FILM STUDY GROUP

SUBJECT INDEX AND REPORT

T.O.M. REEL NO. 3

Prepared by

GULF RESEARCH & DEVELOPMENT COMPANY

RECEIVED
SEP 24 1946
ALBERT E. MILLER

GULF RESEARCH & DEVELOPMENT COMPANY
Pittsburgh, Pennsylvania

ABSTRACT AND INDEX OF TECHNICAL OIL MISSION

MICROFILM

REEL NO. 3

INDEX OF REEL NO. 3

NOTE: The frames of this reel are not numbered; however, continuous frame numbers have been assigned so that subject matter may be located. As there are about twelve frames per foot, approximate location may be estimated by dividing the frame number by twelve.

INDEX OF REEL NO. 3
(Concluded)

Frame No.

PERSONNEL

PLANT OPERATION (Monthly Summaries and Balances)

SCANNING OF REEL #3

U. S. GOVERNMENT TECHNICAL OIL MISSION

NOTE: The frames in this reel are not numbered, and subject reference will have to be made by item location only. The item numbers used below are those listed in the T.A.C. Index. The first part of this reel consists of a continuation of Section 13, Reel 2, Miscellaneous.

BAG 2168 TARGET 30/4.03

ITEM 1: Monthly Summary of Plant Group A (2 Pages)

A monthly report for August, 1943, of the Fischer synthesis plant at Wintershall A.G., Lutzkendorf, showing a summary of 1, coal used; 2, fuel gas; 3, synthesis gas produced; 4, gas purification; 5, synthesis; 6, oxygen and nitrogen by Linde air separation.

The summary is followed by a listing of special plant operating notes such as: A-1, gas production, high sand content of coal caused operating difficulties, plant overhauled and repaired; A-2, synthesis, petroleum oil used in gas washing in place of tar oil in a new column, insufficient gas cooling resulted in higher sulfur content, decreased yields and more rapid catalyst aging.

ITEM 2: Plant Report for June, 1943 (3 Pages)

A monthly report showing material balance under the following headings: coal, powdered coal, coke, fuel gas made, fuel gas used, synthesis gas made, off-gas yields, Linde plant, hydrogen, hydrogenation yields, and lubricating oil.

Monthly Summary of Plant Group C, June, 1943 (1 Page)

Production and use of steam and electricity, and water used.

Monthly Summary of Plant Group B, June, 1943 (2 Pages)

Itemizes operation of Plant 4, hydrogenation; Plant 5, petroleum oil including distillation, deasphalting, dewaxing, clay treating, and sulfuric acid treating; and Plant 6, blending.

ITEM 3: Monthly Summary of Plant Group A, June, 1943 (2 Pages)

Similar to Item 1. Plant summary and operating notes.

ITEM 4: Monthly Summary of Plant Group D, June, 1943 (2 Pages)

Utilities are shown under the following headings: 1, water balance; 2, hours on operation and condition of water in boiler house; 3, hours on operation and condition of water in waste heat boiler; 4, electric balance; 5, steam generator; 6, steam used.

Monthly Summary of Plant Group A, Sept., 1943 (2 Pages)

Similar to Item 1, Part 2. Operating notes.

ITEM 5: Monthly Summary of Plant Group A, Sept., 1943 (1 Page)

Similar to Item 1, Part 1. Plant summary.

ITEM 6: Monthly Summary of Plant Group D, May, 1944 (2 Pages)

Similar to Item 4.

ITEMS 7 and 8: Cover Letter of March 6, 1943, and Attached Register of Chemical and Engineering Personnel (103 Pages)

Employees of Plant Corporation Oberrheim, I.G. (Ludwigshafen, Oppau, Merseburg, Schkopau and Hüls) as of July 1, 1940, for engineers and May 16, 1939, for chemists. Age groups and the number drafted are shown.

ITEM 9: Cover Letter (Marked secret) from Reichsamt für Wirtschaftausbau, Berlin,

of Sept. 9, 1940 to Müller-Conradi at Ludwigshafen for report on "Analytic and Preparative Precision Separation of Hydrocarbon Mixtures" prepared for the "Second Work Conference" on April 5, 1940. (1 Page)

ITEM 10: Letter from Stern to Muller-Conradi of March 20, 1940

stating that a short introductory paper for the above-mentioned report has been prepared. (1 Page)

ITEM 11: Introductory Paper Mentioned in Item 10 (9 Pages)

This paper has been translated completely.

Analytical and Preparative Precision Separation of Hydrocarbon Mixtures

by Stern

Report to the Second Work Conference

Dr. Müller-Conradi

Analytical and Preparative Precision Separation of Hydrocarbon Mixtures

Gentlemen:

Within the bounds of this meeting I have been authorized to report to you on new methods for the separation and determination of hydrocarbons in mixtures.

See supplement p. 1[1]

These methods have been developed by my co-workers and myself within the last decade at the Oppau Works, in order to obtain an insight regarding the composition of pressure oils which are formed under a variety of conditions in the methanol synthesis as well as the products prepared from these and the oils obtained by thermal cracking. The compounds appearing in the latter occur also during coal liquefaction as unstable intermediate members. As cracked oils are prepared in very large amounts abroad so it was important to determine what individual constituents they contain and how to technically evaluate these individual constituents and also to be prepared for the evaluations on the part of foreign countries.

As analytical methods require proof in the form of exhaustive examples I present these to you as supplements to this report.

I shall discuss these methods in about the order they were developed by us: precision fractionation by use of the Oppau distillation head, the smallest model of which I exhibit to you here, the determination of olefines, dienes, the latter, with the exception of butadiene, occurring principally in the products of thermal cracking, and in conclusion I present to you an example of the examination of the multi-component product of alcohol synthesis from CO and H_2 under pressure.

Precision Fractionation
Supplement p. 2

Our fractionation head is the result of the logical development of the principle of the Hahnsehen head: both walls in contact with the vapor stream are surrounded by the boiling bath. The heat supply which

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[1] Refers to page number of German supplement, translation of which is given in Item 12.

keeps this bath boiling does not come from the vapors of distillation but comes from a special uniform heating source - an electric winding. By this means the distilling head becomes equally effective for very small quantities. At first I used only one narrow annular space without the imbedded spiral, then by a built-in, two-way spiral of platinum wire the path of the vapors was lengthened and a positive action obtained even for small vapor velocities. The best solution, however, is represented by the gound-in, glass spiral of the Widmer head which is fused to the inner tube. It can be made tight easily, it requires, however, especially

Supplement p. 5

for the larger types, great technical glass blowing skill. Metal wires, for example, silver, may also be used depending upon the distillate. Sharpness of separation hardly suffers hereby except these distillates according to our experience are not suited for spectroscopic examination. Spun glass cords are unsuitable. The condition for precise separation is constant pressure; it is best to have an individual pump for each

Supplement p. 7

apparatus. A diagram of the arrangement, pressure regulator and various designs are given in the supplement. Temperature is best regulated by diminishing or increasing pressure on the constant boiling bath which pressure can be more accurately measured than the temperature by our frequently inaccurate thermometers.

Supplement p. 8

As an example of precision fractionation I show the separation of equal parts of o, m and p-xylol. After three fractionations about half of the o-xylol in a concentration of 95% was obtained in the last fraction, the first fraction consisting of m and p-xylol free from the o. The ternary mixture of the main runnings could not be further separated. Determination of the xylol content was made by means of the Raman spectra. We got better separations with this laboratory head than was possible with our large industrial columns; up to now the reverse had been true. Now we have also developed this Oppau column on an industrial scale where it performs as well as the smaller ones as far as sharpness of separation is concerned.

Olefines

I shall now discuss the analysis of olefines in mixtures of hydrocarbons. The hydrocarbon chemistry familiar to us in the dye and pharmaceutical technology is primarily the chemistry of aromatics. The cracking of petroleum and tars and the synthetic hydrocarbons from CO and H_2 or their further manufactured products offer a source of raw material in which olefines abound, and as far as reactivity is concerned they are the most important component. Now, how can we, for example, determine the individual chemical isomers such as are represented in a chemical mixture as a cracked oil, which we have separated into individual carbon groups by means of precise fractionation? In order to obtain a working basis we set out to determine the individual isomers of pentene in a mixture with the hope that from these results we could also find methods for the hexenes and heptenes. This problem could not be solved completely; however, we could collectively determine pentenes and hexenes in closely related groups. When we began this problem about ten years ago Professor Mohr, of the Lu Research Laboratory, suggested that we try bromination and fractionation of the bromides. This method did not prove sound; by bromination not only addition but also substitution products are formed which, moreover, are again easily decomposed and thus the mixture becomes more complex which was to be avoided as much as possible in the first place. We then successfully used the addition of HBr and could with the assistance of the reactions observed several decades ago by Michael and Zeidler on the bromination of pentenes, separate the pentenes from each other and from the paraffins thus obtaining four groups. In a suitable reaction vessel, a V-tube with an inner middle leg which you see here, the olefin-paraffin mixture is first shaken with 4-1/2 N HBr, the amount of bromine absorbed is determined and the tertiary bromide which was formed from trimethylethylene and assymetrical methylethylethylene decomposed with water and the resulting HBr determined by titration. Next all olefines are brominated at 0° with saturated HBr solution, the paraffin separated by boiling over into the other leg and determined. If isopropylethylene was present in the mixture, then 48% tertiary bromide is formed from it by rearrangement, from which determination the isopropylethylene can be calculated by using a rearrangement factor of 2. The remaining bromine absorption yields the amount of straight-chain pentenes. We thus obtain besides the paraffin group, three pentene groups: (1) tertiary olefines, trimethylethylene, assymetrical methylethylethylene; (2) isopropylethylene; and (3) straight-chain members.

Supplement p. 11

Supplement p. 9
Analytical procedure

Supplement p. 12
Diagram

In the case of the hexenes besides these three groups there is still a fourth (IIIa) group between the isopropylethylene and the straight-chain groups; namely, tertiary-butylethylene. This now rearranges itself during the saponification of its bromide, because of the retropinacoline rearrangement, into 2,3,dimethylbutanol-2 and this alcohol under these conditions is converted practically completely to tetramethylethylene. Further details are given in the diagram. We have not applied this method beyond the hexenes, the separation by simple boiling in the V-tube being incomplete for higher olefins.

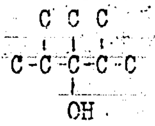
Supplement p. 15

A second method of determination for tertiary olefines is the selective catalytic addition of HCl or HBr to olefine vapors in the presence of a barium chloride or bromide contact (Friedrichsen). It permits, for example, the quantitative separation as halides of small amounts of isobutylene from other butenes.

Supplement p. 16

Supplement p. 18 - Table

A further method originated from the Tauss mercuric acetate procedure. It depends upon the fact that primary, secondary and tertiary olefines react rapidly with mercuric acetate while di-tertiary and tertiary olefines with adjacent quaternary carbon atoms react slowly. By titration of the acetic acid the reaction velocity may be determined. This method is of value when it is desired to determine the amount of 2,4,4-trimethylpentene-1 in the presence of 2,4,4-trimethylpentene-2 as in di-isobutylene, or for example, when it is desired to establish whether 1,1-di-isopropylethylene or 2,3,4-trimethylpentene-2 results from the dehydration of 1,1-di-isopropylethanol.



$$\begin{array}{ccccccccc} & & C & & C & & C & & \\ & & | & & | & & | & & \\ C & - & C & - & C & - & C & - & C \\ & & & & | & & & & \\ & & & & OH & & & & \end{array}$$

Dienes

In the determination of olefines dienes occur as disturbing contaminants, especially in cracked products, and must be determined and removed before making the olefin analysis. After the determination and removal of the dienes traces of peroxides must also be destroyed before precise fractionation since they would interfere with the V-tube analysis.

Supplement pgs. 19-28

We separated the dienes by the stepwise addition of maleic acid anhydride and vacuum distillation after each addition and then identifying them in the individual portions by microchemical reactions or by conversion into phthalic acids.

Supplement p. 19

Supplement pgs. 28, 29

The cyclic dienes, as has been established ~~by Dr. Hoess, may be separated by the addition of a~~ naphthoquinone which reacts but very slowly with straight-chain dienes. The branched chain cyclic (dienes) react first with maleic acid and the straight chains lastly. This method proved good for the separation and identification of the small amounts of dienes in cracked oils. ~~When dienes occur in greater concentrations and the~~ diene is known, then it may be determined titrimetrically

Supplement p. 30 by titrating, with proper precautions, the unconverted
maleic anhydride, which is much more rapidly hydrolyzed
by water than the addition acids.

Paraffines It is especially difficult to determine indi-
vidual isomers in mixtures of paraffins; in some cases,
however, it is of special interest and above all it is
important for the defense economy, as, for example, in
the iso-octane used in aviation gasoline whose resistance
to knocking is dependent on the content of 2,4,4-tri-
methylpentane. As the paraffins are difficultly reactive
chemically it has been proposed many times to use the
Supplement p. 33 molecular spectra especially the easily determined and
evaluated Raman effect. Raman analysis is applicable
to non-aromatics when only a few, at the best not more
than three individual constituents, are present of which
one is clearly preponderant. We also have examined a
number of technical iso-octanes in this manner in order
to explain the unexpected differences in octane values
Supplement p. 36 and in this way arrived at new results. First, the
three samples given on Page 36 of the supplement were
subjected to precise fractionation by means of the Oppau
head, after which the fractions were examined by use
of the Raman effect. The fractions given in the columns
of the table show that Sample II is of very homogeneous
composition while I and III consist of two components
in unequal amounts and the first and last fractions
contain noticeable impurities. The main constituents
were examined by Dr. Timm using the Raman effect and
identified as 2,4,4 and 2,3,4-trimethylpentane and veri-
Supplement p. 37 fied by means of the index of refraction. The first
has an octane number of 100 and the second identified
by us for the first time and synthetically prepared in
Supplement p. 35 pure form had an octane number of 95. The impurities
which decrease the octane number of III are found prin-
cipally in the last fractions; besides this, naturally
also the higher content of 2,3,4-trimethylpentane has
some effect. An octane number of 95 is required, so
this is, therefore, not troublesome.

Synthetic mixtures After just giving you a synopsis of the methods
used by us for the separation and determination of ole-
fines, dienes, and paraffins, I still wish to briefly
~~show you - for details of which I refer you to the sup-~~
plement - how the many CO-H_2 pressure oils of various
compositions can be cleared up. Besides hydrocarbons
Supplement p. 41 these also contain the oxygen constituents above all
alcohols and acids which are separated before the ex-
amination and determined by themselves. This separation
~~for alcohols up to C_4 and for acids was done in known~~
manner. For the higher alcohols and also in general

Supplement p. 42 for the determination of the OH-number our method of using phthalic anhydride instead of acetic anhydride is worthy of mention. After obtaining the ester acids these were converted into the mixed methylesters by means of diazomethane, and since the former are less easily hydrolyzed than the acetic esters, it is easier to determine the amount of unused phthalic anhydride. They are also less volatile and therefore are more easily separated from the other components.

Supplement p. 50 In the next to the last table you see the results on an oil represented graphically and in the last

Supplement p. 52 table are the comparative columns of several oils. In an investigation of this kind it should always be borne in mind that it is impossible to give general rules for analysis and the same is true for these methods. A suitable method must be selected for every product to be examined.

STERN, Op. 200, March, 1940.

ITEM 12: Report mentioned in Item 9 - Supplement to Introductory Paper, Item 11 (51 Pages)

This report has been translated in full.

Enclosure to the Report: Stern

New Methods of Isolation and Identification of Hydrocarbons in Mixtures

Analytic and preparative precision separation of hydrocarbons in the 2nd Working Group:

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[1] The translation page number is noted in the text followed by the corresponding German page number in brackets.

The technical-scientific experiments were carried out by the author in collaboration with: Dr. Ernst Hochschwender (Summer, 1926), Dr. Robert Hasenclever (Fall, 1926-Spring, 1931), Dr. Werner Hoess (Fall, 1931-to date), Dr. Wilhelm Friedrichsen (end of 1934-to date). The physical experiments, especially Raman spectrograms were made by Dr. Bernhard Timm. The chemical and distillation analyses during all this time were made almost exclusively and with greatest perseverance and exactness by my old assistant, Miss Hedwig Lotz. Many thanks to all of them.

OPPAU FRACTIONATING ATTACHMENT

This attachmant for precise fractionating is made wholly of glass to the lower half of which is fused a glass tube provided with electrical heating. This is filled with a liquid of suitable boiling point to just below the upper end of the double inner tube supporting the glass spiral. To avoid delay in boiling, boiling rods[1] are introduced into the inner and outer spaces of the bath. The thermometer is suspended in the outer space of the bath. The upper end of the bath chamber is connected with a reflux condenser by means of a ground glass joint with spring clips to provide for increased pressure.

The desired temperature can be regulated accurately to a fraction of a degree by selection of the bath liquid and the corresponding pressure or vacuum. The liquid flowing back from the reflux condenser must not drop upon the inner spiral tube; it should run down on the outer wall of the bath chamber.

The round-bottomed flask with the liquid to be analyzed is, as usual, connected to the fractionating attachment by means of a ground glass joint and is likewise heated by an electrically heated bath, the temperature of which is measured. The vapors leaving the flask pass, as in the Widmer attachment, through a cylindrical spiral space in which they are in contact for a time with the liquid flowing back and become separated into their constituent parts. By the selection of the distance a-b, the spiral pitch c in relation to a and the length L, it is possible to adjust conditions to a considerable extent to the problem at hand.

According to our experiences, the following are especially to be observed:

The constant boiling liquid must not decompose easily, but it need not necessarily be a pure substance. It must not be inclined to superheat, and besides having a suitable boiling point, must also possess a heat of vaporization which is not less than that of the substance to be fractionated.

For the separation of hydrocarbons we used ether, pentane, carbon tetrachloride, benzene, water, toluene, xylene, pseudocumene, dichlorbenzene and tetralin, the latter very soon showing signs of decomposition. Usually we do not go lower than about 40° below and not more than 15° above the boiling temperature of the bath liquid, at atmospheric pressure. We regulate the pressure by means of a movable tube immersed in mercury.

The liquid to be separated must boil uniformly and sufficiently vigorous; if one fraction has been removed then only very little comes

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[1] or capillary tubing

over. We increased the bath temperature only when with the normal apparatus the dropping rate at the end of the condenser fell below 3-4 drops per minute, and decreased to less than one drop per minute for the smaller apparatus. We never exceeded a rate of over 60 drops per minute as the maximum for the normal apparatus. Since only the bath temperature needs supervision, it is easily possible to carry on a large number of distillations side by side.

We used fractionating attachments of the following dimensions:

	in mm.					
	a	b	c	d	L	L'
No. 1 Small Amounts 5-100 cc.	8	6	5	1	100	150
No. 2 Normal Amounts	14	10	12	2	200	300
No. 3 Long Column	24	20	10	2	200	300

See the attached drawing for the meaning of the letters.

No. 1 - We used this for the separation of small amounts.

No. 2 - Was used for normal conditions.

No. 3 - Was used where especially sharp separations were desirable.

- Oppau, October 16, 1935 Op. 200

Stern

OPPAU FRACTIONATING ATTACHMENT
with adjustable reflux

(Report April 22, 36; April 28, 37, March 10, 40 Stern)

In order to carry out the precision fractionation of larger amounts in a faster and equally satisfactory way, the attachment (described in report of October 10, 1935) was provided with an inner attachment above the column, which could be cooled by water or air (see attached drawing). This attachment is in the form of a test tube and is separated from the column reflux cooling surface by an annulus. Liquid condensate from the constant boiling bath fills the annulus and effects the heat transfer. We use this modification in connection with the 500 mm. columns. In the technical construction of this precision fractionating column, it was not necessary to provide a special device to regulate the reflux. The reflux can be regulated at will by precise setting of the temperature. The determination of the temperature is carried out best and most exactly by determination of the boiling pressure of the constant boiling bath.

For a useful application of this attachment, it is essential to have a convenient regulation of pressure or vacuum. For this we use the floating pressure regulator, which is also shown on the attached drawing: a hollow, cylindrical floating body which, at the upper and lower part, is well guided by three wart-like glass pieces in a fitting glass tube, is ground even at the upper end. This upper end is pasted with a thin plate of oil resisting buna. The regulatory buoyancy of the floating body presses it with the desirable back pressure to a V_2A tube which has a guiding disc on its lower end and which is connected elastically with the inner glass tube by means of a piece of rubber tubing The highest attainable pressure or vacuum depends on the ratio

$$\frac{\text{volume of floating body}}{\text{inner cross-section of tube}}$$

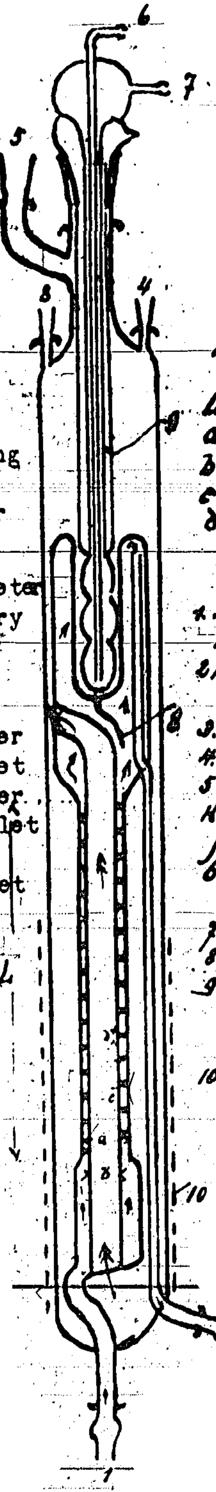
Blg. A. 6

Oppauer Feinfraktionier-aufsatz

n. Ber. v. 21.4.36 ergänzt 2.1.39 Stein.

Fraktionier-aufsatz.

FRACTIONATING ATTACHMENT



1) to distilling flask
2) to condenser
3) for thermometer
4) for capillary tube
5) to reflux condenser
6) cooling water or air inlet
7) cooling water or air outlet
8) reflux tip
9) vacuum jacket
10) electrical heating element

Maße mm

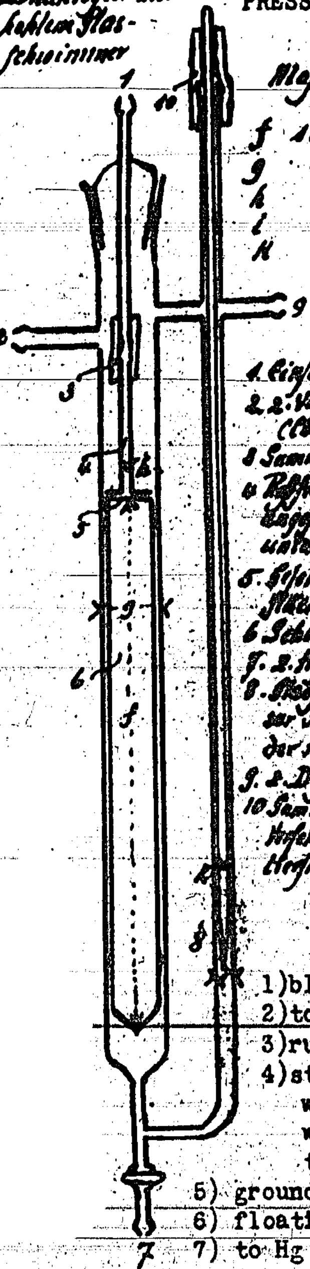
L	350	250	500
a	24	56	54
b	20	50	50
c	10	15	15
d	2	8	8
	[illegible]	Glas	spiral.

1. Schliff z. Destillier-Kolben
2. Schliff z. Destillat-Kühler
3. Thermometerschl.
4. Siedekapillarschl.
5. Schliff z. Rücklauf-Kühler des Konstant siedenden Bades
6. Zulauf des Kühlwassers od. d. Luft
7. Ablauf derselben
8. Abtropfspitze
9. Evakuierter Isoliermantel d. [illegible] Kühlers
10. Elektr. Heizung d. Konstant siedenden Bades

Menge 3.1.39 25 Stück
10.8.39 25 "
10.4.40 50 " (Berlin)

Druckregler mit hohlem Glas-schwimmer

PRESSURE REGULATOR



Maße mm

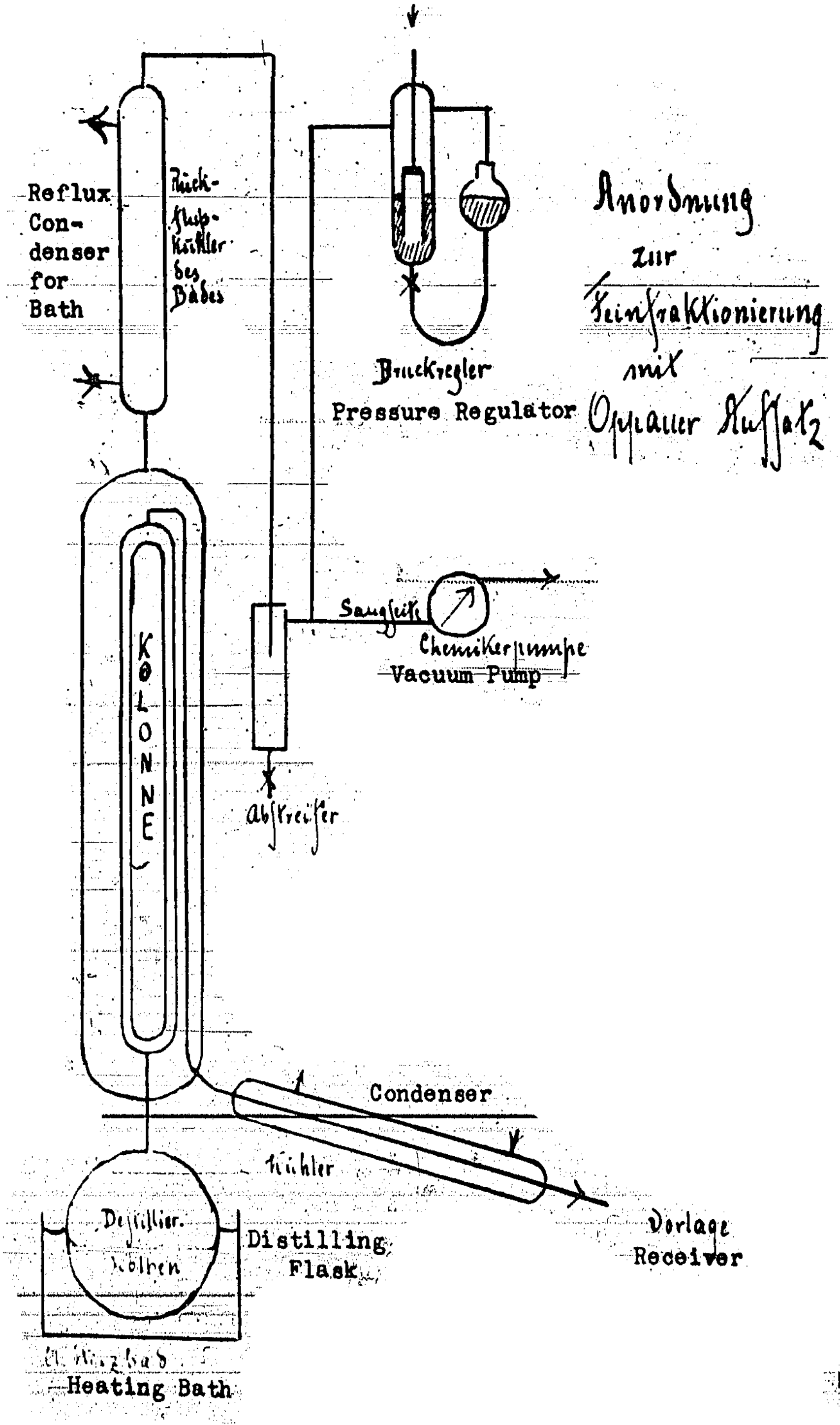
f	180	360
g	24	85
h	4	4
i	–	10
k	–	7

1. Einsaugleitung
2. z. Vakuumpumpe ([illegible])
3. Gummischlauch
4. Rostfreies Rohr mit angeschweißter unten geschliff. Platte
5. Geschliffene Glasfläche
6. Schwimmkörper
7. z. Hg-Niveaugefäß
8. Glasstab m. Spitze zur Feineinstellung der Hg-Höhe
9. z. Destillationsapp.
10. Gummischlauch z. Hochschieben d. Regulierstabes.

1) bleed line
2) to vacuum pump
3) rubber tubing
4) stainless tube with welded on plate, which is ground at the bottom
5) ground glass surface
6) floating body
7) to Hg leveling vessel
8) glass rod with tip for precision regulation of Hg level
9) to distilling apparatus
10) rubber tube

Blge. 5 7

ARRANGEMENT FOR PRECISION FRACTIONATION WITH OPPAU ATTACHMENT



Anordnung zur Feinfraktionierung mit Oppauer Aufsatz

10.5.40 Klm

In order to test the performance of the Oppau attachment for precision fractionation, we made a mixture of equal parts of o-, m-, and p-xylene and fractionated it. Raman spectra were used to determine and estimate the content of the various cuts. The table below shows the results.

A part, about 1/3 - 1/2 of the o-xylene could be obtained in the last cut as about 95 percent o-xylene. The first cut (135°) was free of o-xylene, but contained both m- and p-xylene. The cut 137.2° could not be separated even with four reruns, and it seems to be a constant boiling mixture. The cuts 139° and 140° can probably be further separated.

Boiling Point °C.	Wt.%
135.0	15.2
137.2	54.8
139.2	5.9
139.5	6.0
140.2	8.8
143.2	9.1

INSTRUCTION FOR THE DETERMINATION OF THE PENTENE AND HEXENE FRACTION IN THE V-TUBE[1]

I. Group $-c = \overset{c}{c} - c-$ (Isobutylene group)[2]

Determine Br number in fraction according to McIlhiney.

Rinse tube with water, evacuate, weigh moist. Suck in 4.5 n. HBr eight times the volume of the hydrocarbon, shake 1-1/2 hours, suck off the HBr, suck in water and repeat until the water is no longer acid, let well stratify, suck off water and weigh the tube. Distill the hydrocarbon (pentene 70°, hexene 90°C) from one side tube to the other (0°C.), suck out the residue and weigh the tube.

Repeat treatment with 4.5 n. HBr until decrease in weight of the hydrocarbon is less than 5 per cent.

Saturated Hydrocarbons $c - c - c$

Determine Br number according to McIlhiney. Suck in solution of HBr (saturated at 0°C.) five times the volume of the hydrocarbon, shake two hours, let well stratify, separate the acid.

Collect the hydrocarbon, containing bromides, in a side tube, fill the middle tube partly with KOH 1:1 and leave overnight in order to remove gaseous HBr, suck off KOH and weigh the tube. Determine the Br number of the hydrocarbon bromide mixture to make sure that absorption of HBr was complete. Distill the hydrocarbon bromide mixture (pentene 70°, hexene 90°C.) from one side tube to the other, kept at 0°C. Collect

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[1] After removal of dienes (see encl. p. 19) and of peroxide

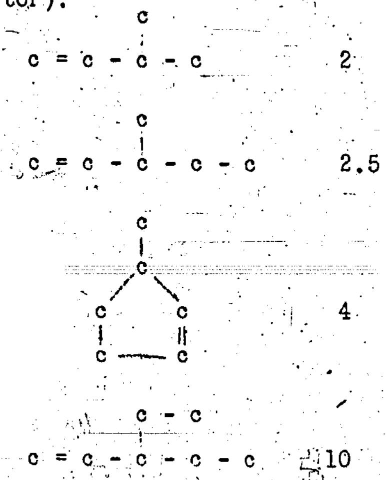
[2] Michael and Zeidler, A. 379, 288, 297; 385, 252, 269

distillate in middle tube, suck off, cool the bromide in the side tube to 0°C. and remove the rest of the hydrocarbon by vacuum until weight is constant.

II. Group $c = c - \overset{c}{c} - c$ Isopropylethylene group

Suck water into the tube with the bromide mixture, shake, suck off and repeat until water is no more acid. Titrate the HBr in the water (and multiply by factor).

Factor for



$c = c - \overset{c}{c} - c$ 2

$c = c - \overset{c}{c} - c - c$ 2.5

4

$c = c - \overset{c - c}{c} - c - c$ 10

Determine the Br number in the residual bromide according to McIlheney, if olefin was formed anew then there is present the

IIIa. Group $c = c - \overset{c}{\underset{c}{c}} - c$ tert-Butylethylene group

From $c = c - \overset{c}{\underset{c}{c}} - c$ is formed in 90 per cent yield $c - \overset{c}{c} - \overset{c}{\underset{Br}{c}} - c$ (retrograde Pinacoline rearrangement)[1] and this gives with water $c - \overset{c}{c} - \overset{c}{\underset{OH}{c}} - c$ which forms $c - \overset{c}{c} = \overset{c}{c} - c$ at room temperature.

Group IIIa occurs in diisobutylenes, but was never found in cracked gasolines.

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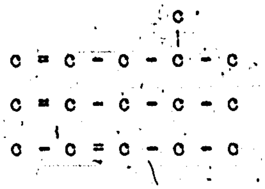
[1] Compare Delacre, C. 1906, II 498

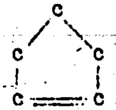
III. Group

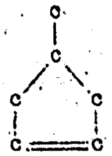


$$c = c - c - \overset{\overset{\textstyle c}{|}}{c} - c$$

$$c = c - c - c - c$$

$$c - c = c - c - c$$



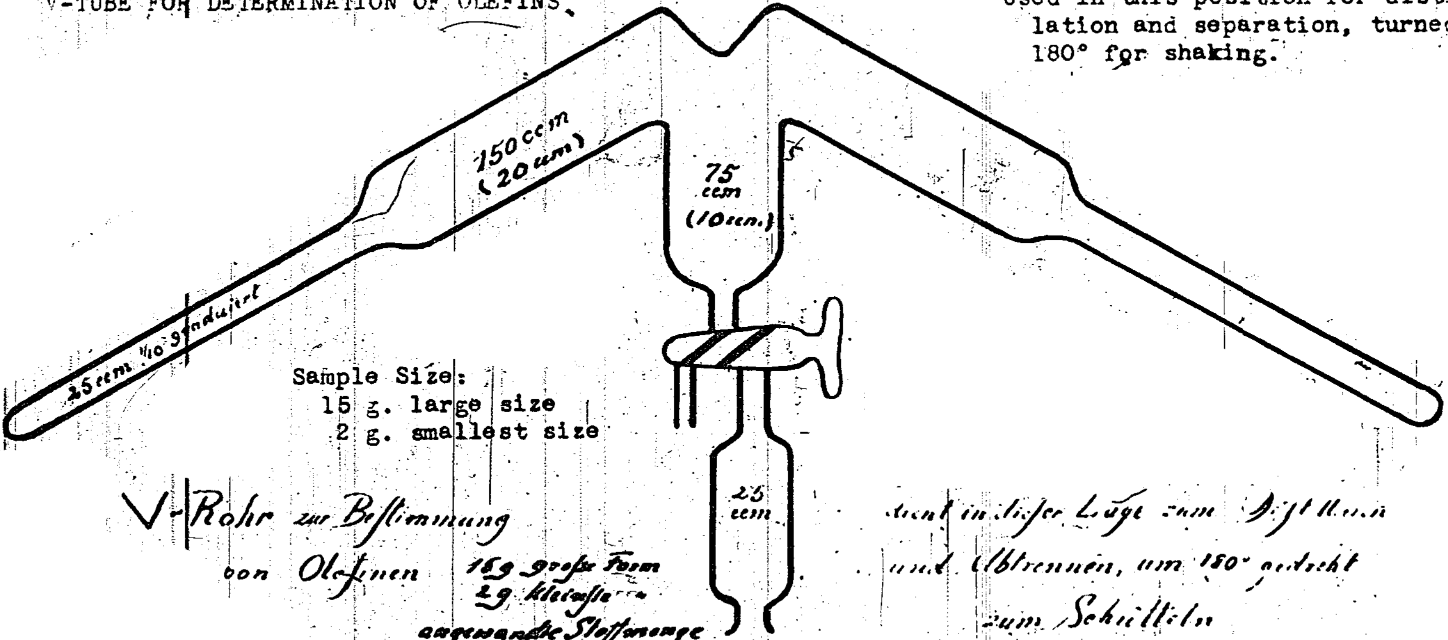


The bromine combined with the hydrocarbon indicates the content of the above olefins with predominantly normal chain.

We use about 10 gr. of hydrocarbons for the analysis in the V-tube with 150 cc. side tube (illustration). We use smaller tubes for smaller quantities.

V-TUBE FOR DETERMINATION OF OLEFINS.

Used in this position for distillation and separation, turned 180° for shaking.



Sample Size:
15 g. large size
2 g. smallest size

V-Rohr zur Beſtimmung von Olefinen

15 g große Form
2 g kleinſte
angewandte Stoffmenge

dient in dieſer Lage zum Deſtillieren und Abtrennen, um 180° gedreht zum Schütteln

Die Zahlen in ( ) ſind Maſse für die kleinſte Form. Verengte, Schenkelverlängerung laſſen wir weg, ſie iſt, wenn alle Werte wie in Vorſchrift gewichtsmäſsig beſtimmt werden, zu entbehren.

Numbers in ( ) are for the smallest size. We omit the narrow extension of the side tube for it is unnecessary if all values are determined by weight according to instruction.

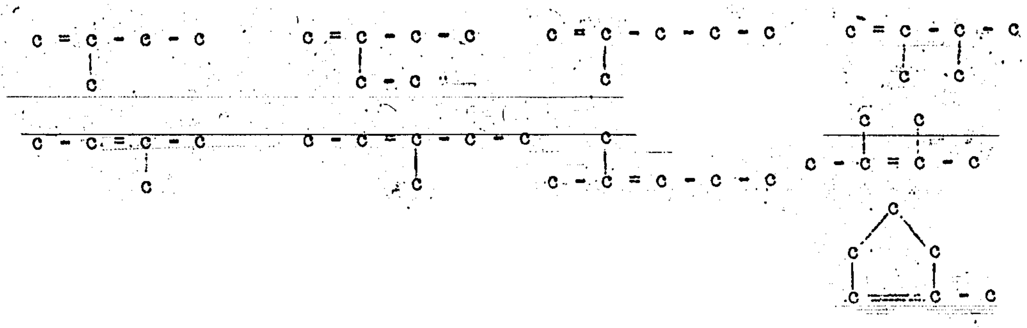
Ergänzt. 22.1.35 Stern

Separation and Determination of Hydrocarbon Mixtures Free from Dienes

Group **Pentenes** **Hexenes**

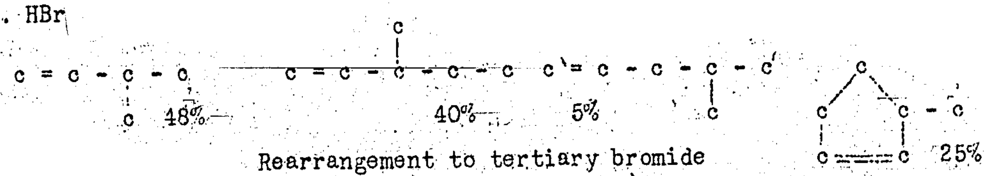
4.5 n. HBr

I



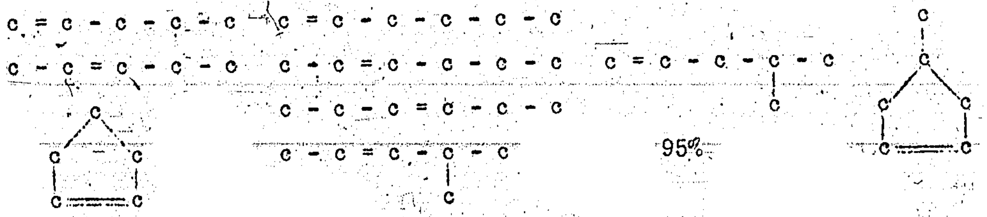
8.5 n. HBr

II

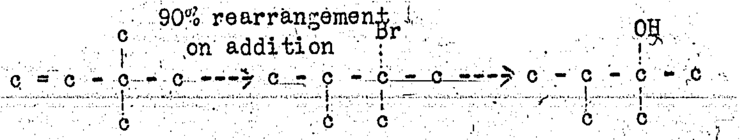


Rearrangement to tertiary bromide
(Michael rearrangement)

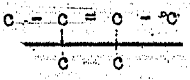
III

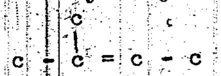
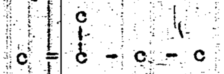
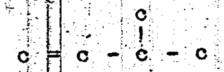


IIIa



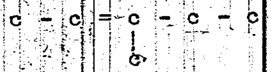
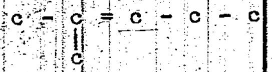
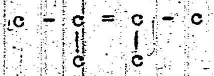
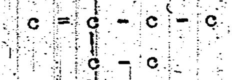
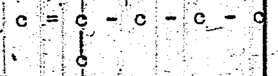
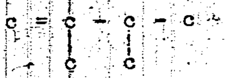
which is converted even in aqueous solution at 40°C. into



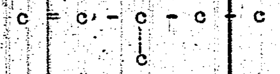
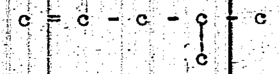
	Br Number According to McIlhiney Addition Calc.	Found	Substitution 20°	40°	Reaction with 4.5 n. HBr	Oxidized at 0°C. with excess of neutr. $KMnO_4$ gives	
Trimethylethylene[1]  $C-\overset{C}{C}=C-C$	228	220	30	35	Soluble	Acetone Acetic acid	
Assym. Methylethylethylene  $C=\overset{C}{C}-C-C$	228	--	--	--	Soluble	Methylethyl ketone (Literature)	
Isopropylethylene[1]  $C=C-\overset{C}{C}-C$	228	225	26	93	None	Isobutyric acid Oxalic acid	
Pentene-1[1] $C=C-C-C-C$	228	--	--	--	None	n-Butyric, Oxalic and Formic acid	No succinic acid, contrary to literature
Pentene-2[1] $C-C=C-C-C$	228	227	6	5	None	Propionic acid, Acetic acid	
Cyclopentene[1] 	236	235	15	20	None	Glutaric acid	

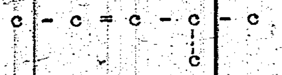
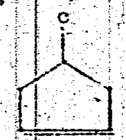
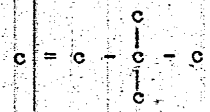
---

[1] Synthetically prepared in a pure condition according to literature.

	Br Number According to McIlhiney				Reaction with 4.5 n. HBr	Oxidized at 0°C, with excess of neutr. $KMnO_4$ gives
	Addition		Substitution			
	Calc.	Found	20°	40°		
3-Methylpentene-2 [1]  $\mathrm{c-c=\underset{c}{c}-c-c}$	190	--	--	--	Soluble	Not tested
2-Methylpentene-2  $\mathrm{c-\underset{c}{c}=c-c-c}$	190	--	--	--	Soluble	Not tested
Tetramethylethylene [1]  $\mathrm{c-\underset{c}{c}=\underset{c}{c}-c}$	190	190	20	35	Soluble if treated repeatedly	Not tested
Assym. Diethylethylene [1]  $\mathrm{c=\underset{c-c}{c}-c-c}$	190	175	60	75	Soluble	
Assym. Methylpropylethylene  $\mathrm{c=\underset{c}{c}-c-c-c}$	190	--	--	--	Soluble	
Assym. Methylisopropylethylene  $\mathrm{c=\underset{c}{c}-\underset{c}{c}-c}$	190	--	--	--	Soluble	

The tertiary alcohol decomposes already at room temp. into olefin and H_2O in the presence of acid. The pure olefin adds H_2O slowly on standing.

	Br Number According to McIlhiney					
	Addition		Substitution		Reaction with 4.5 n. HBr	Oxidized at 0°C. with excess of neutr. $KMnO_4$ gives
	Calc.	Found	20°	40°		
Tertiary Methylcyclopentene[1] 	195	194	68	80	Polymerizes	
3-Methylpentene-1[1]  $c = c - \underset{c}{c} - c - c$	190	185	25	150	None	Ethylmethyl-Acetic acid Oxalic acid
Isohexene[1]  $c = c - c - \underset{c}{c} - c$	190	--	--	--	None	Isovaleric acid Oxalic acid
Active Methylcyclopentene[1] 	195	190	55	180	None	
Hexene-1 c = c - c - c - c - c	190	--	--	--	None	n-Valeric acid Formic acid Oxalic acid
Hexene-2 c - c = c - c - c - c	190	--	--	--	None	n-Butyric acid Acetic acid

	Br Number According to McIlhiney				Reaction with 4.5 n. HBr	Oxidized at 0°C. with excess of neutr. $KMnO_4$ gives
	Addition		Substitution			
	Calc.	Found	20°	40°		
Hexene-3 c - c - c = c - c - c	190	--	--	--	None	Propionic acid
Sym. Methylisopropylethylene  $c-c=c-\underset{\underset{c}{|}}{c}-c$	190	180	15	70	None	Isobutyric acid Acetic acid
Sym. Methylcyclopentene 	195	--	--	--	None	
Tert. butylethylene  $c=c-\underset{\underset{c}{|}}{\overset{\overset{c}{|}}{c}}-c$	190	--	--	--	None	Trimethylacetic acid, Oxalic acid

Syntheses: Dr. W. Hoess

Analyses: Miss Hedwig Lotz

Separation of Tertiary Olefins from other Olefins by Selective-Catalytic Conversion to Halides by Barium Halides

Process of W. Friedrichsen E.P. 473501, Fr. P. 823567, H.P. 351855, U.S.A. 2156070 - O.Z. 11655

About 500 l. of butene-2 containing 10 per cent isobutylene are mixed at 95° with 40 l. of gaseous HCl and passed within 5 hours over 1-1/2 l. of a porous $BaCl_2$ catalyst. A 92 per cent yield is obtained which is at least 98% tertiary-butylchloride and which can be obtained from the mixture by precise fractionation. The catalyst is made by mixing equal parts of $BaCl_2$ crystals and water, drying it at elevated temperature in a vigorous air current to a blistery mass. From this, pea-sized pieces are made and completely freed from water in a stream of HCl at 150-200°C.

Using HBr and $BaBr_2$, the same conversion and the same yield are obtained at 65°C.

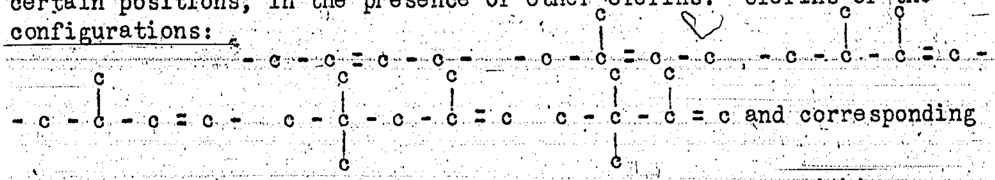
It is as well possible to separate trimethylethylene from isopropylethylene by this process. It can be used not only for the technical, but as well for the analytical separation, because the tertiary olefins can be separated completely from gases containing 2-3 per cent. In technical separation it is best to wash out the halides from the reaction gases or vapors with high boiling hydrocarbons and to drive off the halides from the solution.

Volumetric Determination of Two Groups of Olefins

Expansion of Tauss Method (Dr. W. Friedrichsen)

March 28, 1939

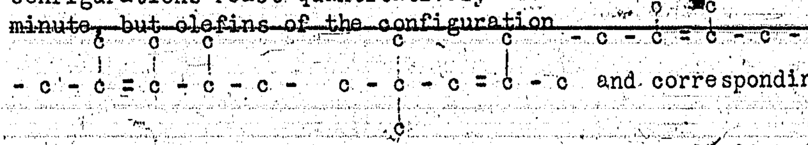
The Tauss method for quantitative determination of olefins consists in reacting the olefins with mercuric acetate and determining volumetrically the equivalent amount of acetic acid. This simple method could be improved in some respects and could be extended mainly for the quantitative determination of branched olefins, with the double bond in certain positions, in the presence of other olefins. Olefins of the configurations:



$-c-c=c-c-$ $-c-\overset{c}{c}=c-c$, $-c-\overset{c}{c}-\overset{c}{c}=c-$

$-c-\overset{c}{c}-c=c-$ $c-\underset{c}{\overset{c}{c}}-c-\overset{c}{c}=c$ $c-\underset{c}{\overset{c}{c}}-\overset{c}{c}=c$

and corresponding configurations react quantitatively with mercuric acetate within one minute, but olefins of the configuration



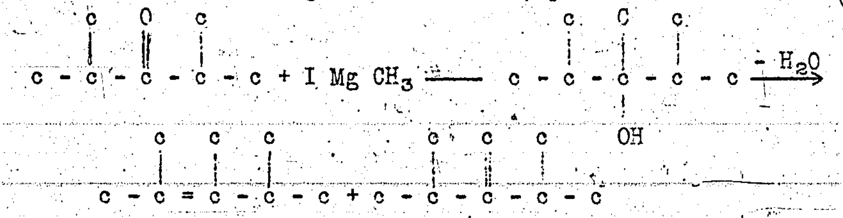
$-c-\overset{c}{c}=\overset{c}{c}-c-$ $-c-\overset{c}{c}=\overset{c}{c}-\overset{c}{c}-c-$ $c-\underset{c}{\overset{c}{c}}-c=\overset{c}{c}-c$

and corresponding configuration react much slower. The differences in reaction velocity of both types are shown in Table I. (It should be mentioned, however, that the olefins of the second group (Curves 1, 3, 4, 5) are apparently contaminated by olefins of the first group due to the method of preparation.)

Experimental: 2 g. of a mixture of 2,4,4-trimethylpentene-1 and -2 are made up to 25 cc. with methanol in a volumetric flask. Two cc. of this solution are mixed in a test tube with 15 cc. of a saturated solution of mercuric acetate in methanol and left for one minute. Then, in order to determine the acetic acid formed, the solution is at once poured into a mixture of 100 cc. of water, 30 cc. saturated NaCl solution and an excess of n/10 NaOH, and this solution is back titrated with n/10 HCl, using phenolphthalein as indicator. Further values are obtained in the same manner after different time intervals. In this way the reaction velocity is obtained and plotted as in Table II. Extrapolation of the straight part of the curve gives an intersection with the abscissa, indicating the composition of the olefin mixture as 50%.

Besides being used for quantitative determination, this method can be used in the determination of the constitution of olefins, e.g. tri-isobutylene, to make statements about the classification of the olefin in question in one of the two groups.

Above all, this method can be used to good advantage in preparative work for the determination of the purity of olefins. For instance, the curves 1, 3, 4 and 5 in Table I show distinctly that the olefins are contaminated by one, which reacts fast with mercuric acetate. These olefins were prepared from the corresponding tertiary alcohol by dehydration with oxalic acid or iodine, e.g. 2,3,4-trimethylpentene-2 as follows:

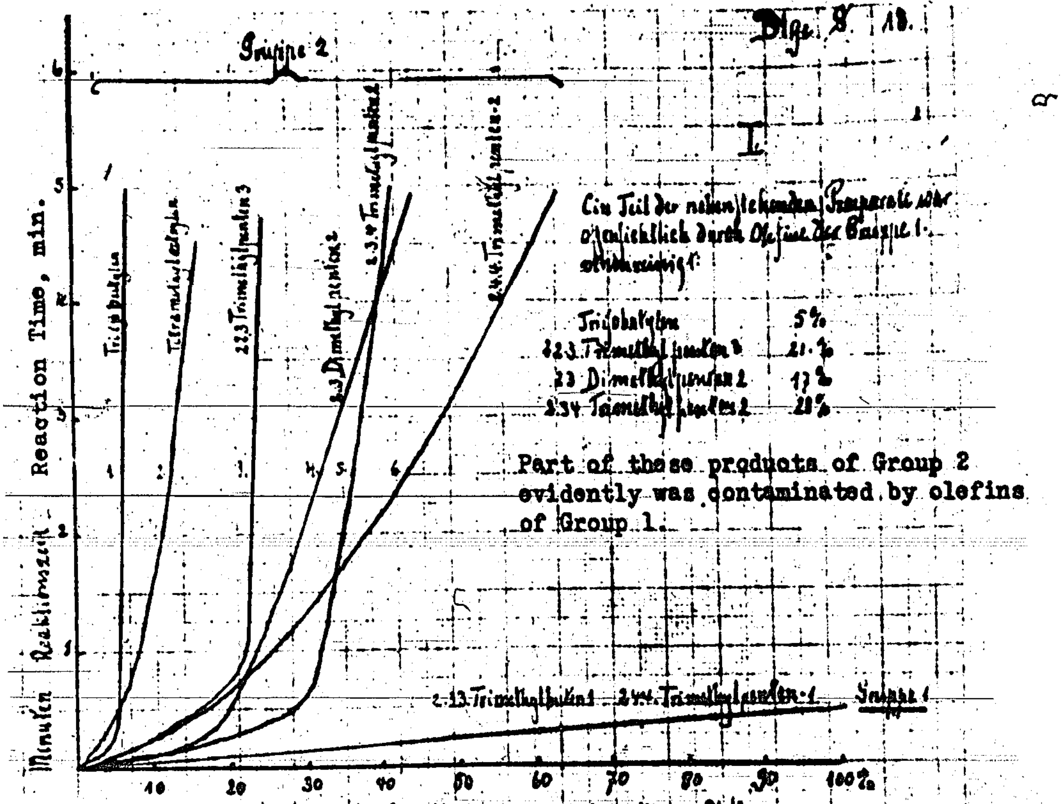


$$\mathrm{c-\overset{\overset{c}{|}}{c}-\overset{\overset{O}{\|}}{c}-\overset{\overset{c}{|}}{c}-c+I\,Mg\,CH_3\longrightarrow c-\overset{\overset{c}{|}}{c}-\underset{\underset{OH}{|}}{\overset{\overset{C}{|}}{c}}-\overset{\overset{c}{|}}{c}-c\xrightarrow{-H_2O}}$$

$$\mathrm{c-\overset{\overset{c}{|}}{c}=\overset{\overset{c}{|}}{c}-\overset{\overset{c}{|}}{c}-c+c-\overset{\overset{c}{|}}{c}-\overset{\overset{c}{\|}}{c}-\overset{\overset{c}{|}}{c}-c}$$

Dehydration, therefore, takes place in two directions. The last olefin, having a terminal double bond, reacts, of course, rapidly with mercuric acetate and was formed in an amount of 28 per cent as the curve shows.

Abb. 8. 18.

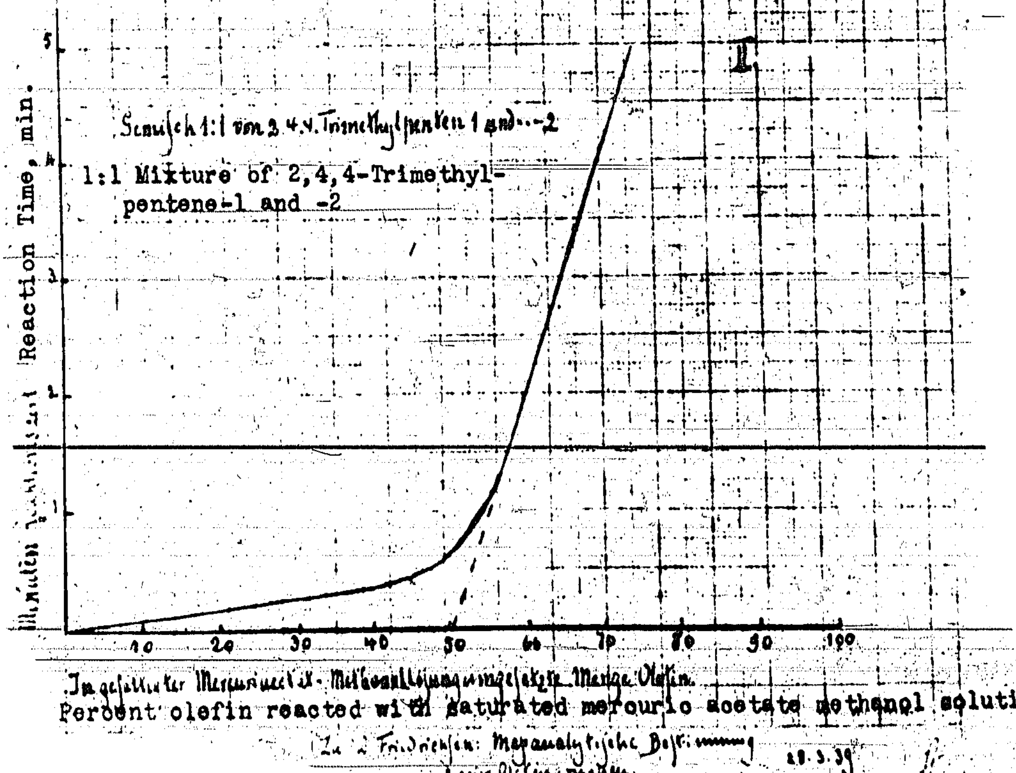


Ein Teil der nebenstehenden Präparate war offensichtlich durch Olefine der Gruppe 1 verunreinigt:

Triisobutylen	5%
2.2.3 Trimethylpenten-3	21 %
2.3 Dimethylpenten-2	17 %
2.3.4 Trimethylpenten-2	21%

Part of these products of Group 2 evidently was contaminated by olefins of Group 1.

In gesättigter Mercuriacetat-Methanollösung umgesetzte Menge Olefin.
Percent olefin reacted with saturated mercuric acetate methanol solution.



Gemisch 1:1 von 2.4.4-Trimethylpenten-1 und -2

1:1 Mixture of 2,4,4-Trimethylpentene-1 and -2

In gesättigter Mercuriacetat-Methanollösung umgesetzte Menge Olefin.
Percent olefin reacted with saturated mercuric acetate methanol solution.

(Zu 2. Friedrichsen: Maßanalytische Bestimmung zweier Olefingruppen. 28.3.39

DETERMINATION OF DIENES

Report of November 23, 1934, Supplemented January 20, 1935
Starting Material: Oil fraction to 120°C.

Course of Determination:

1) Br number according to McIlhiney

Determination of Dienes (with conjugated double bonds) see D.R.P. 646 821.

a. Cyclic: Add α-naphthoquinone, 1 per cent by weight, with vigorous shaking or stirring at room temperature. Allow to stand until yellow color has disappeared and continue the addition until the yellow color persists for 24 hours or, if the oil is colored, until the naphthoquinone can be detected with phenylhydrazine. Separate the addition product from the oil by vacuum distillation at room temperature, maximum temperature of 30°C. The addition product may contain the dimers of cyclopentadiene and methylcyclopentadiene; therefore, it is advisable to distill off after the first addition and to obtain the further addition compounds free from Dimers.

b. Acyclic: As described above, add maleic anhydride percentwise with vigorous stirring until all is dissolved and then leave stand for 24 hours. It is advisable to distill off after each addition, to determine the increase in weight and to crystallize separately the various fractions of addition products. Clay plates of Haldenwanger in Berlin are especially suitable for the separation of the crystals from the mother liquor. These plates permit the separation of small amounts of crystals which will not be contaminated by rubbed-off clay. After further additions of maleic acid, we let stand for 8 days before determining the increase in weight and we stop the additions if there is no increase in weight.

The addition-acids may be examined microchemically according to the enclosed Table I or identified by analysis and melting points of the hydrophthalic acids. (See enclosed Table II.)

With larger samples of benzine we use maleic anhydride as well for the removal of the cyclic dienes (after first determining their percentage with naphthoquinone), in order to avoid the preparation in pure form of larger amounts of the quinone.

Precision fractionation of the oil is carried out after removal of the dienes.

Before analyzing the separate fractions (pentene and hexene fraction) for individual olefins, a test for peroxide is made (especially with the hexene fraction) and peroxides removed in the usual way: $FeSO_4$, iron carbonyl, maleic anhydride at moderate temperature, in many cases it is sufficient to add a high boiling hydrocarbon, e.g. paraffin, about 10 per cent and to redistill. By this means one avoids the dangers connected with the enrichment of the peroxides in the residue from the distillation. Addition of aniline as an artificial high boiling residue (chaser) is to be recommended occasionally, because it can be removed completely by acid.

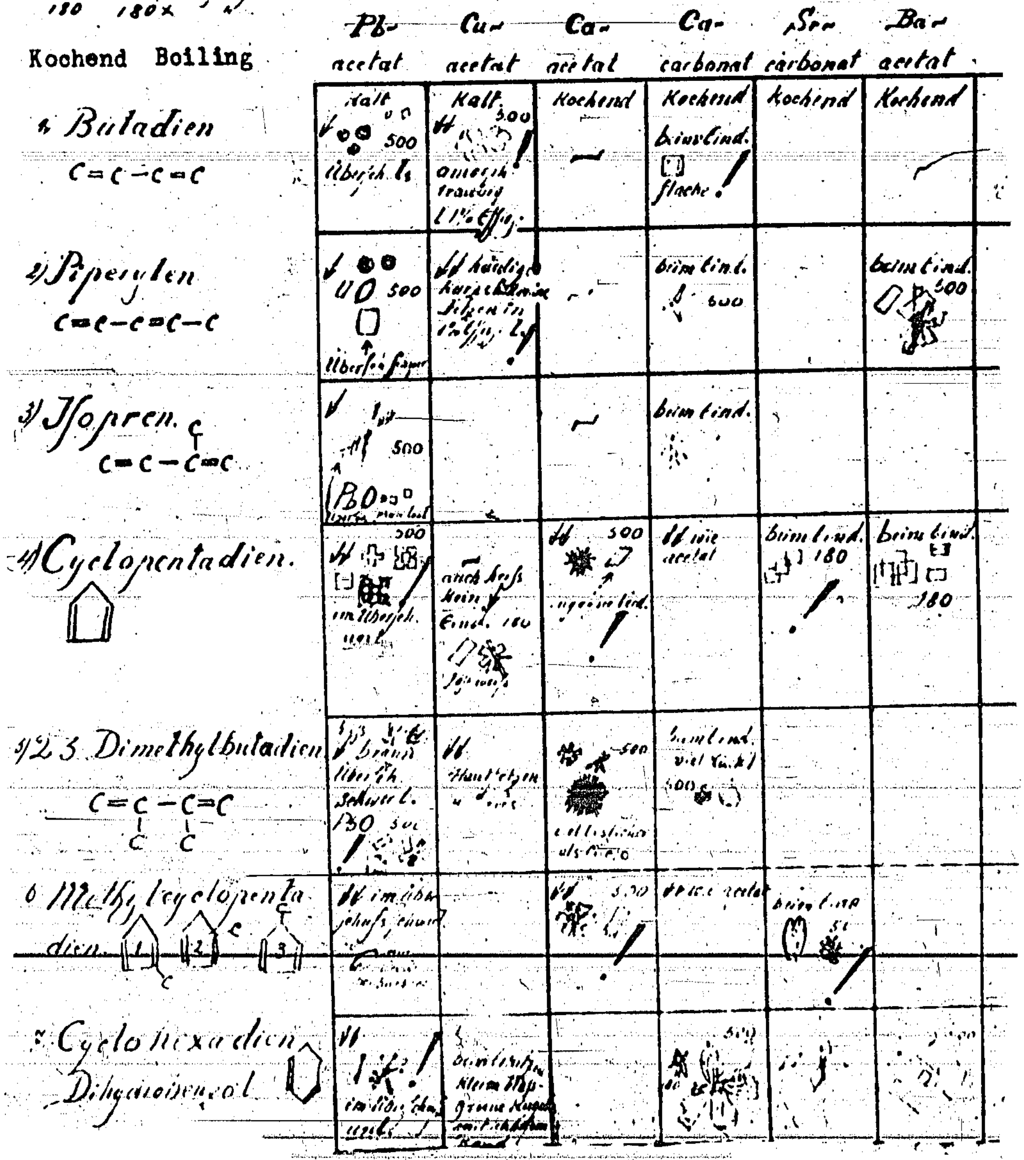
Especially cyclic olefins tend to form peroxides: cyclohexene, methylcyclopentene. Usually the peroxide reaction is already positive one day after purification. Commercial cyclohexene usually contains 1 per cent peroxide; .01 per cent can still be detected. These peroxides are probably responsible for gum formation. For the determination of the individual pentenes and hexenes with the V-tube, it is essential to remove peroxides; otherwise, results for Group I will be much too high.

I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT LUDWIGSHAFEN A. RH.
Stickstoff-Abteilung

Reactions of the Maleic Anhydride Addition Product in Aqueous Solution; Acid Solubility and Cold Saturated Solution Solubility

Reaktionen der Maleinsäureanhydrid-Addukte in H_2O gelöst, saure Lösung, kalt gesättigte Lösungen.

Zeichenerklärung.
↓ Niederschlag Precipitate
l - löslich Soluble
! kennzeichnend Characteristic
500 - 500x vergrößert Magn.
180 180x "
Übersch. Excess Solution
beim Eind. by concentrating
Kochend Boiling



	Pb-acetat	Cu-acetat	Ca-acetat	Ca-carbonat	Sr-carbonat	Ba-acetat
1 Butadien C=C–C=C	kalt ↓ 500 Übersch. l	Kalt 500 ↓↓ ! amorph traubig l 1% Essig.	Kochend —	Kochend beim Eind. flache !	Kochend	Kochend
2) Piperylen C=C–C=C–C	↓ 500 Übersch[illegible]	↓↓ häufige kurze [illegible] Säulen in Essig. l !	–	beim Eind. 500	–	beim Eind. 500
3) Isopren C=C–C(C)=C	↓ ↓↓ 500 PbO [illegible]		—	beim Eind.		
4) Cyclopentadien	500 ↓↓ ! im Übersch. unl.	— auch heiß kein ↓ Eind. 180	↓↓ 500 [illegible] im Eind. !	↓↓ wie acetat	beim Eind. 180 !	beim Eind. 180
5) 2,3 Dimethylbutadien C=C(C)–C(C)=C	↓ braun Übersch. schwer l. PbO 500 !	↓↓ [illegible]	500 [illegible] als [illegible]	beim Eind. viel [illegible] 500		
6 Methylcyclopentadien 1 2 3	↓↓ im Überschuss [illegible]		↓↓ 500 !	[illegible] acetat	beim Eind. 50 !	
7 Cyclohexadien Dihydrobenzol	↓↓ ! im Übersch. unl.	beim Eind. kleine Prismen grüne Kugeln mit [illegible] Rand		500		

Durchschlag

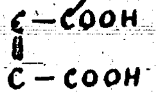
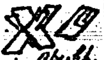
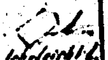
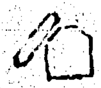
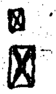
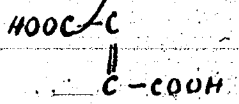
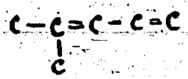
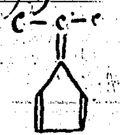
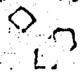
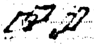
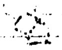
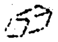
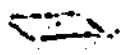
	Pb-acetat	Cu-acetat	Ca-acetat	Ca-carbonat	Sr-carbonat	Ba-acetat
	Kalt	Kalt	Kochend	Kochend	Kochend	Kochend
Maleinsäure-  $\begin{array}{l} C-COOH \\ \| \\ C-COOH \end{array}$	beim 1. Tropfen Kein ↓ dann:  im Abkühl. entsteht.	achtral ◇ □ 500 und kleine Kind.	—	 feinkristall.		 18°
Fumarsäure  $\begin{array}{l} HOOC-C \\ \quad\quad\ \| \\ \quad\quad\ C-COOH \end{array}$	↓  stark licht-brechend. ähnlich oxalat		—			
8) 1,1' Dimethyl-butadien-maleins.  $\begin{array}{l} C-C=C-C=C \\ \quad\ \ | \\ \quad\ \ C \end{array}$	kalt u. heiß ↓↓ hellbraun übersch. L.	↓↓ hellblau	—			
9) Dimethylfulven 	↓↓ ○○ Überschuss	etwas ↓ gelatiniert	↓↓ 500 	wie acetat	500 	↓↓ 180 

Table II

Addition Acids of the Penta and Hexadienes with Maleic Anhydride

1.		$c = c - \overset{c}{c} = c$	Isoprene: beta methyl tetrahydrophthalic acid	M.P. 160°C.
2.		$c = c - c = c - c$	Piperylene: alpha methyl tetrahydrophthalic acid	161°C.
3.		$c = \overset{c - c}{c} - c = c$	2-Ethylbutadiene: beta ethyl tetrahydrophthalic acid	187°C.
4.		$c - c - c = c - c = c$	1-Ethylbutadiene: alpha ethyl tetrahydrophthalic acid	154°C.
5.		$c - c = \overset{c}{c} - c = c$	1,2-Dimethylbutadiene: alpha beta dimethyl tetrahydro phthalic acid	147°C.
6.		$c - c = c - \overset{c}{c} = c$	1,3-Dimethylbutadiene: alpha gamma dimethyl tetrahydrophthalic acid	162°C.
7.		$c - c = c - c = c - c$	1,4-Dimethylbutadiene: alpha delta dimethyl tetrahydrophthalic acid	172°C.
8.		$c = \overset{c}{c} - \overset{c}{c} = c$	2,3-Dimethylbutadiene: beta gamma dimethyl tetrahydro phthalic acid	178°C.

2 - 8 are crystallized from acetic ester.

The determination of the constitution of these acids was carried out by dehydrogenation to phthalic acid and oxidizing to benzenepolycarboxylic acids, which are all known.

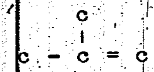
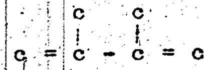
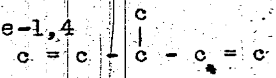
Friedrichsen

Description of the pictures of the crystals:

1) Thin, rhombic flakes	2) Thick, rectangular plates
3) Compact hexagonal plates	4) Short columns with rhombic cross-section
5) Thin, unevenly rhombic flakes	6) Compact plates, tapered on one side and with one truncate corner
7) Hexagonal plates	

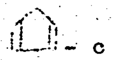
These crystal forms are typical for several times recrystallized purified material. It is suitable to use synthetically obtained substance for comparison.

Analyzed Diolefins

		Br Number according to McIlhiney				Reaction with 4.5 n HBr	Oxidized with excess of neutral KMnO$_4$ at 0°C. gives
		Addition		Substitution			
		Calc.	Found	20°	40°		
Butadiene	$c = c - c = c$	592	--	--	--	No reaction	Not tested
Piperylene	$c = c - c = c - c$	470	450	10	--	Polymerizes	Not tested
Isoprene	 $c = c - \overset{c}{c} = c$	470	410	40	--	Polymerizes & dissolves partially	Not tested
2,3-Dimethylbutadiene x	 $c = \overset{c}{c} - \overset{c}{c} = c$	390	--	--	--	--	Not tested
3-Methylpentadiene-1,4 x	 $c = c - \overset{c}{c} - c = c$	390	370	30	--	Polymerizes	Not tested
Cyclopentadiene x		485	485	50	--	Resinifies	Not tested
Sym. Methylcyclopentadiene xx		400	--	--	--	Resinifies	Not tested

x Synthesized according to literature
xx Synthesized in a new way

Analyzed Diolefins
(Continued)

		Br Number according to McIlhiney				Reaction with 4.5 n HBr	Oxidized with excess of neutral $KMnO_4$ at 0°C. gives
		Addition		Substitution			
		Calc.	Found	20°	40°		
2-Methylcyclopentadiene		400	--	--	--	Resinifies	Not tested
3-Methylcyclopentadiene xx ?		400	--	--	--	Resinifies	Not tested
Dihydrobenzene		400	--	--	--	Polymerizes	Not tested

Dr. W. Stoess
Analyses: Miss Hedwig Lotz

Commission Report, December, 1935 - Dr. Friedrichsen
Project: Cracking Experiments

Separation and Identification of Dienes from Cracked Gasoline

Cracked gasoline is separated into cuts of about 20°; to each cut is added gradually with good shaking 1% maleic anhydride and left to stand for 3-4 days.

The gasoline is then distilled in vacuum at water bath temperature, the residue is dissolved in K_2CO_3 solution and the solution extracted with ether. By acidification and further extraction with ether the addition acids are obtained as oils. The alkaline ether extract is discarded; it contains no acids.

On vigorous frequent shaking about 20-25% tetrahydroacids crystallize after standing for 8-14 days.

Crystals A Mother Liquor B

Working Up and Identification of A.

Separation of the crystalline mixture A by crystallizing from various solvents:

Identification is carried out:

1) by comparison with synthetically prepared material,
2) by bromine dehydrogenation to phthalic acids,
3) by oxidation of the phthalic acids to the corresponding benzene carboxylic acids.

Dehydrogenation was attempted with bromine, sulfur and alkaline solution of potassium ferricyanide; the last two were found to be very little suitable.

The Bromine Method

The usual method of dehydrogenation of hydrogenated aromatic compounds (Willstadter and Einhorn: heating with the calculated amount of bromine to 200° in a sealed tube, yield 75 per cent) could be improved (yield 90-95 per cent) and was worked out for larger amounts.

New Method

Dissolve the anhydride in 5 times the weight of CCl_4, cool to 0°, add Br dropwise until saturation of the double bonds. Distill off the CCl_4 and heat until mass starts to boil, HBr splits off. Now CCl_4 and excess of Br is added. Evaporate the solvent and distill the residue. The unknown phthalic anhydride crystallizes at once. If possible, identify by comparing with homologues of phthalic acid or

Oxidize

with $KMnO_4$ in alkaline solution to benzene carboyxlic acid. Identify by means of the characteristic methyl esters.

Mother Liquors B

The oily mother liquors can be converted by Br in a large part to crystallized phthalic acids. Identification same as above.

Determination of Dienes in a Tar from Low Temperature Carbonization, Fraction 60-80°C.

Sample 3297 g. From this 181 g. oily addition acid corresponding to 2.3 per cent hexadienes was obtained by four additions. 36 g. of crystals were separated from the oily product corresponding to 20 per cent of the addition acids.

	M.P.	g.	Percentage of Amount of Crystals	Diene as Butadiene	Manner of Identification
Addition 1	220°	4.0	About 10%	1,1-dimethyl?	Degradation and oxidation
	187°	11.6	About 33%	2-ethyl-	"
	147°	1.0	About 3%	1,2-dimethyl-	"
Addition 2	154°	12.3	54%	1-ethyl	Degradation and oxidation
Addition 3	154°	4.5			
Addition 4	154°	2.0			

Determination of Dienes in a Propane Oil

Sample 4580 g. From this 100 g. oily addition acid corresponding to 0.8 per cent pentadienes was obtained. 27.1 g. crystals were separated consisting of 38 per cent isoprene maleic acid addition product and 62 per cent piperylene maleic acid addition product.

Determination of Dienes in a Cracked Gasoline Fraction 80-100°C.

Sample 12164 g. From this 742 g. oily addition acid corresponding to 2.5 per cent hexadienes was obtained by four additions. 169 g. crystals were separated from the oily product amounting to 22.8 per cent of the addition acids.

	M.P.	g.	Percentage of Amount of Crystals	Diene as Butadiene	Manner of Identification
Addition 1	207°	0.8	0.5%	cyclic C_6H_8	
	164°	small amt.	--	C_6H_8	
	147°	18.7	45%	1,2-dimethyl-	Crystal form, mixed melting point
	147°	55			
Addition 2	162°	40	24.5%	1,3-dimethyl-	Degradation and oxidation
	174°	small amt.	--	?	
Addition 3	172°	15	9%	1,4-dimethyl-	Degradation and oxidation
	154°	23	21%	1-ethyl	Crystal form, mixed melting point
Addition 4	154°	10,7			

Volumetric Determination of Dienes

Dr. W. Friedrichsen

This method uses the property of maleic anhydride to add to dienes and to form tetrahydrophthalic anhydrides. Compared with other methods using the same principle, it permits the exact determination of dienes with a small number of C-atoms, like butadiene, isoprene, piperylene, etc. The method depends on the observation that the velocity of hydrolysis of maleic anhydride is much greater than of the tetrahydrophthalic anhydrides formed in the reaction.

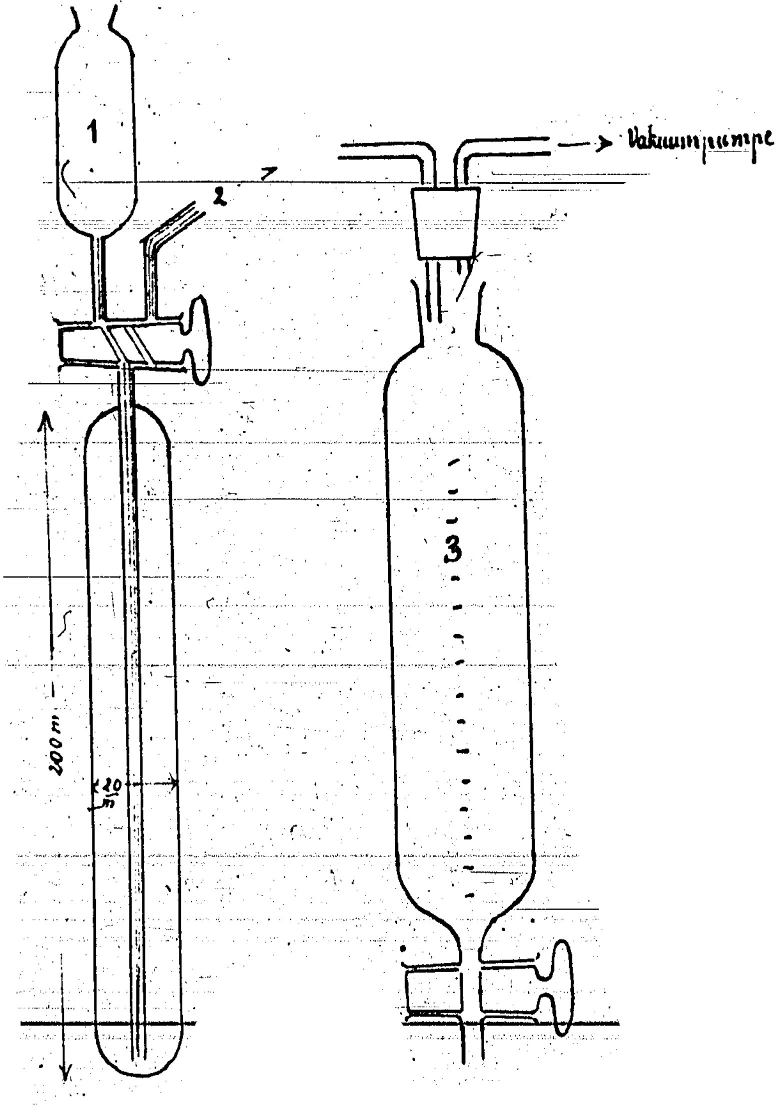
Experimental:

The weighed sample containing dienes is reacted in a tube at ordinary or elevated temperature with an excess of a standardized solution of maleic anhydride in a dry water-insoluble organic solvent such as benzene or toluene. The unreacted maleic anhydride is washed out with water and determined volumetrically. The small amount of tetrahydrophthalic anhydride which dissolves is determined separately (after removal of the maleic anhydride) by a repeated treatment with water and subtracted. The method is accurate for ±0.1 to 0.2 per cent.

Example:

For the analysis, a solution of about 50 g. freshly distilled maleic anhydride is required; small amounts of undissolved material are filtered off. The factor of the solution is determined by shaking with water under exactly the same conditions as the execution of the analysis described below. The factor of the solution should be checked from time to time because it changes gradually due to some evaporation of the solvent.

Two grams of isoprene are weighed into a 25-cc. volumetric flask and filled to the mark with dry benzene. Two cc. of this solution (corresponding to .16 g. isoprene) are mixed in flask 1 with 10 cc. of maleic anhydride solution (equivalent to 108.8 cc. n/10 NaOH) and sucked into the evaporation tube (see illustration). Flask 1 is rinsed out several times with dry benzene and then the three-way cock (which is lubricated with a trace of vaseline) is fastened so tight that it cannot be loosened without applying heat. The tube is then heated to 80° in a constant temperature bath for 5 hours, with higher dienes correspondingly longer. When the reaction is complete, the three-way cock is loosened by heating it slightly with a flame, and by repeated rinsing with benzene the content of the tube is sucked through the attachment 2 into the cylindrical 250-cc. separatory funnel 3. To the benzene solution in the separatory funnel is now added 1.5-2 times the amount of pentane and 70 cc. of water and agitated on the shaking machine for 3 minutes. After separation of the aqueous layer, the operation is repeated under the same conditions three times with the same amount of water. All unused maleic anhydride is now as acid in the combined aqueous layers, plus small amounts of hydrolyzed tetrahydrophthalic anhydride. In order to determine this last amount, the benzene-pentane


1
2
Vakuumpumpe
3
200 m
20 m

solution is shaken once more with 70 cc. of water for 3 minutes, the aqueous layer titrated with n/10 NaOH and 4 times of this result is deducted from the result of the first titration. The number of cc. n/10 NaOH, which corresponds to the amount of maleic anhydride consumed, gives the amount of isoprene according to the formula:

$$\text{g. isoprene} = \frac{.34 \times \text{cc. n/10 NaOH}}{100}$$

It should be mentioned that it was found advantageous to titrate the solution of maleic acid with phenolphthalein as indicator by adding an excess of n/10 NaOH and back titrating to colorless with n/10 HCl.

March 21, 1939

Literature: Diazometric determination of diene hydrocarbons C R (Doklady) Acad. Sci. URSS (nS) 1935 IV 267-72 Moscow Academy of Science: shake the diene with standardized nitrophenyldiazonium-solution and titrate back the excess with n/10 betanaphthol solution.

Titration of dienes in fatty acids: Kaufmann and Baltes; Fette und Seifen 1936, Number 6-7, Page 93; solvent acetone, heating in tubes for about 24 hours, pouring into water and titrating.

USE OF RAMAN SPECTRA FOR THE DETERMINATION OF HYDROCARBONS

Report Dr. Timm and Dr. Stern
On Iso-octane-Leuna

Summary: April 14, 1938
August 25, 1938
March 20, 1939

The spectra of molecules, especially Raman spectra, became important lately, besides the usual physical constants, for the analysis and determination of constitution. We mentioned an example already in the determination of the three isomeric xylenes (enclosure, page 8). These aromatic compounds show especially strong and characteristic frequencies and permit the necessary accuracy. We used Raman spectra previously for the identification of normal hexanol in water gas pressure oils[1] through a suggestion of Dr. F. Winkler and also Dr. Timm in the Physical Laboratory of Dr. Hochheim, and we found that these spectra could be used to advantage for analytical determinations in cases where chemical methods fail and other physical constants are not characteristic enough. This applies especially to paraffin hydrocarbons, for instance the iso-octanes, for which purity specifications are especially rigid for aviation purposes.

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[1] Enclosure, page 39.

In order to use the Raman spectra successfully, a mixture of not more than three components should be used; technical products, therefore, must be split up by precise fractionation, and the spectra of these fractions determined and compared with pure compounds which were prepared synthetically. An extensive split-up into fractions often gives only a few cc., and the pure compounds can usually be synthesized in quantities of not more than 10-50 grams without excessive expenditure of work. Therefore, it was necessary that spectra should not use more than 10 grams with moderate time of exposure. The apparatus of Dr. Timm permits, if necessary the use of one gram.

The intensity of the Raman spectrum increases irregularly with increasing concentration, and with 50 per cent solutions reaches almost the maximum value of the pure compound. Low intensities can be made visible by longer times of exposure. In a similar way, the percentage of the compound in question can be determined in a mixture quantitatively. The exact comparison, by spectra, of an unknown mixture with known pure individual compounds presupposes a very exact measurement of the frequency of the individual lines. One determines then by comparison whether or not a known compound (which can be surmised because of physical or chemical facts) may be present due to the position and intensity of the individual lines.

Literature: Summarized description of Raman spectra.

K.W.F. Kohlrausch; Der Smekal-Raman-Effekt. Berl. 1931 Supplement
Volume 1931-37

F. Goubeau: in Boettgers Physik-Meth. d. Anal. Chemie Volume 3, Leipzig 1939

A. Andant: Application de la spectrographie Raman a l' analyse des essences minerales Publ. sci. Techn. Ministere de l' air, Paris No. 21, 1933 u. No. 99, 1936.

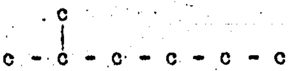
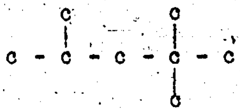
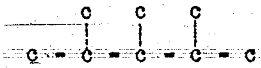
The summary on the next page shows a comparison of three technical iso-octanes:

I - iso-octane polymerized with phosphoric acid O.N. 97

/ II - iso-octane polymerized with sulphuric acid O.N. 100

III - iso-octane by depolymerization of triisobutylene O.N. 91

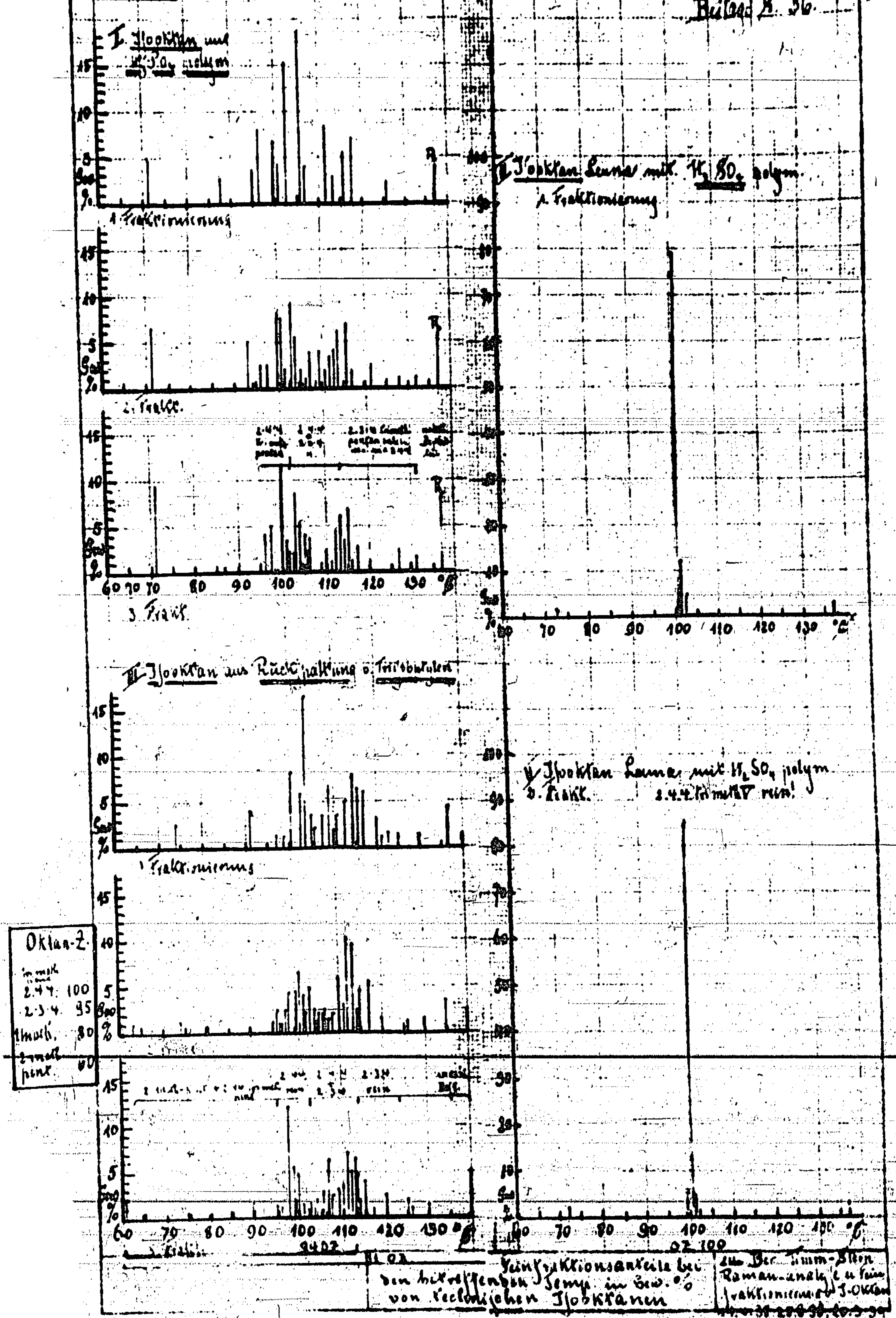
The three samples were precision fractionated by means of the Oppau attachment. I and III were fractionated three times; II, which was already very pure, twice. The cuts in weight per cent are plotted in the summary as columns above the respective temperature. The cuts of I and ~~III are very similar; I had a larger forerun than III; the latter has a~~ larger heavy fraction. Both represent in their main cut a mixture of 2,4,4- and 2,3,4-trimethylpentane and the latter is present in larger amounts in III than in I. The Raman spectra of III were determined by Dr. Timm especially carefully. The forerun very probably is 2-methylpentane. The heavy fractions of I and III consist of two unknown compounds which cannot be derived from triisobutylene. One of them, which is common to both, shows little branching; the second shows more branching; and the latter, which is present in each, is different in I and III. The determination of the refractive indices (see below) confirmed the presence of 2-methylpentane and 2,3,4-trimethylpentane in addition to 2,4,4-trimethylpentane. The presence of the 2,3,4-trimethylpentane can be explained by retropinacoline rearrangement of substituted hydrocarbons with quaternary carbon (see enclosure, page 12) and by the higher temperature of the polymerization with phosphoric acid; 2,3,4-trimethylpentane is very symmetrical and, therefore, very stable.

 $c-\overset{c}{\overset{\vert}{c}}-c-c-c-c$	O.N.	60 x 5%	calc. O.N.= 3	
 $c-\overset{c}{\overset{\vert}{c}}-c-\underset{c}{\underset{\vert}{\overset{c}{\overset{\vert}{c}}}}-c$	O.N.	100 x 40%	calc. O.N.=40	III according to the fractionation analysis and Raman investigation estimated values.
 $c-\overset{c}{\overset{\vert}{c}}-\overset{c}{\overset{\vert}{c}}-\overset{c}{\overset{\vert}{c}}-c$	O.N.	95 x 45%	calc. O.N.=40	
Unknown tail	O.N.	80 x 10%	calc. O.N.= 8	
			91 Octane Number	

Note: 2-methylhexane is shown structurally whereas 2-methylpentane is mentioned in the text.

Vertraulich.

Beilage N. 36



Oktan-Z.	
Trimethyl	
2.4.4.	100
2.3.4.	95
1 methyl	80
2 methyl pent.	60

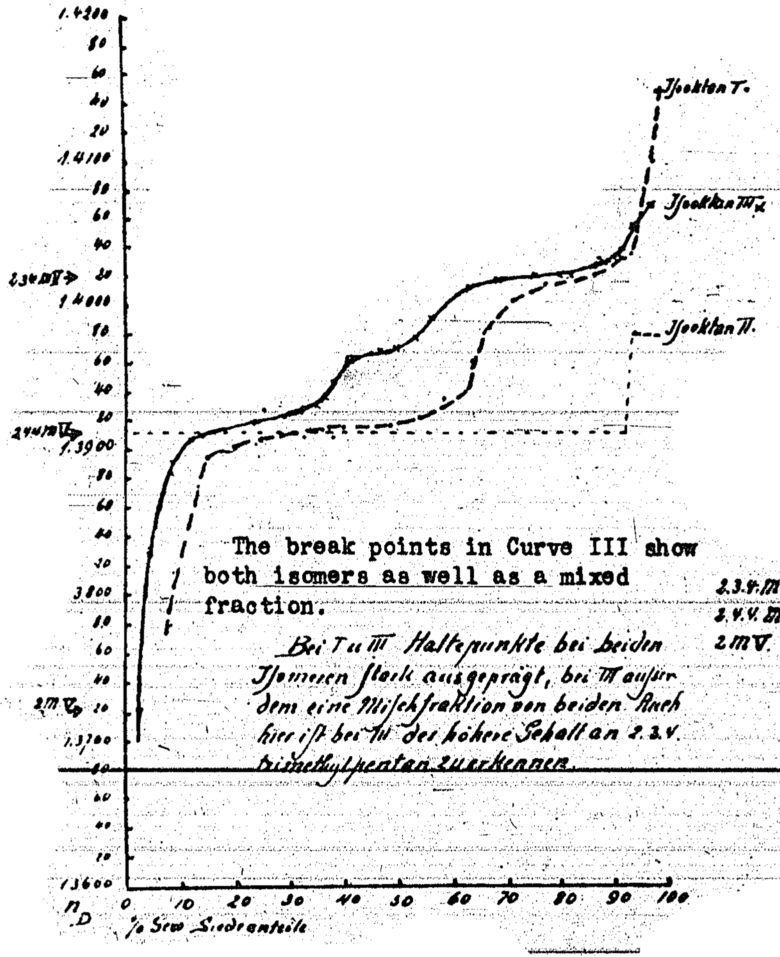
Feinfraktionsanteile bei den betreffenden Temp. in Gew. % von technischen Isooktanen

[illegible] Raman-analyse u. Feinfraktionierung J-Oktan

Refractive Index vs. Boiling Range of Fraction
Leuna Isooctane

Änderung des Brechungsindex mit der Summe der Siedeanteile von Jsooktan Leuna

I. II. III



The break points in Curve III show both isomers as well as a mixed fraction.

Bei I u III Haltepunkte bei beiden Jsomeren stark ausgeprägt, bei III außerdem eine Mischfraktion von beiden. Auch hier ist bei III der höhere Gehalt an 2.3.4 trimethylpentan zu erkennen.

			n_D
2.3.4. MV	2.3.4.	Trimethylpentan.	1.4020
2.4.4. MV	2.4.4.	"	1.3916
2 MV.		2 Methylpentan	1.3720

Dr. Timm.
25.8.38

SEPARATION OF MIXTURES

METHOD OF EXAMINATION

The pressure oil of 1005 was first examined, and in the report of December 3, 1935, part of the results and the methods used were described. The pressure oil contained free acids and alcohols as well as esters. The acids, alcohols and esters were saponified together and then separated from each other. The pressure oil of 997 was first precision fractionated. The small intermediate cuts were added to the main cuts, and in these cuts the free alcohols were converted into ester acids by heating with a small excess of phthalic anhydride, either by boiling under reflux for six hours or in a sealed tube at about 120°. The fractions distilling up to 150° were separated by distillation from the phthalic ester acids. In order to avoid a decomposition of the ester acids formed, the high boiling cuts were converted by diazomethane to the mixed esters of phthalic acid which can be distilled without decomposition and can, therefore, be separated by fractionation even for high boiling cuts. With larger amounts (more than 10 grams), treatment with calcium metal converted them into the calcium salts of phthalic ester acids. The calcium salts precipitated as solids and were filtered and washed with ether, then decomposed by water into alcohols and separately recovered. The mixed methyl esters were decomposed with sodium hydroxide and the alcohols, mixed with methanol, obtained. Using the diazomethane method, any methanol present cannot be determined, and we therefore preferred the calcium method in the course of our investigation. After separation of the free alcohols, the esters which still remained in the oil were saponified with sodium hydroxide and the liquor freed from oil by the use of pentane. The liquor was acidified and the acids extracted by ether. The pentane contains ester alcohols as free alcohols in addition to olefin and paraffin; and these are determined as mentioned before. The olefin and paraffin fractions which boil at 100° and higher are now combined and again precision fractionated. In the cuts thereby obtained, the olefins were converted into the bromides by saturating with HBr gas and allowing them to become warm, and then they were separated from the paraffin by fractionation. The fractions boiling below 80° were examined with the V-tube method described previously (January 20, 1935)[1], first treating with 4.5 n HBr and washing with water, then using 8 n HBr, distilling off of the paraffins, washing with water, and determining the decomposable bromide. These experiments showed that the addition of HBr, using 4.5 n HBr is incomplete from the heptenes on. It is necessary to use at once 8 n or gaseous HBr. Therefore, one obtains the isobutylene and the isopropylethylene group together. The rearrangement of the tertiary-butylethylene and the decomposition, at room temperature, of the resulting tertiary alcohol into olefin and water is still obtained with the octylenes. This is important for the detection of diisobutylene in the cuts. From the heptenes on, the boiling points of the bromides are closer to the boiling points of the respective paraffins, and it is therefore to be recommended to use a fractionating attachment for the separation.

Identification: (Compare report of December 3, 1935.)[2]

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[1] Compare Enclosure, Page 9.

[2] Compare Enclosure, Page 43.

Alcohols: The lower alcohols up to C_5 are separated according to the known methods and identified through their a-naphthylisocyanate. To ascertain the primary normal hexyl alcohol, we compared the Raman spectra of synthetic material with a product obtained with contact (catalyst) Fe_{997}. This method, worked out by Dr. Timm at Dr. Hochheim's laboratory at the suggestion of Dr. F. Winkler, made it possible to ascertain that no other alcohols, especially no isohexyl alcohols, were present.

Acids: The lower acids up to C_5 are separated by fractionation of the free acids, then identified as silver salts and analyzed. There was no indication of iso-acids. The higher acids were converted with diazomethane to the methyl esters. These were fractionatad and analyzed.

Olefins: Up to the heptenes, separation was carried out by means of the V-tube analysis and elementary analysis of the bromides obtained. With the higher members, separation of olefin and paraffin was carried out by means of HBr, fractionation and analysis of the bromides. Here the methods of determination can probably be further improved through Raman spectra if a sufficiently large number of spectra of synthetic compounds are known. Bromides, however, are not suitable for this. They decompose in light and extinguish the Raman lines because of their continuous spectrum.

Determination of Higher Alcohols

C_3 and C_4

Method Dr. Friedrichsen

Sixteen grams of an alcohol mixture are mixed with 150 cc. fuming hydrobromic acid (specific gravity 1.78) in a flask with an Oppau fractionating attachment and heated to boiling, using toluene as the bath liquid. The temperature of the bath is slowly increased during one hour from 20° to 100°C. The bromides which distill off are collected in two wash bottles containing a little water, which are connected to each other and cooled with ice. The bromides are separated in a separatory funnel, washed again with about the same amount of water, and are then dried with a few granules of calcium chloride. The individual bromides are separated by fractionation using a small Oppau attachment. It is advantageous to add 15 grams of pseudocumene or a similar high boiling hydrocarbon before fractionation is started. Fractionation is conducted so that first the temperatures on the attachment are kept somewhat lower than the respective boiling point of the particular bromide. As soon as the velocity of distillation becomes small, the temperature is put higher as the table shows.

		Starting Temperature	Final Temperature
For the bromide of:	Ethanol	38°	44°
	Isopropanol	55°	57°
	n-Propanol	70°	72°
	Isobutanol	90°	92°
	n-Butanol	Residue boiling above 92°	

Every fraction is considered complete if less than one drop per minute distills over. The bromide obtained is weighed and the loss in weight of the distilling flask is determined each time. Ethanol can only be determined by difference. Error ±1 per cent with reference to the mixture. Example:

	Used	Found	
Ethanol	68.8 %	69.5	(by difference)
Isopropanol	18.7	18.0	
n-Propanol	12.5	12.5	
Ethanol	18.25	16.6	(by difference)
Isopropanol	18.75	18.6	
n-Propanol	18.75	19.5	
Isobutanol	18.75	18.5	
n-Butanol	25.00	26.3	
Water	0.5	0.5	

Methods of Determination:

1. Determination of water with phthalic anhydride (freshly recrystallized and finely pulverized).

One-half to one gram of isobutyl alcohol is heated with 1 cc. of benzene in a steam bath in a small sealed test tube (10 x 100 mm.) for 12 hours. Then the test tube is cooled, well dried, opened into an Erlemeyer flask which can be tightly closed and which was flushed with dry nitrogen. The contents of the Erlemeyer are left to crystallize by cooling to 0°. Then 80 cc. of benzene are added and the mass is warmed on a steam bath for a short time with shaking and then again cooled to room temperature. The precipitate formed is separated on a glass filter crucible (1G4), washed with 20 cc. of cold benzene, dissolved in hot water and the solution titrated with n/10 sodium hydroxide. (The freezing out described above avoids supersaturation of phthalic acid in benzene.) Error 0.15 to 0.3 per cent.

Alcohol Number (with Phthalic Anhydride and Diazomethane)

(Diazomethane preparation Z. fur angew. ch. 1930 No. 22 and 1933 No. 2)

One-quarter to one-half gram of alcohol is esterified with excess anhydride as described above, but without addition of benzene. To the opened tube in a 250 cc. flask which has been well flushed with dry nitrogen, are added successively and with shaking, small amounts of diazomethane until it is dissolved and the yellow color persists for some minutes.[1]

Ether and diazomethane are now distilled off (they may be used for further determinations). To the residue in the flask are added about

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[1] With too long contact time of phthalic anhydride and excess diazomethane, losses of phthalic acid occur through a reaction between them.

100 cc. of water, the mass is heated on a water bath for about 15 minutes and titrated warm with n/10 sodium hydroxide. Titration is carried nearly to the end point, then 2-3 cc. of sodium hydroxide excess are added, well shaken and titrated back with n/10 hydrochloric acid. Considering the amount of water determined separately according to 3, the amount of alcohol is calculated.

Alcohol Identification

The oil freed from acids is dried with solid KOH, and heated in a water bath for 5-6 hours with phthalic anhydride. The half esters formed are converted with diazomethane into the mixed phthalic esters, the excess of anhydride removed cold with dilute caustic, then dried and distilled. Phthalic esters stay behind and can be separated from any resin formed by vacuum distillation. The esters are then saponified, extracted with pentane and combined with the alcohols which were obtained before with pentane (see acid determination). Then they are precision fractionated. The individual cuts are converted into the naphthyl isocyanates and the crystalline compounds obtained are exactly identified by melting point and analysis.

Pressure Oil from CO and H_2, Determination of Acid

To the oil is added an excess of solid KOH and some methanol, and the mixture heated for some hours under a reflux. After cooling, water is added, then the oil washed with water. To remove the alcohols, the alkaline solution is extracted with pentane in which the higher fatty acids are much less soluble than in ether. The solution is then acidified, the acid solution extracted with ether and then treated for several days with ether. The first portion of ether contains the monocarbonic acids, the second portion the dicarbonic acids (if they are present). Both ether solutions are then freed from ether in the precision fractionation apparatus and the ether tested for acid. The residue (it amounted to about 10-15 grams) was distilled off with a small precision fractionation attachment at 140°C. Acetic acid and propionic acid come over (see table); the higher acids stay behind and are converted into the methyl esters with diazomethane. The distilling off of acetic acid and propionic acid has the purpose of avoiding losses of the low boiling methyl esters. The methyl esters are fractionated after the ether has boiled off. The cuts of the acids and of the methyl esters are converted into the silver salts, and these are tested microscopically and with elementary analysis for normal and iso acids.

December 3, 1935

Stern

Watergas Pressure Oil Li

Analysis of the acids (Free acids and esterified acids determined together) from oil above 100°C. = 38.5 per cent to 225° + 9.0 per cent over 225°.

I. Fractionated as free acids - analyzed as silver salt

Acid Fraction °C	g	Per Cent C	Per Cent Ag	
	----	19.9	59.4	theor. C_3 Propionic acid
To 125	6.3	21.05	56.2	46% C_4 Calculated from C content
-144	9.8	21.31	56.7	46% C_4
-155	5.7	22.3	56.7	50% C_4
		24.5	55.0	theor. C_4 Butyric acid

II. Fractionated as methyl esters and analyzed

Ester Fraction	gms.	Per Cent C	Per Cent O	Molecular Weight	
To 84	0.34	--	--	--	
-95	4.66	63.08	24.6	82	Calculated as C_3 (still containing ether)
-104	0.4	--	--	--	
(102)	--	58.8	31.3	102	theor. C_4 Butyric ester
-120	1.39	59.46	30.38	100	20 per cent C_5
(127)	--	62.0	27.5	116	theor. C_5 Valeric ester
-135	14.73	62.95	26.81	114	40 per cent C_6
-143	0.67	--	--	--	
-156	2.83	64.43	24.69	125	95 per cent C_6
(150)	--	64.6	24.6	130	theor. C_6 Caproic ester
-165	0.62	--	--	--	
-170	0.72	--	--	--	
-175	6.97	65.69	23.08	131	50 per cent C_7
-182	2.31	66.45	22.62	137	90 per cent C_7
-185	0.79	--	--	--	
(170)	--	66.7	22.2	144	theor. C_7 Oenanthic ester
-195	4.08	67.69	21.3	145	60 per cent C_8
-200	0.72	68.12	20.59	150	85 per cent C_8
(190)	--	68.4	20.3	158	theor. C_8 Caprylic ester
-208	3.34	69.04	20.01	165	45 per cent C_9
		69.8	18.6	172	theor. C_9 Pelargonic ester
10 mm. 127	4.2	70.45	18.15	165	60 per cent C_{10}
" 130	2.0	--	--	--	
	--	70.9	17.3	186	theor. C_{10} Capric ester
" 157	4.15	72.23	15.68	186	30 per cent C_{11}
" 175	1.8	--	--	--	
	--	72.0	16.0	200	theor. C_{11} Undecylic ester
	--	72.8	14.95	214	theor. C_{12} Lauric ester
" 182	7.5	73.4	14.65	212	30 per cent C_{14}
	--	73.2	14.0	228	theor. C_{13} Tridecanoic ester
" 187	1.8	--	--	--	
" 193	0.6	--	--	--	
" 208	4.3	75.05	13.0	255	
	--	75.0	12.48	256	theor. C_{15} Pentadecanoic ester
2 mm. 180	2.45	76.48	11.58	301	
0.4 " 208	3.65	77.73	10.29	330	
R	5.9	--	--	--	

Experiments Li
October 28, 1936
Storn

~~III.~~ Separated as acids and analyzed as silver salt (from oil above 200° = 9 per cent)

Fraction of Oil	Amount g.	C Per Cent	Ag Per Cent	
		32.3	48.2	theor. C_6 Capric acid
20 mm. 75-102	~~4.7~~	33.75	46.7	45 per cent C_7
		35.4	45.4	theor. C_7 Oenanthic acid

IV. Separated as acid and analyzed as such

Fraction of Oil	Amount g.	Per Cent C	Per Cent O	Molecular Weight	
20 mm. 102-107	1.96	61.07	27.8	--	70 per cent C_6
-113	2.1	61.48	28.08	112	85 per cent C_6
	--	62.0	27.5	116	theor. C_6 Caproic acid
-125	3.45	63.28	25.76	126	50 per cent C_7
-162	7.0	64.45	24.81	138	95 per cent C_7
	--	64.6	24.6	130	theor. C_7 Oenanthic acid
-180	3.23	65.87	23.39	149	60 per cent C_8
-185	2.13	65.21	24.1	--	30 per cent C_8
		66.7	~~22.2~~	~~144~~	~~theor. C_8 Caprylic acid~~

V. Separated as acid and fractionated as methyl ester

Ester ~~Fraction~~					
		66.7	24.1	144	theor. C_7 Oenanthic ester
14 mm. -120	0.8	66.85	21.97	--	10 per cent C_8
	--	68.4	20.3	158	theor. C_8 Caprylic ester
	--	69.8	~~18.6~~	172	" C_9 Pelargonic ester
-130	1.37	70.33	17.97		about 50 per cent
	--	70.9	17.3	186	theor. C_{10} Capric ester
-147	0.72	71.52	16.91		about 50 per cent
		72.0	16.0	200	theor. C_{11} Undecylic ester
		73.2	14	228	" C_{13} Tridecanoic ester
-155	0.89	74.03	14.04		
		74.5	13.2	242	" C_{14} Myristic ester
		75.0	12.48	256	" C_{15} Pentadecanoic ester
-165	0.35	75.32	12.73		
-180	0.30	76.6	11.12		
		76.6	10.75	298	" C_{18} Stearic ester
R	1.4	Solid containing asphalt			

Experiments Li
October 28, 1936
Stern

Watergas Pressure Oil Li

Summary of the Alcohols

I. Primary

Per cent Reference to Total Oil		°C.	g.	g.	C Per Cent	O Per Cent	
2.76	Methanol	105-115	.01	.03	61.84	24.88	Propyl-Butyl mixture
		138-142	.03	.02	62.85	23.63	
5.23	Ethanol			--	65.0	21.6	C_4 n-Butyl-
				--	70.8	15.6	C_6 n-Hexyl-
1.0	Propanol	-163	.01	.07	70.85	15.52	
				--	72.6	13.8	C_7 n-Heptyl-
0.2	n-Butanol	177-185	.08	.07	73.56	12.62	
				--	73.9	12.3	C_8 n-Octyl-
0.2	n-Amyl alcohol			--	76.1	10.15	C_{10} n-Decyl-
		190-200	.07	.06	76.26	10.06	
0.23	Alcohol -200°/760			--	77.0	9.35	C_{11} n-Undecyl-
				--	80.0	5.92	C_{18} n-Octodecyl-
0.30	Alcohol 140/3		I	II			
3.2	Higher						

I from Fraction above 200 at 20 mm. 102-185°C

II. Secondary ?

II from Fraction above 200 at 20 mm. 75-102°C

III. Tertiary

2.36 tertiarybutylalcohol
as ester

IV. Water in Alcohols
3.88 per cent

Experiments Li
October 28, 1936
Stern

Watergas Pressure Oil Li

Analysis of the Oxygen-free Hydrocarbons

°C Fraction	Portion Referred to Total Oil		Ester %	Olefin n - %	Isoolefin I - %	Isoolefin II - %	Paraffin %
To 20	20.6	(C_3	--	16.3	--	--	10.3)
		(C_4		36.0	9.0	--	23.5)
-25	10.0	(C_4	--	37.0	12.5	--	20.7)
		(C_5		13.0	3.5	6.5	6.8)
-30a	5.4	(C_4	--	5.5	14.5	--	--)
		(C_5		16.5	4.5	10.0	--)
-30b	3.6	C_5	--	55.0	10.0	10.0	25.0
-36	2.3	)C_5	--	15.0	15.0	10.0	25.0
-40	0.07	)					
-45	0.38	)					
-50	0.6	)C_6	20	45.0	--	10.0	25.0
-55	0.87	)					
-57	0.45	)					
-60	2.7	)C_6	35	25.0	--	10.0	30.0
-62	1.3	)					
-66	0.07	)C_6	23	37.0	--	15.0	25.0
-67	0.11	)					
-68	1.8	)					
-70	0.19	)					
-74	0.35	)C_6 &	50	30.0	--	--	20.0
-78	0.23	)C_7 in-					
-80	0.26	)cluding					
-84	3.62	)alcohol					
-85	0.43	)and					
-86	0.09	)acid					
-87	0.03	)					
-89	0.3	)					
-102	4.65	)C_7					

Experiments Li
October 28, 1936
Stern

Watergas Pressure Oil Li

Analysis of the Oxygen-free Hydrocarbons Fraction 100-200°C - 38 per ct

I Fract. °C	II Fract. °C	Vacuum Fractionation of the Bromides %	°C.	mm	g	% C	% Br	Mol Wt.	% Olefin	% Paraffin
100-150	---	5.32	Not separated				--	---	1.32	4 From Br No.
150-175	150-181		127	20	2.55	65.02	22.9	---	60% Bromide	
	-176	2.8	80	15	4.55	---	--	150		
	-181	0.19	96	7	10.30	54.8	35.7	---	30% C_{11}	
						54.2	36.2	142	theor. C_{10}	
	R	/	R		1.53	--	--	--	--	
186-187	181-89		80	10	7.97		about 13		30% Bromide	
	-185	0.19	104	10	5.49	55.16	35.3	--	50% C_{11}	
	-187	2.37	110	10	2.55	55.6	34.8	--	75% C_{11}	
	-189	0.63				56.1	34.1	156	theor. C_{11}	
			124	10	1.02	--	--			
			125	5	0.83	--	--			
			R		0.62	--	--			
202-204	189-208		90	10	5.52	--	--	168		
			104	10	2.25	65.49	22.7	--	P. 66% Bromide C_{12}	
	-195	0.67	110	10	1.73	--	--			
	-208	2.82				57.8	32.2	170	theor. C_{12}	
			117	10	5.57	58.15	32.0	--	20% C_{13}	
			125	5	4.52	58.76	31.0	--	60% C_{13}	
			R		0.6	--	--	--		

Fraction over 200 (223) = 9 per cent.

°C	mm	g	Br No.
- 94	22	3.65	48
-111	22	2.75	48
-120	22	3.20	48
- 90	7	12.70	48
-108	7	8.4	44
-111	6	7.7	42
-123	6	3.65	44
-123	0.6	10.55	37
-125	0.6	2.55	30
-145	0.6	21.1	23
-190	0.6	1.7	7
R		37.3	

Part of the bromide obtained with HBr is soluble in HBr

About 50% olefin, 50% paraffin

The bromide obtained with HBr is soluble in HBr

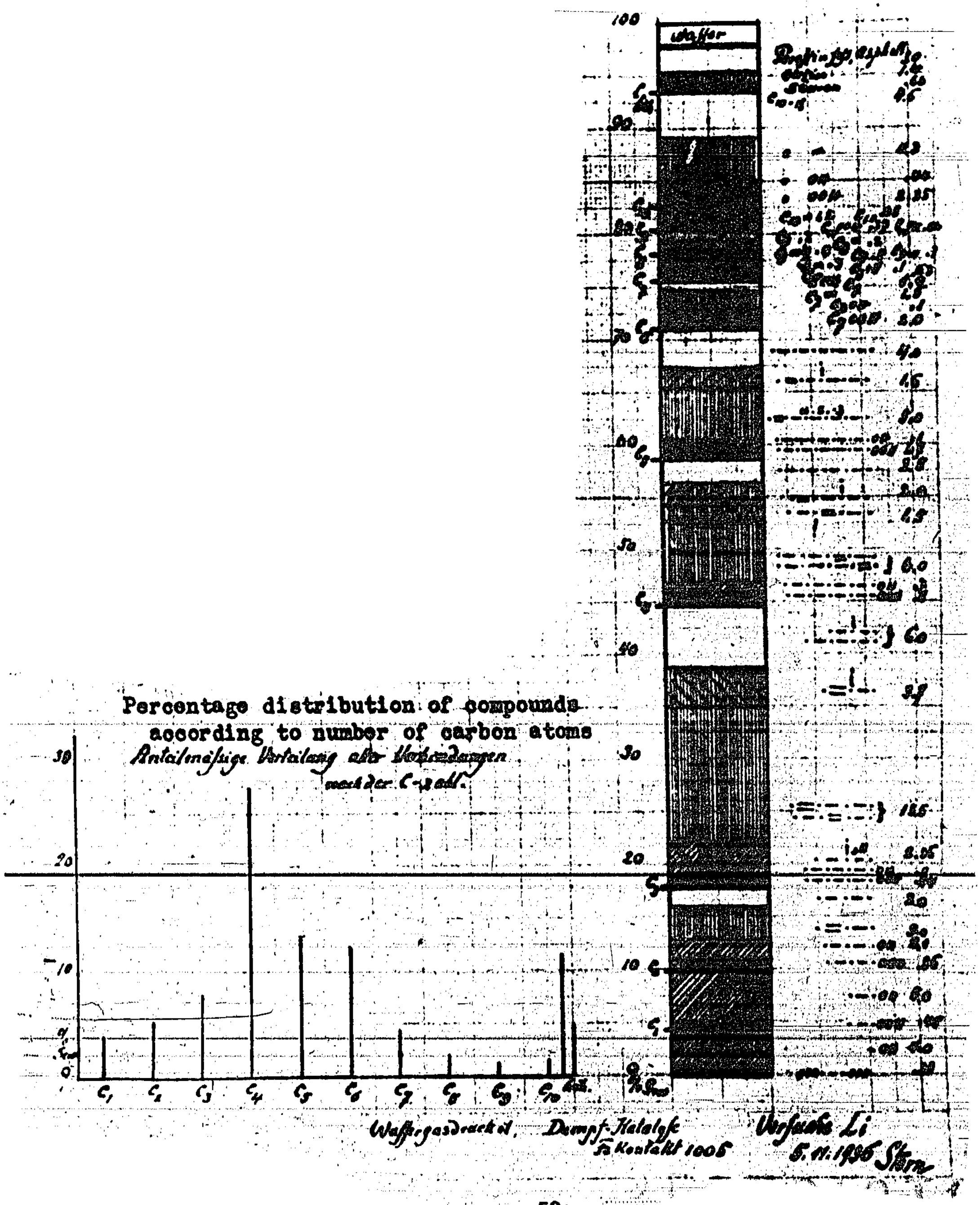
About 50% olefin, 50% paraffin, 6% acid, 10.6% paraffin, 5.7% asphalt, 4% insoluble

October 28, 1936
Stern

I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT LUDWIGSHAFEN A. RH.
Stickstoff-Abteilung

Summary of the Components of Water Gas Pressure Oil Li
Iron Catalyst 1005

Übersicht der Zusammensetzung von Wassergasdrucköl Li
Fe-Kontakt 1005



Percentage distribution of compounds according to number of carbon atoms
Anteilmäßige Verteilung aller Verbindungen nach der C-Zahl.

Wassergasdrucköl, Dampf-Katalyse Fe Kontakt 1005

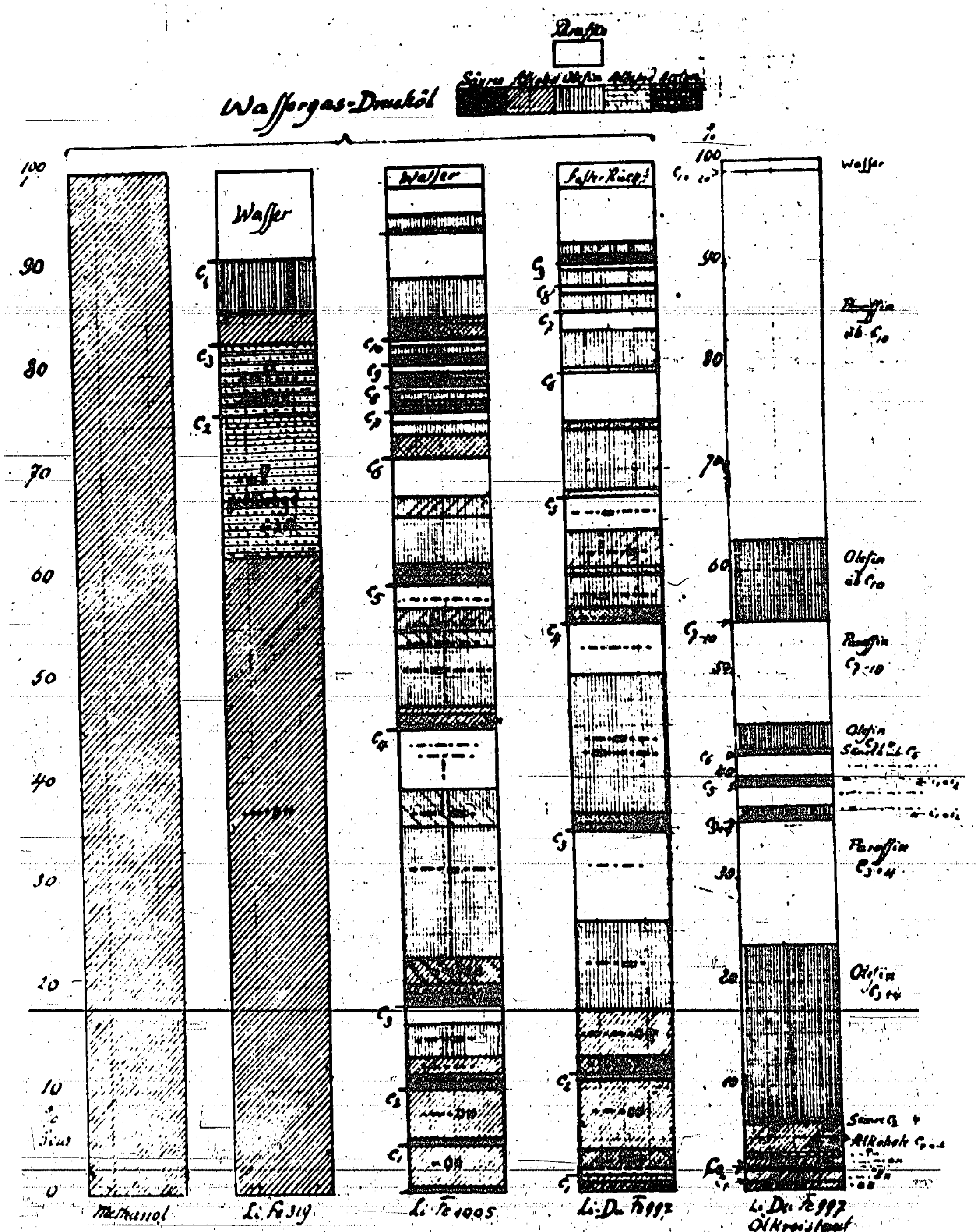
Versuche Li
5.11.1936 Stern

Bl. 551

Components of Water Gas Pressure Oils

Zusammenstellung aller Wassergasdrucköle

Aachlr z Ber 25 11 36 Stein



Zusammenstellung aller untersuchten Wassergasdrucköle

ITEM 13: Paper by K. B. Metzger, March 13, 1940, "On the Change of Explosive Limits of Ethylene and Ethylene Oxide-Oxygen Mixtures by Adding Nitrogen and CO_2, respectively (16 Pages)

The summary of this paper is as follows:

After a study of the literature and experiments in the Union Calorimeter it was concluded that

(1) The explosion limits of C_2H_4-oxygen mixtures are 3.0 to 78 per cent C_2H_4 and ethylene oxide-oxygen mixtures are 2.5 to 99.95 per cent ethylene oxide. These limits apply at room temperature, normal pressure and gas saturated with water vapor at 20°C. This is a considerably higher upper explosive limit for ethylene oxide than is recorded in the literature.

(2) The extinguishing effect of N_2, CO_2 and C_2H_4 on ethylene oxide flames was proven and data is shown in attached tables and curves. Similarly, the extinguishing effect of CO_2 and nitrogen on ethylene flames was recorded.

(3) A discussion of the new explosive limits as applied to the process of direct oxidation of ethylene to ethylene oxide is included. Tabulated results, graphical results and a drawing of the apparatus is attached.

ITEM 14: A Paper by Dr. Jannek, May 24, 1940, "The Synthesis and Conversion of Simple Hydrocarbons" (15 Pages)

This is an elementary discussion of (a) conversion reactions including cracking, dehydrogenation, olefin hydrogenation, isomerization, cyclization and aromatization; and (b) synthesis reactions including polymerization and alkylation. Conventional catalysts and operating conditions are included and structural illustrations given.

ITEM 15: Monthly Summary of Plant Group A, February, 1944 (4 Pages)

Similar to Item 1.

ITEM 16: Monthly Summary of Plant Group B, February, 1944 (1 Page)

Similar to Item 2, Part 3.

ITEM 17: Monthly Summary of Plant Group C, February, 1944 (2 Pages)

Similar to Item 2, Part 2.

ITEM 18: Monthly Summary of Plant Group D, October, 1943 (1 Page)

Similar to Item 4.

ITEM 19: Plant Report for September, 1943 (7 Pages)

Similar to Item 2.

ITEM 20: Monthly Summary of Plant Group C, October, 1943 (1 Page)

Similar to Item 2, Part 3.

ITEM 21: Monthly Summary of Plant Group B, August, 1943 (2 Pages)

Similar to Item 2, Part 3.

ITEM 22: Paper by F. Winkler, July 26, 1939, "Ethylene Enrichment by Alkali Copper Wash of Gas Mixture Obtained by Hydrogenation of Electric Arc Acetylene" (5 Pages)

A summary of this paper is as follows:

During the months March and April, 1938, tests were carried out to enrich the ethylene by hydrogenation of arc acetylene (see report of Dr. Hirchbach of 5-25-38). Thereby, it was found that besides ethylene carbon monoxide was also enriched.

Summary of the results of the continuous test from 4-18 to 5-22, 1939:

(1) The enriching of the ethylene and carbon monoxide at the same time, as found in former tests, was confirmed.

(2) We succeeded in separating by use of copper wash 97 per cent of the ethylene present in the charge gas as rich gas (olefin gas + intermediate gas).

(3) The rich gas quantity amounts to about 27 per cent of the quantity of charge gas.

(4) Contrary to the operation with cracked gases free of carbon oxides, the copper content of the wash noticeably decreases after a few days of operation.

(5) The content of cupric copper stays constant. This shows that a reduction of cuprous copper to copper takes place through the influence of carbon oxides contained in the gas.

(6) A continuous olefin enrichment from CO-containing gases by alkali copper wash is only possible by continuously drawing off part of the wash and replacing it by fresh in order to keep the cuprous copper concentration constant.

The tests were discontinued before the best yields and most favorable operation conditions could be reached.

Test Conditions and Yields

Copper Solution Operation leach Me 106 with 9 to 10 wt.% of total copper and 3 to 4 wt.% of cupric copper

Pressure Washer: 15 atm.

Pressure Release Intermediate 1.8 atm.

Solution:Gas (in M^3) 1:6

	Charged Gas		Intermediate Gas	Olefin Gas		Rich Gas		Vent Gas
m^3/hr	10.0		0.5	2.2		2.7		7.3
Analysis (free of air) in Vol.%								
H_2	48.58		14.92	0.29		3.08		65.20
N_2	1.74		0.54	--		0.10		2.28
CO	2.28	27.99	2.47	9.13	97.94	7.91	93.34	0.28
C_2H_4	22.31		61.23	85.91		81.32		0.94
C_3H_6	1.40		4.66	2.12		2.59		1.19
C_4H_8	2.00		4.74	0.78		1.52		1.73
CH_4	13.01		5.00	0.10		1.01		17.00
C_2H_6	4.60		4.97	1.06		1.78		5.89
C_3H_8	2.82		0.95	0.24		0.39		4.04
C_4H_{10}	1.03		--	0.03		0.03		1.28
C +	0.23		0.52	0.34		0.37		0.17
	100.00		100.00	100.00		100.00		100.00

ITEM 23: Paper by Heinz Heinze, October 6, 1942, on "The Continuous Production of Succinic Acid from Tetrahydrofurane and Nitric Acid" (19 Pages)

This paper may be briefly outlined as follows:

A. Batch Process

1. Previous investigations
2. Plant experiments
3. Laboratory experiments (including tables of results showing the effect of temperature, nitric acid concentration and time)
4. Reaction mechanism and conclusions regarding commercial practice.

B. Continuous Process

1. Planning
2. Apparatus Development (drawing)
3. Oxidation with O_2 (schematic drawing and tabular results comparing nitric acid alone and nitric acid plus oxygen)
4. Absorption tower oxidation (sketch)
5. Pilot plant experiments

C. Summary

No success was obtained in an original 100 kg. plant so a systematic examination of reaction conditions was undertaken. These experiments showed that only at the low temperature of 20°C., acid concentration of 60 per cent and saturation with nitrogen oxides (N_2O_4 and N_2O_3) as well as long oxidation time are good Succinic acid yields obtained as well as nearly complete regeneration of the off-gas. The use of this knowledge on a larger scale resulted in cooling difficulties and considerable loss of time in batch operation. In order to avoid this a continuous operation was developed which resulted in long time trouble-free laboratory runs with improved yield. A pilot plant was planned.

ITEM 24: A Patent Application of March 19, 1943, by I.G. O.Z. (Serial No.) 14083 "Production of Normal and Iso-Butyraldehyde or the Corresponding Alcohols" (4 Pages)

The propane-propylene mixture obtained by incomplete dehydrogenation of propane is converted catalytically (fuller's earth plus 0.5% copper plus 1% cobalt reduced with hydrogen at 300°C.) at 100-250 atmospheres pressure, temperature of 180-250°C. by admixture with carbon monoxide and hydrogen to produce a butyraldehyde mixture or a butyl alcohol mixture is obtained by the hydrogenation of the aldehyde. The separated propane and unconverted propylene is recycled to dehydrogenation.

ITEM 25: Patent Application of March 6, 1943, I.G. O.Z. 13960 "Production of Polyhydric Alcohols" (1 Page)

Allyl alcohol is oxidized with hydrogen peroxide in the presence of 0.01 per cent OsO_4 at 25°C. to give a yield of 74 per cent glycerine after a reaction time of 12 hours. Equivalent yields of glycerine are obtained with 0.2 per cent manganous acetate in five hours.

ITEM 26: Patent Application of November 23, 1943, by I.G. O.Z. 13808 "Production of Dichlorethane" (2 Pages)

Ethane is chlorinated in the gas phase in the normal manner to ethyl chloride. This product is further chlorinated in the liquid phase with liquid chlorine under pressure and in the presence of the catalyst to yield dichlorethane. No recommended conditions or catalysts are stated.

ITEM 27: Patent Application of July 9, 1942, by I.G. O.Z. 13545 "Production of Ethylene Glycol" (7 Pages)

Formaldehyde is reacted with methyl alcohol to yield formaldehyde dimethyl acetal. This product is converted with CO and H_2 (1:2) catalytically (20 per cent cobalt on silica gel) under pressure (200 atmospheres) and at elevated temperature (125°C.) into oxygen-containing compounds including ethylene glycol monomethyl ether and methoxy acetaldehyde dimethyl acetal. Ethylene glycol is obtained from this mixture by hydrosaponification (200 atmospheres hydrogen pressure, 0.3 per cent acetic acid, nickel-on-silica gel catalyst and 270°C.)

ITEM 28: Patent Application of March 26, 1942, by I.G. O.Z. 13342 Continuation in Part "Production of Halogen Acid Solutions" (4 Pages)

The addition compound of carbonamide (diethylformamide) with HX is used as a solvent which contains per mol of carbonamide about one mol of HX. This solvent is used for treating mixtures of halogen acids, hydrocarbons and in certain cases halogenated hydrocarbons.

ITEM 29: March, 1942, Steam and Electricity Production at Lutzkendorf (8 Pages)

This paper discusses the maximum steam and electricity at full production and presents several schemes to meet the demand.

Contract Construction Data, Technical Data and Requirements for the Installation of Propane-Butane Recovery Plant (3 Pages)

ITEM 30: Letter of November 25, 1940, from the Ministry of Industry (2 Pages)

In answer to a request to connect the Lutzkendorf power plant to another power circuit refusing the request with reasons.

ITEM 31: Report on Power Production (2 Pages)

This states that the boiler plant is operating at 100 per cent of capacity and reasons for changes to provide relief are given. Coal dust production units are unsafe.

ITEM 32: Directive on Work Schedule (1 Page)

This directive lists operations to be performed when outside power is cut off.

END OF BAG NO. 2618, TARGET NO. 30/4.03

BAG 2745 TARGET 30/4.08 GELSENBERG

This section is prefaced with a summary sheet in English listing 20 items from Bag 2745.

ITEM 1: Monthly Reports on Operating Data from the Hydrogenation Plant (26 Pages)

These reports are general data from plant operation for the months of March, 1943, to April, 1944, exclusive of April, 1943, and November, 1943.

ITEMS 2 and 3: Monthly Material Balance Sheets for the Hydrogenation Plant (22 Pages)

These material balances are for the months of January, 1940, to October, 1941.

ITEM 4: Monthly Gas Balances for the Hydrogenation Plant (16 Pages)

These gas balances are for the months from January, 1940, to September, 1941.

ITEM 5: Monthly Shipment Totals from the Hydrogenation Plant (10 Pages)

These reports show product shipment for the months of January, 1941, to October, 1941.

ITEM 6: Monthly Barge Shipments (8 Pages)

These reports show shipments for the months of February, 1941, to September, 1941, excluding June, 1941.

ITEM 7: Monthly Summaries for the Isobutane Plant (8 Pages)

These reports are for September, 1941, and August, 1941. There is also included under this item summaries for Distillations A and B, Stabilization C and Benzene Wash I for the months of July, 1940, to December, 1940.

ITEM 8: Monthly Summaries for Middle Oil A Distillation (14 Pages)

These reports are for the months of December, 1939, to June, 1940. There is also included under this item monthly summaries for Distillation B, Stabilization and Wash C for the months of December, 1940, to June, 1941.

ITEM 9: Monthly Summaries for the Distillation and Stabilizing Units (11 Pages)

These reports are for the months of January, 1941, to October, 194

ITEM 10: Monthly Summaries for the Centrifuge Plant (24 Pages)

These reports are for the months of January, 1940, to October, 1941.

ITEM 11: Monthly Summaries for the Carbonization Plant (24 Pages)

These reports are for the months of January, 1940, to October, 1941.

ITEM 12: Monthly Summaries of the Coal Grinding Plant (10 Pages)

These reports are for the months of January, 1941, to October, 1941.

ITEM 13: Monthly Summaries for the Light End Recovery Plant (23 Pages)

These reports are for the month of February, 1940, to July, 1941.

ITEM 14: Monthly Summaries of Coal Stall Operation (22 Pages)

These reports are for the months of January, 1940, to October, 1940, and January, 1941, to December, 1941.

ITEM 15: Monthly Summaries for the Saturation and Splitting Stalls (22 Pages)

These reports are for the months of January, 1940, to October, 1941.

ITEM 16: Operating Data and Yield Curves (3 Pages)

These curves are for the months of August, 1942, to September, 1943.

The first curve shows per cent operating capacity at monthly intervals indicating reasons for decreased operation.

The second curve shows the throughput of Rhine ground coal (0.34-0.40) and yield efficiency (Leistung 0.22-0.32) for benzine in gas-phase operation for monthly intervals.

The third set of curves shows the end point of Middle Oil A and yields in per cent indicating reasons for loss of yield which include hydrogen deficiency, change in coal charge, bombings, etc., at monthly intervals.

ITEM 17: Effect of Ash, Hydrogen Loss and Oil Injection on Coal Stall Operation (7 Pages)

1. Effect of Ash. When the ash content of the coal increases, the centrifuge charge should always be diluted to 16.5 per cent solids and the solid content of the centrifugal oil and residue should be kept the same. This allows the same proportion of oil to residue (80:20).

2. The amount of released oil is 6.5 per cent greater than calculated by the solubility, and the amount of hydrogen in solution is higher than

the assumed value by over 50 per cent. A summary of this report is as follows:

> From the data of the last months (normal gas analysis and monthly quantity of gas) it was found, that the gasification and the solubility of hydrocarbons is on the average about as high as calculated, while the solubility of H_2 and N_2 are about 1.5 times higher.
>
> In the report of 6.18.40 "the solubility of components of the waste gas of the coal phase" similar values were found by Dr. Fries for H_2 and N_2 through normal analysis. The values for the single hydrocarbon components, for which Pod-analysis has to be used, were however also high.
>
> At higher N_2 content of the fresh gas about 50 per cent more N_2 gets into the system; the N_2 partial pressure reaches therefore, despite increased solubility, the assumed value of 55 atm. As the solubility of H_2 and N_2 are about the same, the H_2 losses increase with increasing amounts of N_2.
>
> If it would be possible to decrease the N_2 content of the fresh gases to an average of 2%, the amount of wash-oil could be reduced from 3.8 cbm/t of raw coal by .55 cbm. and the H_2 loss thereby would be decreased by about 60 cbm/t of gasoline.

3. The paste charge rate at Scholven was increased from 23 to 25 tons by eliminating the cold gas cooling of the hot exit (formerly done to prevent carbonization) and substituting injection of cold thinning oil into the pressure side of the hot circulation system. This allows an increased temperature. When paste was injected through the cold gas inlets, the temperature decreased. By charging through ~~the emergency outlet line~~ to Oven Two, the temperature could be increased.

ITEM 18: Operating Reports for Saturation and Splitting Stalls

1. Catalyst age record, operating difficulties of the individual stalls, catalyst changes, etc., for the months of January, 1944, to June, 1944, exclusive of March, 1944. (8 Pages)

2. Discontinuation of splitting stall 301 and its conversion to a three-section stall. (4 Pages)

> The performance of this stall had become increasingly poorer during the long period of operation so that it was not satisfactory even at the high temperature of 23.7 mv. The stall was ~~shut down March 7, 1943, after 738 days of operation (catalyst~~ age: 936 days for Reactor 1 and 864 days for Reactor 2). The catalyst screens were difficult to remove because FeS_2 had formed a tight union with the reactor wall. The catalyst from both reactors was in good condition; however, the seventh compartment showed slightly greater dust quantities. The pills and dust were ~~separated and examined.~~

	Reactor 1		Reactor 2		New
	Pill	Dust	Pill	Dust	Catalyst
Wt. % S	3.20	17.92	3.84	18.24	4.08
Ign. Res.	6.03	10.31	6.20	9.99	7.76
SiO_2	70.86	32.78	70.86	23.20	69.36
Fe_2O_3	3.67	49.50	4.47	59.88	6.63
Al_2O_3	13.93	15.50	13.99	13.52	9.90
WO_2	10.92	Trace	10.44	Trace	8.70
TiO_2	0.16	Trace	0.12	Trace	0.07
CaO	Trace	0.45	Trace	0.56	1.25

There was very little difference between the carbon and hydrogen content of the pills and dust - carbon 1.23-1.77 and hydrogen 0.20-0.36. The K factor of the heat exchanger for Reactor 1 had decreased from 350 to 100 and for Reactor 2 from 250 to 150, due to accumulation of FeS_2. An additional reactor was added bringing the number in the stall to three and new catalyst charged.

3. Test data on Stall 301 showing pressure drop through parts of the unit. (1 Page)

4. Machine shop forms. (3 Pages)

5. New equipment numbers for 301 stall. (1 Page)

6. Discontinuation of splitting Stall 305 on account of an air raid October 15, 1940. (1 Page)

The reactors and regenerators of 305 were rebuilt as part of 301 stall.

7. Operating report for splitting Stall 301. (9 Pages)

This report is for the rebuilt 301 stall (three reactors) from March 13, 1943, to May 31, 1944. Each reactor was charged with 5.8 tons of 6434 catalyst; the pressure drop through each reactor was 52-77 mm. water.

Charge: 187,700 tons B + C Middle Oil = 7,830 tons/m.^{3} catalyst
740 tons = 0.39% elemental sulfur
25-50,000 m.^{3}/hr. of gas

A table is included showing conditions on representative days and illustrating decreasing catalyst activity due to the ~~addition of tar oil to the charge. A table shows charge rates,~~ hydrogen partial pressure, temperature, products and throughput. Operating data for Stall 301 (two reactors) for the period December, 1940, to March, 1943, is also shown.

8. Report on remodeling of experimental Stall 302 after ninth period of operation, February, 1943. (3 Pages)

The reactors were opened and the catalyst in Reactor 1 replaced, FeS_2 deposits removed and heat exchange bundles repaired.

9. Machine shop forms. (3 Pages)

10. Equipment for experimental hydrogenation Stall 302, February 20, 1943. (1 Page)

11. Preliminary testing of pressure drop in experimental Stall 302, February, 1943. (2 Pages)

12. Shut-down of Stall 302, April 21, 1941. (1 Page)

Phenols apparently had produced leaks in the regenerator and deposits had plugged the heat exchangers. An aluminum test sample had been converted to yellow powder (aluminum phenolate). The stall was put back on-stream May 24, 1941.

13. Report on operation of Stall 302 covering the first to tenth periods of operation. (29 Pages)

This sub-item is similar to sub-item 7 and covers the following intervals.

Feb. 21, 1943 - June 12, 1944	10th period
Apr. 24, 1941 - Feb. 9, 1943	9th period
Jan. 19, 1941 - Apr. 21, 1941	8th period
Dec. 20, 1940 - Jan. 9, 1941	7th period
Nov. 5, 1940 - Dec. 15, 1940	6th period
Sept 20, 1940 - Oct. 15, 1940	5th period
July 15, 1940 - Sept 4, 1940	4th period
Mar. 9, 1940 - June 30, 1940	3rd period
Dec. 16, 1939 - Dec. 30, 1939	2nd period
Oct. 27, 1939 - Nov. 20, 1939	1st period

14. Shut-Down of Chamber 303, March 17, 1944. (3 Pages)

Catalyst sampled, damage and unit condition discussed, repairs made, unit reassembled and tested.

15. Discussion of repair work, advisability of new catalyst, etc., for Chamber 303. (1 Page)

16. Memorandum concerning damage to Chamber 303 during air raid August 12, 1943. (1 Page)

17. Flow Sheet for Chamber 303. (1 Page)

18. Memorandum stopping work on coal chamber 707 to concentrate effort on Chamber 303, August 24, 1942. (1 Page).

19. Production results with hydrogenation catalyst 7846W at Politz. (1 Page)

This memorandum confirms other experience that gasoline yield and prehydrogenation with catalyst 7846W is less than with catalyst 5058. Up to 150°C. the saturated gasoline from bituminous and brown coal results from phenols and amines and therefore consists principally of naphthenes. It contains, in contrast to catalyst 5058, little gasoline from splitting.

20. Operation with catalyst 7846W250 at Politz, August 20, 1942. (5 Pages)

Five months' operation with the first reactor charged with catalyst 5058 and the second two with catalyst 7846W250 was satisfactory. The catalyst was stable physically and chemically. As less cracking took place in the prehydrogenation stage, an additional load was placed on catalyst 6434 in the splitting stage.

21. Tables showing charge and operating conditions using catalyst 7846 in different plants. (3 Pages)

22. Operation of catalyst 7846W250 with bituminous coal middle oil. (3 Pages)

No pressure drop or temperature control difficulties were experienced. 50 per cent less gasoline (155°C. E.P.) was obtained than with catalyst 5058. It was concluded that the 6434 catalyst was not damaged by substituting 7846W250 for catalyst 5058.

23. Pilot plant hydrogenation run with catalyst 7846W250, May, 1942. (2 Pages)

It was found necessary to fill one reactor with 5058 to avoid decrease in the quality and quantity of gasoline. However, a low end point gas oil is obtained which after washing with 50 per cent H_2SO_4 can be split to higher quality gasoline.

24. Visit of Dr. Schick concerning catalyst 7846W250 at Leuna, March, 1942. (1 Page)

The catalyst operated satisfactorily with a slightly larger preheat furnace than was normally used with catalyst 5058 due to the higher operating temperature required.

25. Operating report for experimental Chamber 303. (7 Pages)

This report covers the periods from March 24 to April 23, 1944, and November 3, 1942, to March 17, 1944 using catalyst 8376 and 5058.

26. A short report of the last (ninth) operating period for Chamber 304. (2 Pages)

This covers the period April 16, 1943, to June 12, 1944, using catalyst 5058 and 8376.

27. Preliminary testing of experimental chamber 304, December, 1943. (3 Pages)

28. Operating difficulties of Chamber 304, April, 1942. (6 Pages)

29. Repair and remodeling of Chamber 304, March, 1942. (1 Page)

30. Discontinuation of experimental chamber 303 due to bombing attack, June, 1941. (1 Page)

31. Operating report for Chamber 304. (3 Pages)

This report covers the period November 18, 1940, to June 2, 1941, using catalyst 5058.

32. Operating report for Chamber 304. (4 Pages)

This report covers the period of June 14, 1941, to April 6, 1942, using catalyst 5058.

33. Operating report for Chamber 304. (5 Pages)

This report covers the period April 16, 1943, to June 12, 1944, using catalyst 5058 (age 310 days) in reactor one, new catalyst 5058 in reactor two and new 8376 in reactor three.

34. Preliminary testing of Chamber 305. (3 Pages)

35. Repair of Chamber 305, October, 1942. (2 Pages)

36. Removal of catalyst from Chamber 305. (3 Pages)

The upper basket (7th) was tipped at a 45 degree angle and contained a dust layer 10 cm. thick which was in a solid cake.

37. Discontinuation of splitting chamber 305, October 7, 1941. (2 Pages)

A new splitting oven was installed.

~~38. Shut-down of splitting chamber 304 due to bombing October 15,~~ 1940. (1 Page)

39. Operating report for Chamber 305. (4 Pages)

This report covers Period 1 for November 19, 1939, to ~~February 29, 1940.~~

40. Operating report for Chamber 305. (4 Pages)

This report covers Period 2 for March 9, 1940, to October 15, 1940.

41. Operating report for Chamber 305. (4 Pages)

This report covers Period 3 for November 9, 1940, to October 7, 1941.

42. No item.

43. ~~Operating report for Chamber 305. (2 Pages)~~

This report covers Period 4 for October 11, 1941, to December 1, 1941.

44. Operating report for Chamber 305. (4 Pages)

This report covers Period 5 for December 7, 1941, to March 20, 1943.

45. Operating report for Chamber 305. (4 Pages)

This report covers Period 6 for March 27, 1943, to May 1, 1944.

46. Reconstruction of Chamber 306, September 2, 1943. (2 Pages)

The reactors were blown with nitrogen in an attempt to eliminate dust which was producing an excessive pressure drop. This was unsuccessful, so the catalyst was discharged, screened and recharged.

47. Shut-down of splitting Chamber 306. (4 Pages)

~~Attempts were made to decrease the pressure drop by blowing~~ the reactors. New catalyst 7846 was charged to Reactor 3.

48. Reconstruction of Chamber 306, December 10, 1942. (3 Pages)

This chamber was shut down and reconstructed to a three-reactor system. The drawing of the new chambers is included.

49. Memorandum on catalyst charge to Chamber 306, February 17, 1942. (1 Page)

50. Shut-down of Chamber 306, February, 1942. (5 Pages)

This chamber was shut down due to pressure drop in Reactor 2. The catalyst was changed.

51. Discontinuation of Chamber 306, January 10, 1942. (3 Pages)

This chamber was shut down and Catalyst 7019 replaced with Catalyst 5058.

52. Catalyst charge to Chamber 306. (1 Page)

Quantities of Catalyst 5058 charged and pressure drop through reactor.

53. Operating report for Chamber 306. (17 Pages)

~~This report covers the following periods: first period,~~ January 16, 1942, to February 2, 1942; second period, February 11 1942, to December 1, 1942; third period, December 9, 1942, to July 2, 1943; fourth period, August 17, 1943, to July 12, 1944

54. Pressure-drop testing of Chamber 307, May, 1944. (1 Page)

55. Shut-down of Chamber 307, November, 1943. (2 Pages)

Regenerator tubes were encrusted with 1 mm. of FeS_2 and injection pump packing.

56. Examination of raffinate reactor in Chamber 307, December, 1942. (2 Pages)

This reactor contained catalyst 7360 and had developed a high pressure drop. Some of the catalyst pellets were coated with a white film and others had been penetrated with a brown discoloration. Samples analyzed as follows:

	Ign. Res.	Al_2O_3	Mo
White	7.71	90.16	1.23
Brown (MoS_2)	14.21	74.12	7.72

Catalyst 7360 showed no advantage over catalyst 7019 in hydrogen consumption or octane number of gasoline.

57. Raffination of coal benzine. (5 Pages)

A curve of yields and octane numbers by months is shown for the raffination of naphtha from middle oil prehydrogenation (5058) using catalyst 7360 in an attempt to prove the advantage of this catalyst over catalyst 7019.

58. Catalyst filling of chamber 307 with 6434, February, 1942. (1 Page)

59. Operating reports for Chamber ~~307. (10 Pages)~~

This report covers the following periods: first period, February 19, 1942, to October 14, 1942; second period, October 16, 1942, to June 30, 1943; third period, October 29, 1943, to June 12, 1944.

60. List of reactors and regenerators in various chambers, March 24, ~~1944. (2 Pages)~~

61. Shut-down of gas-phase system, October, 1942. (5 Pages)

The gas phase was shut down temporarily to pipe in Chamber 303 which had been completed.

62. Pressure release and flushing of chambers. (1 Page)

This memorandum indicates which valves to operate during pressure release.

63. Plant shut-down scheme, October, 1942. (2 Pages)

The liquid-phase chambers are shut down before the gas-phase.

64. Memorandum on shut-down, October, 1942. ~~(3 Pages)~~

This memorandum describes the shut-down mentioned in Sub-item 61.

65. Repairs during shut-down. (2 Pages)

Memorandum discussing repairs of gas-phase equipment during shut-down mentioned in Sub-item 61.

END OF REEL