proved to be without effect on the knocking properties of fuels. Even lead compounds of this sort are ineffective, lead tetrastearate and lead tetraacetate[82] having no effect on the knocking characteristics of fuels. No attempt was therefore made to investigate compounds of this type.

Chromic cyanide ($Cr(CN)_3$) is known to be insoluble in most aqueous solvents and this suggested the possibility that the chromium-carbon bond might have sufficient non-polar characteristics to permit the compound to dissolve in non polar solvents such as hydrocarbons. Chromic cyanide was accordingly prepared by precipitation from concentrated solutions of potassium cyanide (KCN) and hydrated chromic chloride ($CrCl_3 . 6H_2O$), the potassium cyanide being in excess. The green blue chromic cyanide was filtered and dried at 300°C. in an inert atmosphere. The compound proved to be completely insoluble in non-polar solvents so its use as a fuel additive was not possible.

Conclusions - Section IV.

Chromium hexacarbonyl is the most suitable chromium

compound for testing as a fuel additive.

SECTION V

HEXACARBONYL AS A FUEL ADDITIVE.

One of the prin... objections to the use of
metallic anti-knock compo... ... ...n their deleterious
effects on the engine. ... ...concerned are ...
corrosion, and erosion. ... ...tetraethyl was first
as an anti-knock additi... ... ...was found that t
valves deteriorated afte... ... ...hours at ...
due to the deposition o... ... ...
of the valves. With ...
were encountered and in this ...
the cylinder sides **SECTION V.** ... ...
To affect the effects of ... ...
of ethylene dichloride, ...added to
fuel in order to remove the ... ...ly vola
bromide or chloride. A large ... ...gen compoun
however, be harmful to the engin... ... ...ated haloge
may cause corrosion.

Before using chromium ... ...doped fuels
... knock No 86 engine it was con... ...dvisable to tes
whether the corrosion, erosion an... ...ection effects of
compound were sufficiently serious to damage the engine.
... therefore decided ... ...

SECTION V.

ENGINE DEPOSITS CAUSED BY THE USE OF CHROMIUM HEXACARBONYL AS A FUEL ADDITIVE.

One of the principal objections to the use of metallic anti-knock compounds has been their deleterious effects on the engine. The effects concerned are deposition, corrosion, and erosion. When lead tetraethyl was first used as an anti-knock additive to petrol it was found that the valves deteriorated after several hundred hours of running due to the deposition of lead and lead oxides on the faces of the valves. With iron carbonyl similar deposition effects were encountered and in this case the valves were eroded and the cylinder sides scored by iron and iron oxide particles. To offset the effects of lead tetraethyl on the engine a mixture of ethylene dichloride and ethylene dibromide was added to the fuel in order to remove the lead as its relatively volatile bromide or chloride. A large excess of halogen compounds may, however, be harmful to the engine since liberated halogen acid may cause corrosion.

Before using chromium hexacarbonyl doped fuels in the Ricardo E6 engine it was considered advisable to test whether the corrosion, erosion and deposition effects of the compound were sufficiently serious to damage the engine. It was therefore decided to carry out a series of tests on a model engine working on the same principles as the larger internal combustion engine. The engine selected for this

purpose was the "C.I. Special" manufactured by Messrs. J. & G. Jensen of Jersey.   This engine is a four-stroke, 10 c.c., O.H.V. engine suitable for running on Pool Petrol. It follows motor cycle practice, being made of the same or similar materials. "Clearances" are sealed down in proportion to the reduced size of the engine.

1) Engine Tests to Determine the Extent of Corrosion, Erosion and Deposition Effects.

A series of tests were performed on the "C.I. Special" engine using pool petrol doped with varying concentrations of chromium hexacarbonyl.   After each test the engine was stripped and the cylinder head, valves, and cylinder walls examined.   It was found that at concentrations of chromium hexacarbonyl under 0.5 g./l. there were no noticeable effects on the engine even after four hours running.   At concentrations of 1 g./l. and over small green deposits were observed on the sparking plug and exhaust valve when the engine was run for periods over 30 minutes.   These deposits consisted of chromium sesquioxide presumably formed by oxidation of the hexacarbonyl:-

$$4 \; Cr(CO)_6 \; + \; 15 \; O_2 \longrightarrow 2 \; Cr_2O_3 \; + \; 24 \; CO_2 .$$
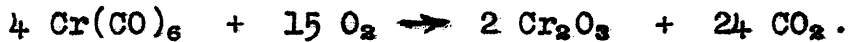
A 500 cc. Pool Petrol sample containing 3 g./l. chromium hexacarbonyl (saturation concentration) was used in an engine test.   The engine was run at 2,500 r.p.m. under light load.   Under these conditions the C.I. Special consumed the fuel in five hours.   Examination of the engine after the tests revealed fairly heavy deposits of chromium sesquioxide on the valves, cylinder head and plug, the deposits on and

around the exhaust valve being particularly heavy.   The
valves, cylinder head, and sparking plug were weighed before
and after the test.   Despite the fact that 1.5 g. chromium
hexacarbonyl (equivalent to approximately 1 g. Cr_2O_3) had
been burned in the engine the increase in weight due to
deposits was only 0.05 g.   The deposits were by no means
wholly composed of chromium sesquioxide, considerable quantities
of soot being deposited in the path of the exhaust gases.
This test showed that at least 95% of the chromium was being
carried out of the engine in the exhaust.   After cleaning
off the deposits the valves, cylinder head, and plug were
re-weighed and found to have returned to their original weight.
There was no visible sign of damage to the engine.

The above results were taken as indicating that
chromium hexacarbonyl doped fuels could be used in a full size
engine without appreciable risk of damage to the engine.

2) Attempts to Prevent Deposition of Sesquioxide.

One of the difficulties in studying deposition was
to devise an accurate method of measuring the amount of
sesquioxide deposited.   The weighing of the parts of the engine
on which deposition occurred was not wholly satisfactory since
much of the deposit consisted of carbon.   The method adopted
was to weigh the exhaust valve before and after tests but
it was established from tests on undoped fuel that the weight
of carbon deposited varied considerably from one test to
another ($\underline{v}$. Table XVll.)

Since chromic chloride and chromic bromide are

Table XVll.

The Effect of Ethylene Dibromide on Engine Deposits.

Engine used ... "C.I. Special"

Fuel used ... Pool Petrol

Vol. of fuel used per test = 100 cc.

Nature and Concn. of Fuel Additive.	Increase in weight of exhaust valve (g.)	Average increase in weight of exhaust valve. (g.)
Nil.	0.0012	
"	0.0012	
"	0.0002	0.0007
"	0.0006	
"	0.0009	
"	0.0000	
3 g./1. $Cr(CO)_6$	0.0020	
	0.0014	0.0020
	0.0024	
	0.0021	
3 g./1. $Cr(CO)_6$ 5 g./1. $C_2H_4Br_2$	0.0012	
	0.0017	0.0011
	0.0004	
	0.0012	

relatively volatile ($CrCl_3$ sublimes at 1065°C.) it was decided to add ethylene dibromide and ethylene dichloride to the doped fuel with a view to removing the chromium from the engine in the form of chloride or bromide.   Both compounds were added in slight excess of the amount required to convert all the chromium in the fuel to the halide.   Visual examination of deposits after the tests indicated that both compounds reduced the deposits considerably although neither compound eliminated them.   An attempt was made to perform rough quantitative tests with ethylene dibromide, the results being given in Table XVll.

The results in Table XVll indicate that ethylene dibromide is almost certainly reducing deposition though it is not possible to draw quantitative conclusions from the results.

Conclusions - Section V.

The presence of chromium hexacarbonyl in a fuel causes little appreciable deposition in the engine until the concentration of hexacarbonyl is greater than 0.5 g./l.   At higher concentrations chromium hexacarbonyl causes appreciable engine deposits after several hours running.   These deposits can be reduced but not eliminated by the addition of ethylene dibromide or ethylene dichloride to the doped fuel.   Chromium hexacarbonyl does not appear to cause any excessive corrosion or erosion effects on the engine.

----------oOo--------

A brief description of the engine with some detailed drawings has been given by Ricardo & Clyde[ ]. The more detailed description known to the author is supplied with each engine by the manufacturers (Messrs. Engineers (1927) Ltd.).

The engine can be run either as a petrol or a with interchanging the cylinder head and by altering similar adjustment to a universal piston engine with a sleeve type poppet valve, controlled by the actual speed range

APPENDIX I

compression ratio in the diesel retained as varied from in the diesel engine usually fixed.

In the petrol engine the combustion chamber is at all stages, the one side formed by the flat of the cylinder head and the other. This gives a very chamber of good anti-knock qualities and also chamber having the same general form as the required. The sparking plug is situated at combustion chamber, between the valves. That is

APPENDIX I.

THE RICARDO E6/S VARIABLE COMPRESSION ENGINE.

A brief description of the engine with reasonably detailed drawings has been given by Ricardo & Glyde[88]. The only more detailed description known to the author is the Report supplied with each engine by the manufacturers (Messrs. Ricardo & Co., Engineers (1927) Ltd.).

The engine can be run either as a petrol or a Diesel unit by interchanging the cylinder head and by alternatively fitting a magneto or a fuel pump to a universal platform. The engine is of the single cylinder, poppet valve, four-stroke type, having a bore of 3 in. and a stroke of 4.3/8 in. The normal speed range of the engine is 1000 - 3000 r.p.m. The compression ratio in the petrol version can be varied between 4.5 and 20; in the Diesel version it is usually fixed at about 20.

In the petrol version the combustion chamber is cylindrical in shape, the ends being formed by the flat surfaces of the cylinder head and the piston. This gives a very compact combustion chamber of good anti-knock qualities and also ensures that the chamber retains the same general form as the compression ratio is varied. The sparking plug is situated at the side of the combustion chamber, between the valves. Thus maximum flame travel is affected very little by change of compression ratio. A similar hole on the other side of the combustion chamber enables a pressure recording instrument to be fitted.

In the Diesel version, a head having a Ricardo Comet Mk 11 Compression Swirl combustion chamber is fitted. The fuel is injected into the Comet chamber via a pintle type nozzle, and the organised swirl of the air in the combustion chamber ensures that there is maximum contact between the fuel particles and the air and therefore maximum utilisation of the air supplied.

The cylinder, which is cast iron, is fitted with a hardened high-phosphorus cast iron liner. The cylinder may be raised or lowered relative to the crankshaft, thus enabling the compression ratio to be varied while the engine is running. The movement of the cylinder is measured by a micrometer and the compression ratio can be obtained from a calibration graph supplied by the makers.

The lubricating system is of the wet sump type, the oil being circulated by an externally driven pump. An electric oil heater is provided in the crank case for the purpose of shortening the period required for the oil to reach the desired temperature. An oil-water heat exchanger enables the temperature of the oil to be controlled at any value desired. A filter ensures that only clean oil is delivered to the bearings.

The valves, one inlet and one exhaust, are operated by an overhead camshaft driven from the crankshaft through two pairs of bevel gears.

The magnete, in the petrol version, and the fuel pump in the Diesel version, are driven from the end of the

camshaft.   The timing of ignition or injection can be varied whilst the engine is running.

The carburettor is fitted with a **variable main jet**, consisting of a taper needle valve which permits the mixture strength to be varied between wide limits during operation. In the petrol version an electric air heater is fitted which permits air inlet temperatures 40°C. above room temperature to be attained while the engine is running at 2500 r.p.m. This extra heat is sufficient to enable most fuels to be vapourised completely before passing into the engine, and approximately represents the induction heating furnished by the "hot spot" of a road vehicle engine.

In both petrol and Diesel versions liberal cooling areas are provided in the cylinder head and barrel.   The circulation of water is by a centrifugal pump of large capacity driven off the same motor that drives the oil pump.   The high rate of circulation ensures a uniform temperature distribution in the head and this temperature can be controlled at any desired value by adjustment of a cooler.

Description of Test Equipment.

The engine is coupled to a swinging field electric dynamometer of sufficient capacity to absorb the maximum power produced by the engine at all normal speeds.   Simple switch gear enables the dynamometer to be operated as a motor to start or motor the engine.   The engine torque is measured by the usual counteracting weight and spring balance system;

the balance is capable of being read to the nearest 0.01 lb.
The radius of the torque arm is 18-in.   Five weights of 5
lb. each are supplied. The spring balance is mounted on a
davit arm and reads up to 7 lb.   From these constants and
the dimensions of the bore and stroke of the engine the
following equations exist:-

$$\text{B.M.E.P.} = 7.31\ W\ \text{lb./sq.in.}$$

$$\text{B.H.P.} = \frac{W \times \text{R.P.M.}}{3500}$$

where W = nett weight on torque arm in pounds.

A bank of resistance grids having a negligible
temperature coefficient of resistance absorbs the energy
developed by the dynamometer.   A series of knife switches
enables the amount of resistance in the armature circuit to be
varied thus varying the load on the engine.   Two rheostats,
one coarse and one fine, enable the field current to be altered
within fine limits thus providing a further control of the load.

The fuel measuring apparatus consists of a two
gallon tank for the main supply, a quart tank for fuel samples
and a flow-meter equipped with the necessary cocks to enable
the change over from one fuel to another to be made rapidly.
The fuel flow is measured by noting the time taken for 50 or
100 cc. of fuel to be consumed by the engine.

A tachometer driven from the dynamometer shaft and
located in a position convenient to the observer is provided
for speed measurement.

Method of Determining H.U.C.R.s.

In determining the H.U.C.R. of a fuel, a sample of the fuel to be tested is added to the sample tank, the main supply tank being filled with Pool Petrol. The oil heater and oil circulation pump are switched on about an hour before the start of the test in order that the oil may be at a suitable temperature during the test. At the start of the test the fuel cocks are adjusted so that the engine will run on fuel from the main supply tank. The engine is started and the controls adjusted until the engine is running at 2500 r.p.m. under full throttle. The engine is maintained at this speed throughout the test by appropriate alteration of the load. The engine is allowed to run until the oil and water temperatures are 150°F. During all engine tests the cooling water temperature was maintained at 155 $\pm$ 5°C. and the oil temperature at 150 $\pm$ 5°C.

When the oil and water temperatures have reached the desired value the fuel cocks are changed so that the engine draws fuel from the sample tank, the load is readjusted to maintain the speed at 2500 r.p.m. and the compression ratio is raised until knock becomes audible. The fuel flow is then varied until the mixture strength giving maximum intensity of detonation is obtained. At this mixture the compression ratio is lowered to a value just below that at which detonation is audible. A number of power readings are then taken at small increments of compression ratio. As the ratio is increased

the power output and intensity of detonation increase. When
the detonation exceeds a certain intensity the power output
ceases to rise and, if the compression ratio is raised beyond
this point, a fall in power will occur.   The readings are
plotted as shown in Figure 20 and the H.U.C.R. is indicated
by the peak of the curve.   At each point the ignition timing
is varied to obtain maximum power.   This ignition timing
is obtained from a graph of compression ratio against ignition
advance supplied by the engine manufacturers.

Method of Determining Ignition-lags.

When using the compression ignition version of the
engine to obtain ignition-lags from indicator cards the
cooling water temperature was maintained at $150 \pm 5°C$. and the
oil temperature at $140 \pm 5°C$.   Details of the method are
given in the text of the thesis.

— — — — — — — —

	Refined Straight Run Spirit		Coal Tar Spirit 327	
S.G. at 20°c.	0.7016			
	23		78	
	43		85	25
			90	32
	78		65	128
	73	73	73	
	83	43	94	234
	98	47	104	271
	105	104	110	293
	114	114	112	307
	121		129	327
	132	145	143	252
F.B.P. (°c.)	160	173	170	370
Total Distillate	98%	98%	95%	98
Residue	1%	1%	1%	2
Loss	1%	1%	1%	0

APPENDIX 11.

BOILING RANGES AND SPECIFIC GRAVITIES OF HETEROGENEOUS FUELS REFERRED TO IN THESIS.

	'Refined Straight' Run Spirit.	'Pool Petrol (A)'	'Pool Petrol (B)'	'Pool Gas Oil'
S.G. at 20°C.	0.7060	0.7321	0.7200	0.8400
I.B.P.(°C.)	39	38	39	198
2% recovered at(°C).	41	47	49	219
5% " " "	52	55	56	229
10% " " "	58	63	63	240
20% " " "	69	73	75	249
30% " " "	79	81	85	258
40% " " "	89	89	94	266
50% " " "	98	97	103	278
60% " " "	105	105	110	290
70% " " "	114	114	118	307
80% " " "	121	127	129	327
90% " " "	132	145	143	352
F.B.P.(°C.)	160	178	170	375
Total Distillate	98%	98%	98%	98%
Residue	1%	1%	1%	2%
Loss	1%	1%	1%	0%

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