A STUDY OF THE EFFECT OF TEMPERATURES BETWEEN 100° C.
AND 250° C. ON THE PHYSICAL AND CHEMICAL
PROPERTIES OF GAS OIL

by

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INTRODUCTION

This study was undertaken in order to determine the cause of the exothermic reaction which had been observed in several oils while being heated from room temperature to the cracking temperature which is about 425° C.

This phenomenon was observed by Hedrick (1) while determining the specific heats of various petroleum fractions. These fractions included gas oil, cracked gas oil, red oil, mineral seal oil, water white distillate, and motor oil. As a result of this exothermic reaction, which adds heat to the oil, the calculated specific heat values were lower between the temperature range from 150° C. to 250° C. than the actual specific heat values.

This reaction was observed while the oil was being heated under constant pressure, as well as when the pressure was allowed to build up autogenously during the heating. When curves of the calculated specific heats are plotted against temperature, a dip appears in the curve in the temperature range from 150° C. to 250° C. This investigation was carried out between these temperatures.

For this investigation, a Kansas virgin gas oil was

selected because it was more easily handled in the equip-
ment and also because the previous investigation had
shown that gas oil was a good representative of the petro-
leum fractions which manifest exothermic reactions. It
was not possible to use the same gas oil in this study as
was used in the specific heat determinations because there
was none of that sample available. However, that did not
prove to be a difficulty since the specific heat data
always showed an exothermic reaction with such oils as gas
oil.

REVIEW OF LITERATURE

A search of the literature has revealed no other
report of an exothermic reaction's being detected during
specific heat determinations on oil other than the thesis
by Hedrick (1). There are two instances in the literature
where exothermic reactions have been reported as occurring
in oil when at the cracking temperature. Nelson (2) re-
ports that occasionally a rise in temperature is observed
in oil while being held in the soaking drum of the crack-
ing process. Weir and Eaton (3), in their determination

of the heat of reaction of cracking, observed in two instances an exothermic reaction at about 650° C. These observations were at cracking temperatures and therefore do not necessarily have any relation to the exothermic reaction which has been detected considerably below the cracking temperature.

Mondain-Monval and Quanquin (4) report that when pentane, hexane, octane, or gasoline are oxidized in the vapor state at 300° C. or slightly lower temperatures with air there were obtained, in addition to the gaseous products, an oily liquid which possessed marked oxidizing properties. When this oil was heated to 200° C., it underwent an exothermic change with the production of a blue luminescence and white fumes. Large quantities of aldehydes, particularly formaldehyde, were formed. This oily liquid was considered to be a mixture of peroxides.

Since this investigation was conducted as a consequence of the results reported by Hedrick (1), a brief review of his paper will be given. In the first part of his work, a bomb calorimeter was used in which the volume was kept constant and the pressure was allowed to increase autogenously within the bomb. Briefly, the apparatus consisted of the following: a 25 cubic centimeter bomb made

of Carpenter's Stainless Steel No. 4 and fitted tightly into a special Dewar flask. The hot junction of one of the thermocouples was placed just outside the bomb and within the Dewar flask. The bomb and Dewar flask, when charged for a run, were placed inside a special insulated steel box which formed an air bath for the bomb and flask. A baffle plate separated the bomb and flask from the heating coils over which a fan drove the air to be heated. The temperature of the air bath was measured by means of a thermocouple fastened to the outside of the Dewar flask. Two water cooled rheostats were used to regulate the temperature of the bath. The heating of the oil in the bomb was a continuous process during which several readings could be taken for the specific heat calculations. The heating coil within the bomb was supplied with electrical energy from large storage batteries. The measurement of this energy was made with the use of a volt box and a Leeds and Northrup type "K" potentiometer. The temperature readings were also taken with the potentiometer.

The time for each run was 60 minutes; that is, the time necessary to heat the oil from room temperature to well within the cracking range. The experimental method consisted in measuring the change of temperature when a

definite amount of electrical energy was put into a known
amount of oil. By subtracting the heat equivalent of the
calorimeter at the mean temperature of the reading from
the recorded electrical input, the specific heat may be
calculated.

That is:

Energy input $=$ $\dfrac{\text{Watts x time in sec.}}{4.182}$ $=$ Calories

Net calories to oil $=$ $\dfrac{\text{Calories}}{t}$ $-$ Heat equiv. of
$^{\circ}C.$
calorimeter $=$ Calories corrected

$\dfrac{\text{Calories corrected}}{\text{Grams of oil}}$ $=$ Specific heat at the mean tem-
perature

The oils used in this first investigation were:

	Sp. Gr. 60° F.	A. P. I.
Gas oil	0.855	34.0
Cracked gas oil	0.9057	24.7
Red oil	0.9229	21.8
Mineral seal (Penn. stock)	0.8275	39.5
W. W. distillate	0.8204	41.0
Motor oil	0.9021	25.4

The results of this investigation showed that with
each of these oils there was an exothermic reaction oc-

curring in the temperature range from 150° C. to 250° C. This is shown by the dip in the curve of Figure 9.

After obtaining the results, it was thought desirable to verify them by conducting the heating in different apparatus and under different conditions. It was therefore decided to heat the oil at constant pressure. A larger bomb was constructed of the same material as the first bomb. This was heated by means of a heating coil on the outside of the bomb. The bomb was placed in a tightly sealed metal container which was kept evacuated by means of a mercury vapor pump. A thermocouple measured the temperature of the oil. A pressure line passed from the top of the bomb through the metal cover to a tee connector into which was fitted the pressure gage and then to a needle valve used in controlling pressures within the bomb. The oil passed from the pressure line into a glass bulb containing mercury which was displaced into a capillary tube. This part of the apparatus was used to record volume changes. The time for each run was about 75 minutes. The method of taking readings and calculating results was the same as used in the first investigation.

The curves plotted from data in this investigation showed that the exothermic reaction does take place at

about the same temperatures as in the first series of
tests. The thermal expansion curves are also sub-normal
indicating that polymerization is taking place. By
measuring the area under the specific heat vs. tempera-
ture curves an approximate value for the amount of heat
liberated may be calculated. They are as follows:

	Calories per gram of oil charged
Gas oil	118
W. W. distillate	93
Mineral seal	177
Red oil	117
Motor oil	80
Cracked gas oil	69

EXPERIMENTAL

Part I

Plate I shows the diagram of the pressure equipment
which was used in the first part of this investigation.
In this equipment, the oil could be heated to any desired
temperature up to well within the cracking range and under

pressures from zero to 900° pounds per square inch gage.
The system was entirely closed and adaptable to the use
of gases other than air above the oil in the reservoir.
A is a glass separatory funnel into which the oil sample
was placed prior to a run. A small glass tube extended
to the bottom of the funnel and was connected by a flex-
ible connection to the intake pipe of the special gear
pump. This pump forced the oil through the heating sec-
tion, B. This section was molybdenum steel rubing 3/16
inch inside diameter, 9/16 inch outside diameter, and 36
inches long designed to withstand high pressures and tem-
peratures. Surrounding this pipe was an electrical heat-
ing coil made of No. 16 nichrome wire and suspended on the
pipe by means of porcelain insulators thus allowing the
coil to heat the pipe by direct radiation. The coil was
insulated from the air by a box made of 85 per cent mag-
nesia brick and lined with mineral wool. The amount of
electrical energy to this coil was controlled by means of
a water cooled rheostat. A thermocouple extending
through the coil and in contact with the pipe measured
the surface temperature. C is the reaction chamber fas-
tened to the end of the heating section. This chamber
was made of Carpenter's Stainless Steel No. 4, 233 cubic

centimeter capacity and capable of withstanding high
pressures. Inserted in this chamber was a thermocouple
well into which a thermocouple was placed to measure the
temperature of the oil. D is the pressure gage for meas-
uring the pressure in the system. E is a water cooled
jacket surrounding the pressure tubing for the purpose
of cooling the oil. After cooling, the oil passed through
the needle valve, F, where the pressure was released.
The oil then discharged back into the funnel where it be-
gan the cycle again.

To make a run, 500 cubic centimeters of the oil
sample was placed in the funnel. If a gas other than air
was to be used, a rubber tube was placed on the outlet of
the funnel and the gas bubbled through the oil until the
air was all flushed from the system at which time the
system was closed. The pump was started and the flows
regulated with the needle valve until the pressure was
steady at 150 pounds per square inch. The flow was 140
cubic centimeters per minute under that pressure. The
heating coil was turned on and regulated in such a manner
that the surface of the pipe was maintained at a constant
predetermined temperature. The temperature in the re-
action chamber immediately began to increase. When the

desired temperature was reached, a sample was taken and
the rheostat adjusted. At intervals of one-half hour
thereafter for any desired period of time, samples were
withdrawn from the bottom of the separatory funnel with-
out interrupting the heating process. If the run was for
a very long period of time, a larger sample was used.
Before each run, the system was thoroughly flushed with
fresh gas oil.

Gases other than air which were used were nitrogen,
ammonia, and carbon dioxide.

This equipment was so constructed that it could be
used for cracking oils. It was originally fitted with a
gas meter for recording the volume of cracking gases
produced, but in these runs no gas was produced and,
therefore, that part of the equipment was not used.

Part II

After a number of samples were secured with the above
apparatus, it was thought desirable to compare these with
oil which had been heated for the same period of time and
temperature but at atmospheric pressure in glass. The
equipment used consisted of a 500 cubic centimeter round

bottom Pyrex flask suspended in a cottonseed oil bath
which was heated with a Bunsen burner. Experience with
this apparatus enabled the operator to control the tem-
perature within a range of ±2 C. The oil in the flask
could be heated at various temperatures up to 250° C. and
for any desired length of time. Various atmospheres,
including air, ammonia, nitrogen, and carbon dioxide,
were used above the oil. These atmospheres were main-
tained both by bubbling gas into the oil throughout the
run and by closing the flask with a stopper after heating
the gas. A few runs were made with various materials in
the flask to determine their catalytic properties. These
were nichrome turnings, copper turnings, copper acetate,
manganese acetate, and resorcinol.

Part III

In this part of the investigation, an attempt was
made to detect the exothermic reaction with the hope of
treating the oil in such a manner that the exothermic re-
action could be eliminated. Thus, a knowledge of the
treatment used would add to our information concerning
this reaction. In order to determine this data, it was

not considered feasible to construct a sensitive bomb
calorimeter such as was used by Hedrick (1). Therefore,
it was decided to construct an apparatus by means of which
temperature vs. time data could be determined. If an
exothermic reaction occurred, a definite curve would be
obtained and if the reaction was eliminated, a change in
the position of the curve should be observed.

Plate II shows the diagram of the apparatus con-
structed for this purpose. A is the outside container
holding the liquid mercury. B is a glass air condenser
for condensing and returning excess mercury to the bath.
The top of this condenser was connected to a bottle partly
filled with water as a safety precaution to prevent any
danger of mercury vapor escaping to the room. C is a
smaller cylinder which fits inside A and furnishes the
surface for the mercury to transfer its heat to the air
bath inside. This part of the equipment thus far described
is a unit by itself and enables the operator to establish
a uniform temperature in the air bath before the oil
sample is inserted. The oil sample (5 cubic centimeters)
is placed in D which is a cylinder smaller than C. D fits
inside C without touching except at the threaded connection
at the top. A thermocouple extends from the top of E

through a small hole in the bottom for a distance of one-half inch. A cement made of litharge and glycerine anchors the thermocouple firmly at the top and bottom of E. The junction therefore is immersed directly in the oil. Also extending through the center of E is a small stirrer made of No. 16 nichrome wire. This stirrer gently agitates the oil sample during heating. The thermocouple is connected to a Leeds and Northrup potentiometer. Temperatures could be measured with an accuracy of $\pm .5^{\circ}$C.

After considerable practice, the following procedure was developed for operating this apparatus. Five cubic centimeters of mercury were placed in A and heated with a Bunsen burner. The burner was regulated until the mercury was condensing steadily at a definite height in the reflux condenser. Five cubic centimeters of oil were placed in D and E containing the thermocouple and the stirrer was inserted in D. This oil must be at a definite temperature before the run. It was found that this could be conveniently obtained by holding D in the hand until the oil had reached body temperature as indicated by the potentiometer reading. With the bath at constant temperature and the sample at a definite temperature, the run could be begun. D was quickly inserted in A, the stop

watch started and the stirrer connected to the stirring
motor by means of a rubber connection. When the watch
read 15 seconds, the stirrer was started. At 30 seconds,
the first potentiometer reading was taken. Thereafter,
a temperature reading was taken every 30 seconds until the
oil had been heated to the desired final temperature. D
was then removed and quickly cooled with cold water. It
was then allowed to reach body temperature and the pro-
cedure repeated. It was believed that successive sets
of data on the same sample of oil would give curves that
would eventually approach a minimum as the reaction con-
tinued to completion.

Figures 5 and 6 are examples of data that were ob-
tained. These curves show that no consistent results
were obtained. It is not known whether this variation is
due to experimental errors or to some peculiar phenomenon
in the oil itself. All that can be said concerning the
results is that no two identical curves were ever obtained.
Insufficient time prevented further work on this appara-
tus.

Part IV

Various physical tests were run on the samples.
Viscosity was determined in a viscosity pipette at 100° F.
The viscosity in centistokes was calculated from the re-
corded time.

Specific gravity was determined at room temperature
(28° C.) using a Westphal balance. Care was taken to use
exactly the same amount of oil in each determination.

The refractive index was determined at 25° C. with an
Abbe refractometer.

The color was measured by means of a Tag-Robinson
colorimeter using a color disk as the standard color for
comparison.

An absorption curve was run on the original oil with
a Bausch and Lomb spectrophotometer. Optical density was
plotted against wave length, Figure 2; a curve was also
plotted from data determined from oil which had been
darkened by heating, Figure 2.

The material in the oil which caused the very dark
color was removed by agitating with two volumes of fuller's
earth to one volume of oil. The fuller's earth was re-

moved by centrifuging. The occluded oil was removed from the fuller's earth by washing with petroleum ether and centrifuging. The washed fuller's earth was then extracted for several hours with benzene in a Soxhlet extraction apparatus. The benzene solution was evaporated and the dark oily material recovered and weighed.

The black precipitate was recovered by decanting off the oil and washing the precipitate with petroleum ether to remove oil. The ether was evaporated and the carbene residue was weighed.

Several chemical tests were used on the samples. It was found desirable to know something of the chemical nature of the gas oil. Because of the very complex nature of petroleum only an approximate idea of its constituents could be determined. The percentage of aromatics and olefins together was determined using the method proposed by Wells and Hedrick (5). Using the method outlined, 50 cubic centimeters of the original gas oil was shaken with 100 cubic centimeters of 91 per cent sulphuric acid for 10 minutes under cold water, two minutes shaking and two minutes between shaking. The oil was allowed to settle; the sludge drawn off. The oil was washed with 10 per cent sodium hydroxide and finally with water. Polymers were

removed by distillation. The distilled oil was treated
with three volumes of 97 per cent sulphuric acid, shaken
for 10 minutes as before under the tap water and then for
five minutes in air. The sludge was drawn off and the
volume of oil recorded. The loss in volume multiplied by
two was the percentage of olefins and aromatics together
in the original sample.

To determine the amount of unsaturates present, the
Francis method (6) with Bacon's (7) modification was used.
Using this method, five cubic centimeters of the oil are
diluted with 10 cubic centimeters of benzene and placed
in a 200 cubic centimeters separatory funnel. Twenty-five
cubic centimeters of 10 per cent sulphuric acid were
added and the mixture shaken. To this mixture was added
.2 cubic centimeter of a .2 normal potassium bromide-po-
tassium bromate solution. When vigorously shaken, bromine
was slowly liberated by the action of the sulphuric acid
on the potassium bromide-potassium bromate solution. If
unsaturated linkages were present, the bromine would be
added. The slow liberation of bromine minimized substi-
tution reactions. A slight excess of potassium bromide-
potassium bromate solution was added as determined by a
trial titration. The titration mixture was shaken for

three minutes with two cubic centimeters of saturated po-
tassium iodide solution. The excess bromine liberated an
equivalent amount of iodine. The free iodine was then
removed by adding one or two cubic centimeters excess of
standard .1 normal sodium thiosulfate. The water layer
was separated and the excess thiosulfate was titrated
with standard iodine solution with starch indicator. The
bromine number which is the number of grams of bromine
absorbed per gram of oil was calculated as follows:

$$N = \frac{.08}{VD} (T_1 N_1 - T_2 N_2 - T_3 N_3)$$

N — Bromine number in grams of bromine per gram of oil

V — Volume of sample

D — Specific gravity of sample

T_1 — Cubic centimeters of potassium bromide-potas-
    sium bromate solution

N_1 — Normality of potassium bromide-potassium
    bromate solution

T_2 — Cubic centimeters of iodine solution

N_2 — Normality of iodine solution

T_3 — Cubic centimeters of sodium thiosulphate
    solution

N_3 — Normality of sodium thiosulphate solution

The gas oil used in this investigation was found to

have practically no unsaturates. Therefore, the results
obtained by the sulphuric acid method for determination of
olefins and aromatics together represents the percentage
of aromatics.

The presence of an oxidizing agent was detected by
means of a solution of potassium iodide in dilute sul-
phuric acid (8). Iodine was found to be liberated and
was titrated with standard sodium thiosulfate. Further
confirmation of the presence of an oxidizing agent was
made by using a solution of ferrous sulfate and ammonium
thiocyanate in an ethanol solution. Vigorous shaking of
this solution with the oil resulted in a red precipitate
being formed as a result of the oxidation of the ferrous
ions to ferric ions by the oxidizing agent in the oil.

By shaking one volume of original oil with two vol-
umes of a five per cent sodium bisulfite solution followed
by two washings with two volumes of 10 per cent sodium
hydroxide and two washings with two volumes of water in a
carbon dioxide atmosphere, it was found that oil so
treated, when heated at 200° C. in a carbon dioxide at-
mosphere, underwent no color change. Such a sample also
gave negative results with the two tests for oxidizing
agents. However, when the treated sample was shaken

vigorously in the air, it again gave positive tests for
the presence of an oxidizing agent.

Total sulfur was determined by the oxygen bomb method.
One gram of oil was burned in an oxygen atmosphere. The
sulfur dioxide was absorbed in water and the sulphurous
acid was oxidized to sulphuric acid by using 10 cubic
centimeters of saturated bromine water and two cubic cen-
timeters concentrated hydrochloric acid. Then 10 cubic
centimeters of 10 per cent barium chloride was added to
precipitate barium sulphate. The precipitate was weighed
and the per cent of sulphur calculated.

DISCUSSION OF RESULTS

Figure 1 shows the curves for color vs. time at
various temperatures for gas oil when heated in the pres-
sure equipment at 150 pounds per square inch pressure.
The color changes from a light red through darker shades
of red to practically a black color. It may be seen that
the curves approach a maximum color change at about
200° C. and that all the curves tend to converge, indicat-
ing that after a certain time of heating, depending upon
the conditions, the color reaches a maximum intensity.

The curves in Figure 1 show that the color change, when using an inert gas, is definite but not as great in degree as when using air which indicates that at least part of the color change is due to oxidation. The heated samples all showed a small amount of brown gum deposited on the sides of the flask after standing. A black, finely divided precipitate is also deposited in the bottom of the flask. This precipitate was separated by decantation and washed with petroleum ether. It was insoluble in petroleum ether and carbon tetrachloride but soluble in benzene and carbon disulfide thus classifying it as carbenes according to Ellis (9). The amount of black precipitate increased as the color became darker. The separatory funnel in the pressure equipment always showed a small amount of water condensed on the sides, after cooling to room temperature, indicating that water was formed during the heating. This was observed when both air and inert gases were used.

Figures 3 and 4 are the curves of color vs. time for the samples of oil heated in glass flasks at atmospheric pressure. They show that oil heated in air undergoes a greater color change than oil heated in an inert atmosphere for the same period of time and at the same

temperature. The samples heated in air reached the same
maximum color change as did the samples heated under
pressure except that it took a much longer time of heat-
ing. For instance, at 150° C. under pressure of 150
pounds per square inch, the maximum color change was
reached in five hours while at 150° C. under atmospheric
pressure, using air above the oil in both cases, the same
maximum color change was reached in 14 hours. It should
be noted here that the difference in color vs. time
curves for the pressure and glass apparatus may be due
to several factors. Although care was taken to prevent,
as far as possible, overheating of the heating tube in
the pressure equipment, it is possible that there may
have been local overheating in the oil film next to the
metal. Another effect which would account for the color's
changing more rapidly in the pressure equipment was the
decrease in the volume of oil during the run caused by
samples being taken thus the remaining oil would recir-
culate more often toward the end of the run. Pressure
may also have accelerated any polymerization reaction.

In the glass apparatus, several materials, including
nichrome shavings, copper turnings, copper acetate,
manganese acetate and resorcinol, were used separately in

in various samples to determine whether or not the change
in color could be accelerated. It was found that none of
these materials caused the color of the oil to change any
more rapidly than when heated alone in the flask. It was
observed, however, in the use of resorcinol that the color
change was decreased somewhat. It is known that phenolic
compounds, such as resorcinol, act as antioxidants. This
was further evidence that the color change was at least
partly due to oxidation.

Figure 2 shows the absorption curves for the origi-
nal oil and for a sample which had been darkened by heat-
ing. There are no characteristic peaks in these curves
and consequently they have no apparent significance ex-
cept to show that the curve was displaced upward by heat-
ing the oil. An interesting observation in connection
with this work was that the Tyndall effect was observed
in the original oil and to a much greater degree in the
heated oil. Oil which had been decolorized with fuller's
earth showed practically no Tyndall effect. This indi-
cated that at least part of the dark coloring matter in
the oil was of colloidal dimensions.

The refractive index did not change to any measurable
extent. Figure 7 shows that the specific gravity has de-

creased slightly up to a color change of about 8.45 and
then has increased slightly.

Figure 8 shows that the viscosity decreased very
slightly in most of the samples. This may have been due
to precipitation of the carbenes and gum.

Figures 5 and 6 are temperature vs. time curves for
the heating of the oil in the apparatus described in
Part III. It may be seen from these curves that in Fig-
ure 5 the curves fall successively below one another as
the heating is repeated on the same sample. However, in
Figure 6 the curves come successively above one another.
These curves are typical examples obtained from many runs
with this apparatus. In no run were any two curves ex-
actly alike, nor were the trend of successive curves
consistent. The causes for these inconsistent results
have not been determined.

Table 10 shows the results obtained from physical
and chemical tests on the gas oil. The analysis for the
black coloring matter in the oil shows 26.43 per cent by
weight. However, this value is undoubtedly too high be-
cause the fuller's earch held a certain amount of the un-
reacted oil which could not all be removed before extrac-
tion. This black coloring matter, because of the Tyndall

effect and its adsorption on fuller's earth, appears to be an oily polymer which is an intermediate step in the formation of the highly polymerized carbenes which are precipitated.

The chemical tests on the oil samples showed that there was an active oxidizing agent in the original gas oil. This oxidizing agent possessed the ability to liberate iodine from a solution of sulphuric acid and potassium iodide and to oxidize ferrous ions to ferric ions. It was found that the reducing agent, sodium bisulfite, removed this oxidizing agent as indicated by the potassium iodide and ferric thiocyanate tests. When this oxidizing agent was removed and the oil heated in an inert atmosphere, there was no color change or precipitate formed. When oil which has been treated with sodium bisulfite is shaken in air, the oxidizing properties are restored. Treatment of the oil with aqueous sodium hydroxide alone did not remove the oxidizing agent. However, the color change was less which may have been due to the removal of acidic compounds. A small amount of soap was formed when the original oil was treated with sodium hydroxide.

The results of this investigation indicated that the observed changes in the gas oil were due to the action of

molecular oxygen from the air with subsequent polymeriza-
tion of oxygenated products. The presence of the active
oxidizing agent in the oil suggested that autoxidation
was the type of oxidation which occurred during the heat-
ing. This was further suggested by the fact that the gas
oil was stable at room temperatures but underwent a
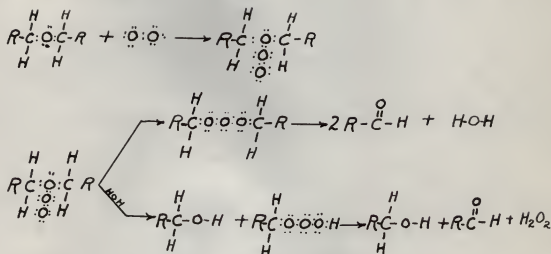change when heated.

By autoxidation is meant, according to Moureu and
Duffraise (10), the combination of the whole molecule of
oxygen with an autoxidizable substance to form a primary
peroxide which may then change in a number of ways to
yield stable oxidation products. The theory proposed by
there investigators assumes that autoxidation starts with
the union of an oxygen molecule, O_2, with a molecule of an
autoxidizable substance, A, to yield the peroxide (AO_2).
Such peroxides are formed with the absorption of energy
and may then decompose to yield various products such as
aldehydes or react with other molecules of the autoxi-
dizable substance. These investigators also suggest that
antioxidants catalyze the reverse reaction, the destruc-
tion of these peroxides.

Milas (11) has proposed a theory by which peroxides
may be formed from saturated compounds. This theory

assumes the addition of molecular oxygen to compounds containing molecular valence electrons comparable to valence electrons in atoms. For ethers, he proposed the following mechanism:

1.

$$R-\overset{H}{\underset{H}{C}}:\overset{..}{\underset{..}{O}}:\overset{H}{\underset{H}{C}}-R \; + \; :\overset{..}{O}:\overset{..}{O}: \; \longrightarrow \; R-\overset{H}{\underset{H}{C}}:\overset{..}{\underset{:\overset{..}{O}:H}{O}}:\overset{H}{\underset{H}{C}}-R$$

$$\longrightarrow R-\overset{H}{\underset{H}{C}}:\overset{..}{O}:\overset{..}{O}:\overset{H}{\underset{H}{C}}-R \longrightarrow 2 R-\overset{O}{C}-H \; + \; H\text{-}O\text{-}H$$

$$R\overset{H}{\underset{H}{C}}:\overset{..}{\underset{:\overset{..}{O}:H}{O}}:\overset{H}{\underset{H}{C}} R \overset{H_2O}{\longrightarrow} R\text{-}\overset{H}{\underset{H}{C}}\text{-}O\text{-}H \; + R\overset{H}{\underset{H}{C}}:\overset{..}{O}:\overset{..}{O}:H \longrightarrow R\overset{H}{\underset{H}{C}}\text{-}O\text{-}H + R\text{-}\overset{O}{C}\text{-}H + H_2O_2$$
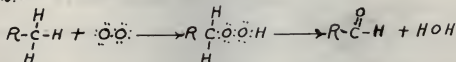
Milas (12) states that the molecular valence electrons are exposed either as a result of excitation or the dissociation of the molecule into free radicals. Whether the final product is an alkyl hydro-peroxide or dialkyl peroxide depends entirely upon the hydrocarbon in question and the strength of the bonds involved.

Stephens (13) states that the reactions of molecular oxygen can be placed in two categories comparable to the addition and substitution reactions of halogens. In both cases, however, the result is addition of oxygen; there-

fore, unsaturation is not necessary for such additions. With saturated molecules, such as paraffins, he proposes the following mechanism for peroxide formation from saturated compounds:

2.

$$R-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}-H + :\overset{..}{O}:\overset{..}{O}: \longrightarrow R\ \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}:\overset{..}{O}:\overset{..}{O}:H \longrightarrow R-\overset{\overset{\textstyle O}{\|}}{C}-H + HOH$$

The theory of autoxidation is of considerable value in explaining the results obtained in this investigation. Although the method used for detecting the exothermic nature of the reaction was not successful in this work, it is known that autoxidation reactions are exothermic, (Mondain-Monval and Quanquin, 4). Also the subsequent polymerization of the oxidized products is an exothermic reaction. The combination of these two types of reactions would account for at least part of the exothermic reaction observed by Hedrick (1). No attempt was made to measure the amount of dissolved oxygen in the oil; however, bubbles were observed to escape when the oil was placed under a vacuum indicating the presence of air which had dissolved during storage. In the work of Hedrick (1), the oil was not de-aerated before heating since the amount of dissolved oxygen was considered to be too small to cause the

observed exothermic reaction. However, in the light of
this investigation, that assumption was not entirely jus-
tified.

As previously discussed, the color vs. time curves
at a definite temperature were shifted upward as the
amount of available oxygen was decreased. Without chem-
ical treatment, the minimum color change was observed when
the oil was ds-aerated and heated in an inert atmosphere.
However, according to the theory of autoxidation, Moureu
and Duffraise (14), there will be a certain amount of
molecular oxygen held in loose combination with autoxi-
dizable molecules which cannot be removed by vacuum. Con-
sequently, one would expect the reaction to take place to
a certain extent even when the oil was de-aerated and
heated in an inert atmosphere, Figure 4. The presence of
this active oxygen was detected by the two tests for an
oxidizing agent which have been described. By treating the
oil with the reducing agent, aqueous sodium bisulfite,
the active oxidizing agent was removed and the color change
prevented when the oil was heated in an inert atmosphere.

Equation 1 suggests that a chain reaction could be
instigated by a small amount of oxygen which forms a perox-
ide which then decomposes to give stable oxidation products

and hydrogen peroxide. The hydrogen peroxide which is produced may then form other peroxides and continue the cycle until all the oxygen is used. The aldehydes which are produced polymerize to form complex molecules such as gum, carbenes, and oily polymers. In the complex mixture of molecules which make up petroleum fractions such a reaction would be possible. Equation 2 shows the mechanism for peroxide formation from saturated compounds which could be aromatic, naphthenic, or paraffin hydrocarbons.

This investigation did not reveal a great deal concerning the type of compounds involved in the reaction. However, a few statements may be made concerning them. It is generally conceded that carbenes are cyclic in structure which indicates that they are formed from aromatic and naphthenic compounds. Paraffin chains attached to ring structures are more easily oxidized than is the ring structure. The oily polymer or coloring matter was extracted with benzene from the fuller's earth whereas it resisted extraction with petroleum ether. This may be some indication that the oily polymer is cyclic in structure. It is probable that there are many types of compounds involved. Further work on these products may

establish their structure more definitely.

It must be emphasized that due to the very complex nature of petroleum fractions no claim can be made that the results of this investigation prove that autoxidation is the only reaction that occurs which could account for an exothermic reaction in the temperature range studied. As suggested by Hedrick (1), the naphthene rings may also be breaking and then polymerizing with the liberation of heat. Future investigators will, no doubt, reveal much additional information concerning the reactions which occur in petroleum fractions when heated.

SUMMARY

Color vs. time curves at various temperatures were determined at 150 pounds per square inch pressure and at atmospheric pressure using the following atmospheres above the oil: air, nitrogen, ammonia, and carbon dioxide. These curves show that the color vs. time is greatest at about 200° C. when heated at 150 pounds per square inch with air above the oil in the reservoir. Atmospheric pressure, lower temperatures, and inert atmospheres gave less color change per unit time as shown by the color vs.

time curves being shifted upward.

The oil did not change in color during storage for one year at room temperature.

The viscosity and specific gravity changed slightly during the heating.

No measurable amount of unsaturates were detected in the gas oil.

Bubbles of air were removed from the oil by vacuum. The amount of dissolved air was not determined.

Temperature vs. time curves did not yield consistent results. The causes for the inconsistent results have not been determined.

The optical density vs. wave length curve was shifted upward by heating the oil. No characteristic peaks were observed. The Tyndall effect was observed in the original gas oil and to a much greater extent in heated oil. Decolorized oil gave practically no Tyndall effect.

Table 10 gives the physical data for the original oil, heated oil, and decolorized oil.

The presence of an active oxidizing agent was detected by the liberation of iodine from a solution of sulphuric acid and potassium iodide.

The active oxidizing agent was removed with the reducing agent, a five per cent aqueous solution of sodium bisulfite.

Gas oil which had been treated with sodium bisulfite underwent no color change when heated in an inert atmosphere. The use of resorcinol as an antioxidant decreased the color change but did not prevent it.

Gas oil which had been treated with sodium bisulfite and then shaken in air underwent a color change when heated and also gave a positive test for the presence of an oxidizing agent.

CONCLUSIONS

The observed changes in the oil were due to autoxidation.

The original oil had observed oxygen during its storage which cannot all be removed by vacuum or inert gas.

Part of the dissolved oxygen was combined at room temperature with autoxidizable molecules to form peroxides. At higher temperatures, the remaining dissolved oxygen combined with more autoxidizable molecules to form

peroxides.

This combination was stable at room temperatures.

At higher temperatures, the active oxygen was re-
leased and oxidized the autoxidizable molecules to stable
compounds.

The products of oxidation tended to polymerize to
higher molecular weight compounds such as carbenes, gum,
and oily polymers.

If an inert gas were used above the oil during the
heating, the color change and precipitate are less since
less oxygen is available for the oxidation.

ACKNOWLEDGMENT

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Explanation of Figure 1

The relation of color to time of heating at 150 pounds
per square inch pressure.

   Curve 1 - Gas oil heated to 93° C. with air above the
             oil in the reservoir and held at that temper-
             ature for four hours.

   Curve 2 - Gas oil heated to 150° C. with carbon dioxide
             above the oil in the reservoir and held at
             that temperature for four hours.

   Curve 3 - Gas oil heated to 121° C. with air above the
             oil in the reservoir and held at that temper-
             ature for four hours.

   Curve 4 - Gas oil heated to 150° C. with air above the
             oil in the reservoir and held at that temper-
             ature for four hours.

   Curve 5 - Gas oil heated to 163° C. with air above the
             oil in the reservoir and held at that temper-
             ature for four hours.

   Curve 6 - Gas oil heated to 200° C. with air above the
             oil in the reservoir and held at that temper-
             ature for four hours.

Explanation of Figure 1

The relation of color to time of heating at 150 pounds per square inch pressure.

Curve 1 – Gas oil heated to 93° C. with air above the
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Curve 3 – Gas oil heated to 121° C. with air above the
oil in the reservoir and held at that temper-
ature for four hours.

Curve 4 – Gas oil heated to 150° C. with air above the
oil in the reservoir and held at that temper-
ature for four hours.

Curve 5 – Gas oil heated to 163° C. with air above the
oil in the reservoir and held at that temper-
ature for four hours.

Curve 6 – Gas oil heated to 200° C. with air above the
oil in the reservoir and held at that temper-
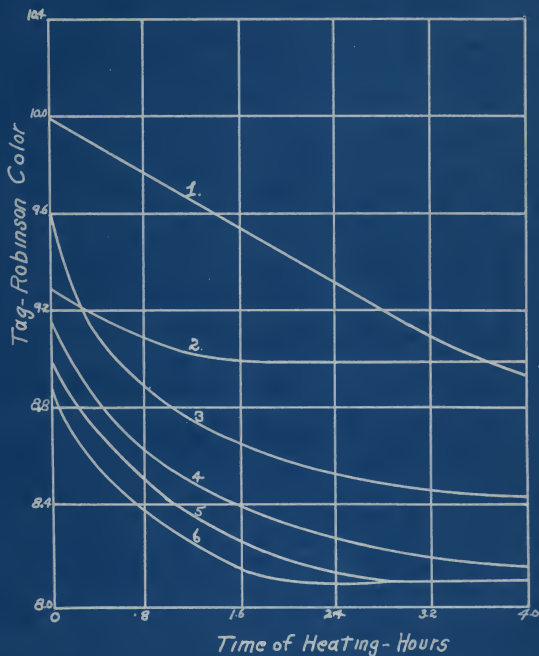ature for four hours.

Figure 1. The Relation of Color to Time of Heating in the Pomace of Sugar Beet Pressure.

Table 1. The relation of color to time of heating at 150 pounds per square inch.

Time – hours	Tag-Robinson color
Plotted as No. 1 in Figure 1	
93° C.	
0.0	10.00
0.5	9.80
1.0	9.70
1.5	9.60
2.0	9.44
2.5	9.30
3.0	9.15
Plotted as No. 2 in Figure 1	
150° C.	
(CO_2 atmosphere)	
0.0	9.30
0.5	9.20
1.0	9.10
1.5	9.00
2.0	9.00
Plotted as No. 3 in Figure 1	
121° C.	
0.0	9.60
0.5	9.10
1.0	8.80
1.5	8.70
2.0	8.65
Plotted as No. 4 in Figure 1	
149° C.	
0.0	9.30
0.5	8.80
1.0	8.60
1.5	8.45
2.0	8.30
Plotted as No. 5 in Figure 1	
163° C.	
0.0	9.15
0.5	8.75
1.0	8.45
1.5	8.25
2.0	8.15
2.5	8.10
Plotted as No. 6 in Figure 1	
200° C.	
0.0	9.00
0.5	8.50
1.0	8.18
1.5	8.10
2.0	8.10

Explanation of Figure 2

Optical density of gas oil at various wave lengths.

    Curve 1 - Optical density at various wave lengths for a
           sample of gas oil which had been heated to
           200° C. and held at that temperature for one
           hour. The Tag-Robinson color was 9.10.

    Curve 2 - Optical density at various wave lengths for a
           sample of the original unheated gas oil. The
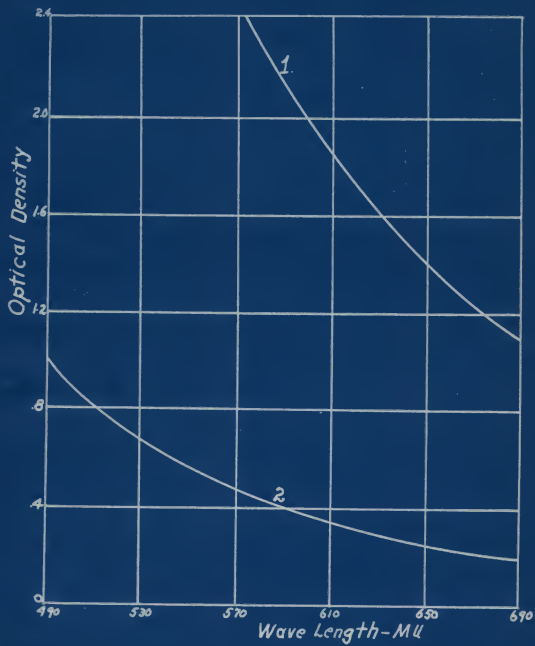   Tag-Robinson color was 10.25.

Figure ... Optical Density of Gas Oil At Various Wave Lengths.

Table 2. Optical density at various wave lengths.

Wave length	Optical density	
	Unheated gas oil	Gas oil heated at 200° C. for one hour
490	0.98	
500	0.85	
510	0.75	
520	0.68	
530	0.65	
540	0.58	
550	0.52	2.90
560	0.48	2.80
570	0.44	2.50
580	0.42	2.24
590	0.37	2.05
600	0.37	1.90
610	0.36	1.80
620	0.32	1.65
630	0.24	1.60
640	0.24	1.44
650	0.24	1.38
660	0.21	1.28
670	0.21	1.20
680	0.21	1.12
690	0.21	1.10
700	0.18	1.02

Explanation of Figure 3

The relation of color to time of heating in glass apparatus
at atmospheric pressure with air above the oil sample.

Curve 1 - Gas oil heated for six hours at $110°$ C.

Curve 2 - Gas oil heated for six hours at $150°$ C.

Curve 3 - Gas oil heated for six hours at $200°$ C.
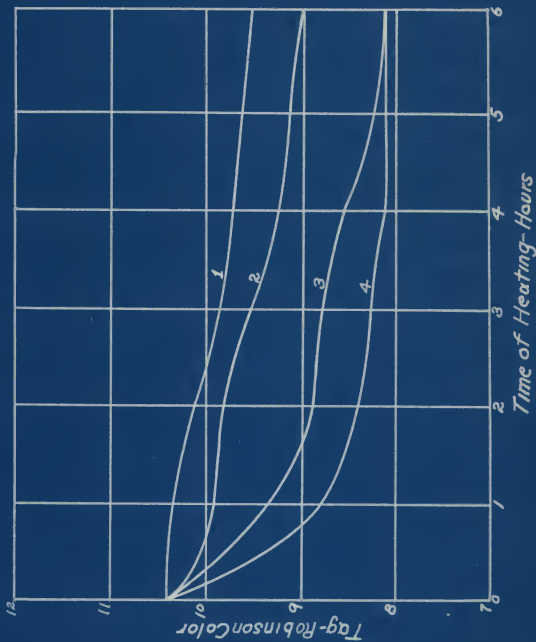
Curve 4 - Gas oil heated for six hours at $250°$ C.

Time of Heating- Hours

Tag-RobinsonColor

Table 3. The relation of color to time of heating in glass
apparatus in air.

Time - hours	Tag-Robinson color
Plotted as No. 1 in Figure 3 110° C.	
1	10.35
2	10.10
3	destroyed
4	9.70
5	9.60
6	9.50
Plotted as No. 2 in Figure 3 150° C.	
1	9.90
2	9.80
3	9.50
4	9.20
5	9.10
8	8.75
10	8.40
12	8.30
14	8.30
Plotted as No. 3 in Figure 3 200° C.	
1	9.50
2	8.85
3	8.75
4	8.50
5	8.20
6	8.10
Plotted as No. 4 in Figure 3 250° C.	
1	8.75
2	8.45
3	8.25
4	8.10

Explanation of Figure 4

The relation of color to time of heating in glass apparatus under various conditions.

Curve 1 - Gas oil which had been treated with five per cent aqueous sodium bisulfite in an inert atmosphere and then heated at $200°$ C. in a carbon dioxide atmosphere for three hours at atmospheric pressure.

Curve 2 - Gas oil heated at $150°$ C. in an ammonia atmosphere at atmospheric pressure for three hours.

Curve 3 - Gas oil heated at $150°$ C. with air above the oil at atmospheric pressure except that the flask was stoppered to prevent additional air from entering.

Curve 4 - Gas oil heated under the same conditions as Curve 3 except that the temperature was $200°$ C.

Curve 5 - Gas oil heated at $150°$ C. after being de-aerated in a vacuum. The vacuum was maintained during the heating.

Curve 6 - Gas oil heated at $150°$ C. with carbon dioxide at atmospheric pressure above the oil and resorcinol placed in the oil.
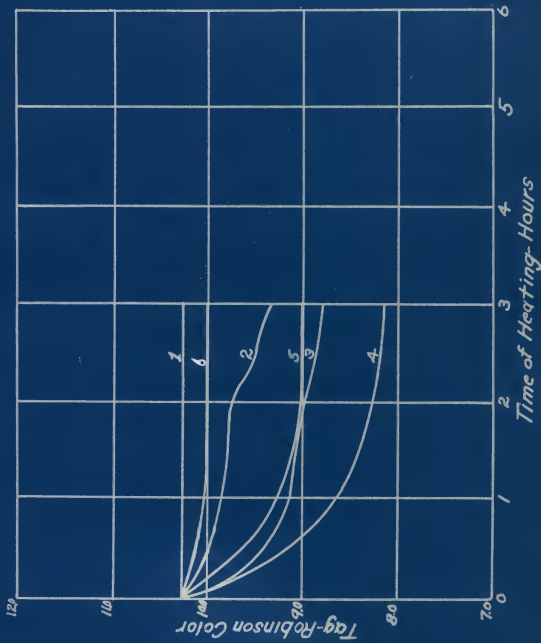
Figure 4. The Relation of Color to Time of Heating Various Products.

Table 4. The relation of color to time of heating in vacuum in ammonia atmosphere and when sealed from the air in glass apparatus.

Time - hours		Tag-Robinson color
	Plotted as No. 1 in Figure 4	
	200° C.	
0.0	(Sod. bisulfite treated)	10.25
0.5	(CO_2 atmosphere)	10.25
1.0		10.25
1.5		10.25
2.0		10.25
2.5		10.25
	Plotted as No. 2 in Figure 4	
	150° C.	
0.5	(Ammonia atmosphere)	10.00
1.0		9.80
1.5		9.80
2.0		9.80
2.5		9.50
3.0		9.40
3.5		9.00
	Plotted as No. 3 in Figure 4	
	150° C.	
1.0	(Sealed)	9.30
2.0		9.00
3.0		9.80
	Plotted as No. 4 in Figure 4	
	200° C.	
1.0	(Sealed)	8.75
2.0		8.30
3.0		8.25
	Plotted as No. 5 in Figure 4	
	150° C.	
1.0	(Vacuum)	9.10
2.0		9.00
3.0		9.00
	Plotted as No. 6 in Figure 4	
	150° C.	
0.5	(Carbon dioxide atmosphere)	10.00
1.0	(Resorcinol treated)	10.05
1.5		10.00
2.0		10.00

Explanation of Figure 5

The relation of temperature to time when gas oil was heated
in a constant temperature bath (Plate II).

Curve 1 - Temperature at various times during the first
heating of the sample of gas oil.

Curve 2 - Temperature at various times for the same sample
of oil when heated under the same conditions a
second time.

Curve 3 - Temperature at various times for the same sample
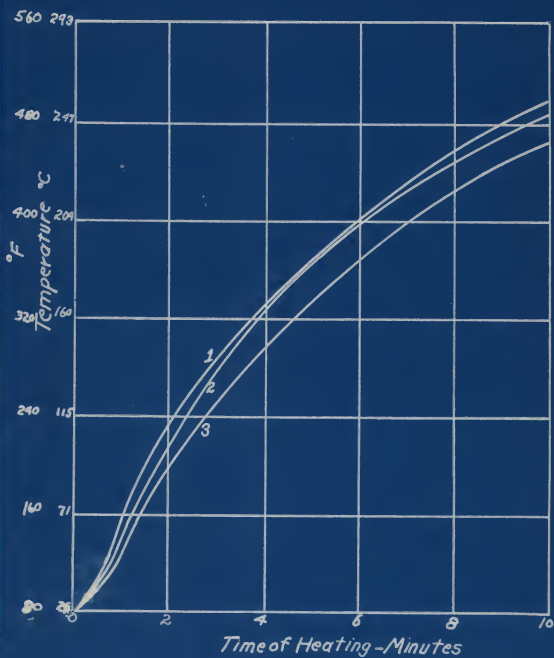of oil when heated under the same conditions a
third time.

Figure 5. The Relation of Temperature to Time When Heated In A Constant Temperature Bath.

Table 5. The relation of temperature to time when heated
in a constant temperature bath.

Plotted as Figure 5

Time in minutes	Temperature in degrees F.		
	First heating	Second heating	Third heating
0.0	84	84	84
0.5	109	101	96
1.0	151	139	128
1.5	194	176	163
2.0	229	212	196
2.5	260	245	223
3.0	290	274	248
3.5	314	300	275
4.0	336	325	304
4.5	358	347	321
5.0	374	367	337
5.5	390	385	348
6.0	405	406	365
6.5	422	416	380
7.0	436	430	393
7.5	447	443	411
8.0	456	455	428
8.5	467	467	436
9.0	476	477	446
9.5	481	486	460
10.0	489	496	467

Explanation of Figure 6

The relation of temperature to time when heated in a constant temperature bath (Plate II).

Curve 1 - Temperatures at various times during the third heating of the sample of gas oil.

Curve 2 - Temperatures at various times during the second heating of the sample of gas oil.

Curve 3 - Temperatures at various times during the first heating of the sample of gas oil.

As in Figure 5, the sample was cooled between successive heatings and placed in the bath at the same temperature for each set of data.
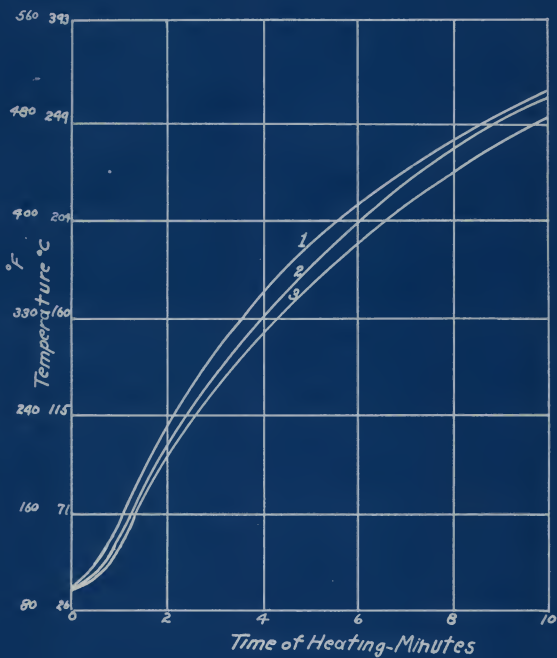
Figure 6. The Relation of Temperature to Time When Heated in a Constant Temperature Bath.

Table 6. The relation of temperature to time when heated in a constant temperature bath.

Plotted as Figure 6

Time in minutes	Temperature in degrees F.		
	First heating	Second heating	Third heating
0.0	98	98	98
0.5	110	107	116
1.0	144	144	155
1.5	180	179	194
2.0	207	214	225
2.5	232	242	258
3.0	257	271	288
3.5	285	296	316
4.0	306	322	341
4.5	328	345	362
5.0	349	365	380
5.5	368	385	398
6.0	386	402	412
6.5	402	418	426
7.0	416	430	439
7.5	429	443	455
8.0	446	454	470
8.5	454	437	473
9.0	465	476	495
9.5	475	488	499
10.0	486	500	506

Figure 7. Specific Gravity of Lube Oil at Various Colors.

The chart plots Specific Gravity (y-axis, ranging from .83 to .89) against Tag-Robinson Color (x-axis, ranging from 10.2 to 8.2), with a nearly horizontal curve labeled "1" near .86.
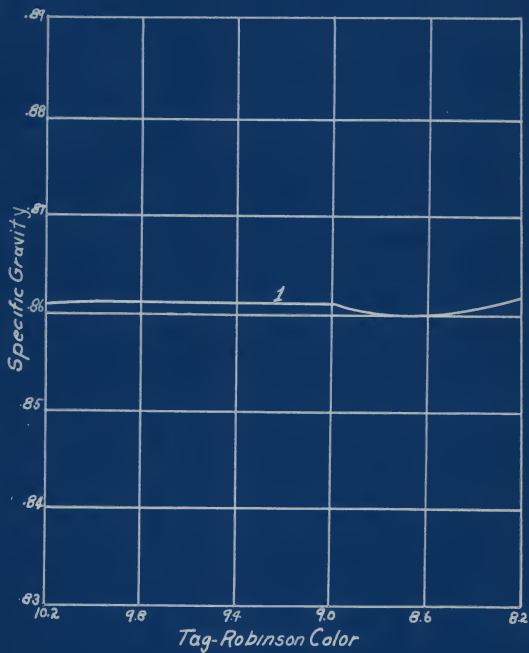
Table 7. Specific gravity at various colors.

Plotted as Figure 7	
Specific gravity	Tag-Robinson color
0.8608	10.25
0.8612	10.00
0.8612	9.80
0.8610	9.00
0.8602	8.75
0.8609	8.45
0.8625	8.10
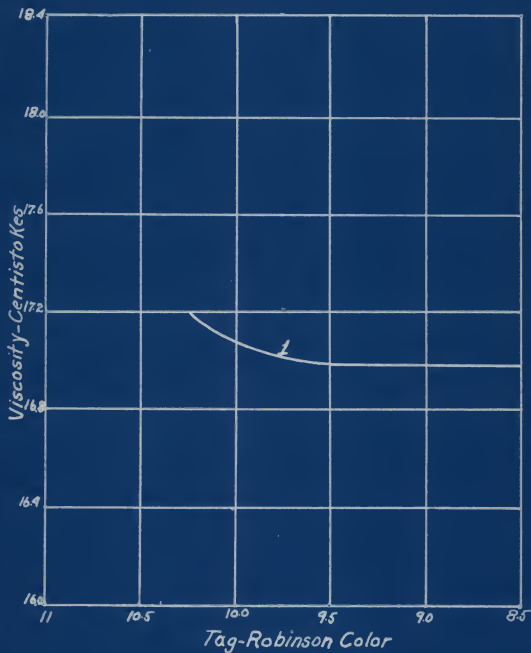
Plate 6. The Viscosity of a Oil with Change in Color.

Table 8. Viscosity at various colors.

	Plotted as Figure 8	
Viscosity in centistokes		Tag-Robinson color
17.25		10.25
17.09		10.00
17.00		9.30
17.00		8.80
17.00		8.30
17.00		8.10
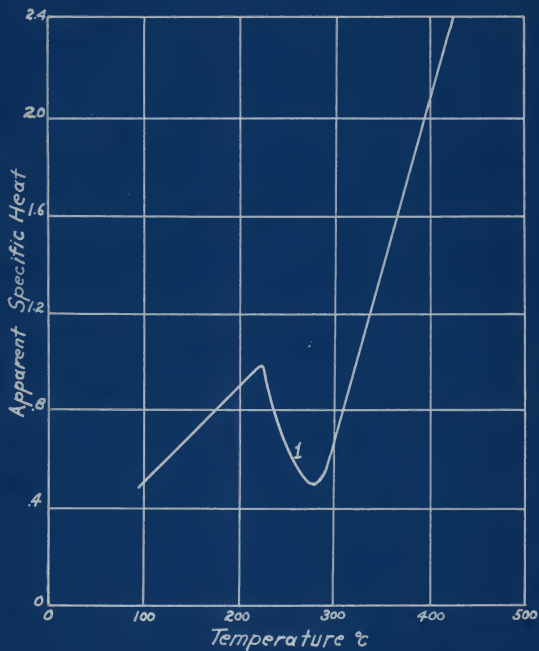
Table 9. Apparent specific heats at various temperatures
for 34.0 A. P. I. gas oil, Hedrick (1).

Plotted as Figure 9	
Temperature	Specific heat
100	0.50
150	0.60
225	1.00
250	0.55
275	0.40
300	1.00
340	1.40

Table 10. Specifications of gas oil.

| | :Unheated:gas oil | Gas oil heated to maximum color change | |
		:Not decolorized	:Decolorized
Specific gravity	: 0.8608:	0.8625	: 0.8594
A. P. I. gravity	: 32.7 :	31.3	: 33.5
Mean boiling point °F.	:545.0 :	545.0	:545.0
Tag-Robinson color	: 10.25 :	8.10	: 17.00
Viscosity at 100° F. (centistokes)	: 17.20 :	17.00	: 17.00
Refractive index	: 1.4721:	1.4721	: 1.4592
Aromatics (per cent±2):	16.00 :	16.00	: 15.00
Unsaturates (per cent):	0.00 :	0.00	: 0.00
Sulphur (per cent)	: 0.25 :	0.25	: 0.23

Products of reaction when heated to maximum color change:

    Black oily material extracted from fuller's
   earth .   .   .   .   26.43 per cent by weight

    Black precipitate classified as car-
      benes .   .   .   .   .   0.042 per cent by weight

    Gum   .   .   .   .   .   Trace

Explanation of Plate I

Apparatus for heating oil under pressure with continuous
recycling of the oil.

A - Oil reservoir (glass separatory funnel).
B - Pipe still made from pressure tubing surrounded by an
    electrical heating coil suspended on porcelain insulators.
C - Reaction chamber designed to withstand high pressures.
    This serves to hold the heated oil for a few seconds
    before cooling.
D - Pressure gage which reads up to 900 pounds per square inch.
E - Water jacket to cool the oil leaving the reaction chamber.
F - High pressure release valve.
G - 85 per cent magnesia brick insulation around the heat-
    ing coil.
H - Thermocouple inserted in a well which protrudes into
    the center of the reaction chamber.
I - Pipe leading to gas meter to record volume of gas pro-
    duced when gas is produced.
J - Sample container.
K - High pressure gear pump.
L - Thermocouple inserted through the insulation to measure
    the surface temperature of the pipe.

FIG 5

I

F

A

J

E

D

L

K

G

C

B

H
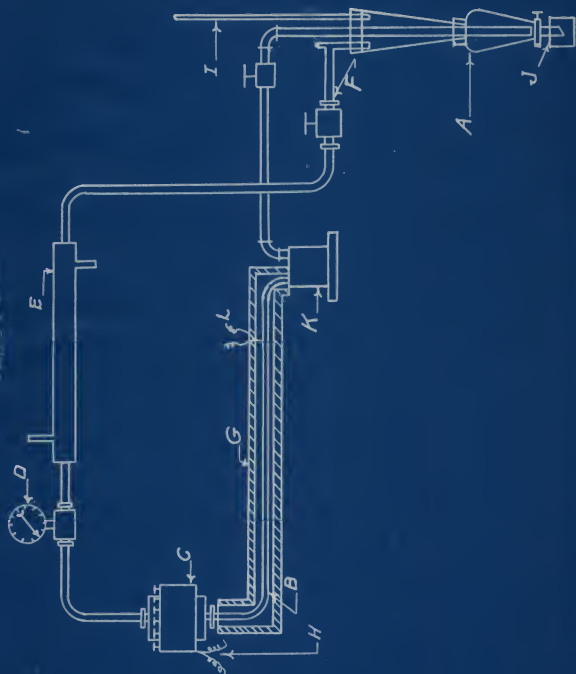
Explanation of Plate II

Constant temperature bath for determining temperature at
various times during the heating of the gas oil.

A - Jacket which contains the boiling mercury or other
    liquid used to maintain a constant temperature.
B - Reflux condenser for condensing and returning excess
    vapors to the system.
C - Reflux wall upon which the vapors condense and trans-
    fer heat to the air bath inside.
D - Container for the oil sample. This container does
    not touch the jacket C and thus a constant temperature
    air bath is maintained between D and C.
E - Cylindrical guide for the stirrer and thermocouple.
F - Thermocouple inserted directly into the oil for
    measuring the temperature of the oil.
G - Flexible connection for connecting the stirrer to the
    stirring motor at the beginning of the run.
H - Leeds and Northrup potentiometer for recording the
    temperature.

    This apparatus was made of mild steel pipe and cast
    iron fittings.

PLATE III.

G

B

D

H

A

E

F

D

C

Oil

Mercury