

FILM STUDY GROUP

REPORT

T.O.M. REEL NO. 46

Prepared by

THE TEXAS COMPANY

(Bar 3446, Target 30/5,01 - Ruhrchemie A. G. Sterkrade-Holten)

Item 24. Miscellaneous Analytical Methods.

000063-65      Precise purification of synthesis gas  
(Fischer-Tropsch) and sulfur determination methods.

000066-70      Determination of the thermal conductivity  
of catalysts (Fischer-Tropsch).

000070-71      Apparatus necessary for desulfurizing  
experiments.

~~000072-3      S determination.~~

000074-      Determination of gas oil content in  
product gas by titration of the olefins (at  
Rheinpreussen).

~~000075-8      General instructions to be followed for  
any method of manufacturing gasoline and specific-  
ations on quality, analyses, etc.~~

000079-89      Standard method of determining the boiling  
behavior of gasoline, heavy benzine, petroleum and  
similar products (A.S.T.M. D86-35).

000090-1      Determination of gas oil content in pro-  
duct gas by titration of the olefins (at Rhein-  
preussen).

~~000092-7      Colorimetric determination of carbon  
disulfide in gas or in motor fuels.~~

~~000098      Determination of the boiling behavior in  
gas oils and distillation residues from fractiona-  
tion equipment.~~

~~000099      Determination of acetone (method of Robineau  
and Rollin, improved by Kehler Ann. J. Pharm 69, 65,  
(1910)).~~

000100      Examination of fresh precision-purifier  
masses: (Feinreinigungsmasse).

- 1) Water content
- ~~2) Determination of soda~~
- ~~3) Porosity determination~~

000101-2	Peroxides in motor fuels (Yalc & Wilson Ind. Eng. Chem. 1931, 1254).
000102-4	Determination of degree of reduction (of Co Catalysts) - "Reduktionswertbestimmung".
0000105	Method of distinguishing between "sweet" and "sour" natural gas (Smith & Crowell - Oil Weekly <u>Ed</u> (10) 36-43 Feb. 2, 1938).
000106	Determination of total sulfur (in Fein-reinigermassen).
000107-10	Hydrogen sulfide determination.
000111-2	<del>Comparison of determinations on degree of reduction according to methods and sampling.</del>
000113-7	Determinations of organically bound sulfur as hydrogen sulfide.
000118	Preliminary carrying out of ammonia determinations in product gas.
000119	Determination of iron carbonyl.
000120-1	Determination of NO in coke gas - modified method of Schuffen?
000123-3	Total sulfur determination in $\text{H}_2$ containing substances.
000124	NGAA Experimental method for qualitative determination of water content in commercial propane using cobalt bromide.
000127-8	Determination of total sulfur in liquid fuels, according to Dr. Hurdelbrink's method.
000129	(Advertisement for) Hurdelbrink's apparatus.
000130-1	Determination of moisture content in synthesis and product gases.
000132-4	Description and method of using the wet control-gasometer according to plan 24 4/74.
000135-6	<del>Comparison apparatus for the determination of coking residues.</del>
000137	Determination of the C number (number of C atoms) during gas analysis.

- ~~000138-40~~ Sulfur determination in synthesis gas.
- 000141 Calculation of coke.
- 000142-50 Determination of gaseous paraffinic hydrocarbons.
- 000151-8 Common determinations and analytical methods of the thorium convention with modifications from the later convention of 12,31,21.
- 000159-63 Methods of investigating thorium products for catalyst manufacture.
- 000164-5 Sulfur determination (in gas).
- 000166 Necessary apparatus for experiments on desulfurizing.
- 000167-72 Gas analysis methods (with 40% oxygen and 5% H<sub>2</sub>S).
- 000173-3 Solidifying point.
- 000176-7 Method of determining water in mineral oils.
- 000178-31 Potentiometric cobalt titration.
- 000182-95 Determination of a small concentration of sulfur dioxide and hydrogen sulfide in the atmosphere (translation of article by Gurevitch & Wendt J. Gen. Chem. (U.S.S.R.) 6 962-71 (1936)).
- 000196-9 Apparatus for the quantitative determination of hydrogen sulfide impurities in gases. (translation of article by Kaminski H. scioboin schirowoje Delo 12 332-3 (1937)).
- 000200-2 Description and method of using the wet control-gasometer according to plan 5/74/74.
- 000203-4 Apparatus for the determination of moisture in commercial gases.
- ~~000205-7~~ Gas analysis methods with phosphorus pentoxide-sulfuric acid.
- ~~000208-17~~ Olefin determination with phosphorus pentoxide-sulfuric acid.
- ~~000214-20~~ Method for the determination of water in coke oven gases with large and small water contents.

000221-33	Methods for determining the amount of water in coke even gases with large and small water contents.
000224-33	Instructions for methods of various samples and research methods.
000231	Determination of the iodine number (of unsaturated compounds) in gasoline according to H. P. Kaufmann.
000232	Apparatus for determining the iodine number of gasoline.
000233	Rapid determination of the gasoline content in liquefied gaseous fuels.
<del>000234</del>	<del>Rapid determination of the iodine number of liquefied gaseous fuels.</del>
000237	Standards for the purification of oil samples.
000238	Determination of viscous content.

Statement of James Earl Ray, also during the period July 20, 1957 to Sept. 10, 1955 (4 pages)

1. Name of the person or persons interviewed

2. Title of the individual or individuals

3. Title of the person or persons interviewed  
at the time of the interview

4. Date of the interview

5. Place of the interview

6. Name of the person or persons interviewed

7. Title of the individual or individuals

8. Title of the person or persons interviewed  
at the time of the interview

9. Date of the interview

10. Place of the interview

11. Name of the person or persons interviewed

12. Title of the individual or individuals

13. Title of the person or persons interviewed  
at the time of the interview

14. Date of the interview

15. Place of the interview

did not see the handwriting of the subject and

did not see the handwriting of the subject in any of the letters which were sent to him only if they were sent at New York, and did not see any of the letters which were sent to him in New York.

And in New York City.

Respectfully,  
W. J. [Name]

W. J. [Name] [Address]

T O N 44

Item 22 (date 000248-000250) Kieselguhr Analyses and Catalyst Activity

Thorsen-Holten, 4/9/36  
Abt. BVA F/Ro.

Isobenzol nst.-lsg.  
B. 21 ml

Concerning Thorium-Kieselguhr - Samples from the Kieselguhr Co.  
B. 714

The thorium impregnated and thorium nitrate obtained from the Kieselguhr Co. on 3/9/36 were found to be suitable for the production of contact material in synthetic experiments carried out over periods of two hours. Also the construction (type) were found to be suitable.

A sample of kieselguhr supplied at the same time was also tested for use as contact base and it was found that after 300 hours activity decreased rapidly.

Analytical data on Kieselguhr 5 II, 120 and Kieselguhr are given in - table.

Tests of various kieselguhrs are described and results compared.

Other contact carriers such as zeolite, ~~and~~ charcoal, activated carbon and decolorizing earth were also tested. Decolorizing earth is least desirable, activated carbon next, charcoal and zeolite are better, but none of these materials stands up for long periods of time.

Catalysts with as low as 1% of thorium oxide were tested. Previous tests show that lowering of the thorium content has no harmful effect on the activity.

Various methods of precipitation and washing were tried with a view to determining the effect on the activity of the catalyst.



T O K 46

Page 30 (page 000251) / Ni-Mn-Al catalyst

Industriell Akt. Ges.  
Hambörsen - Holten  
Task I F/WCHA

Holten, 5/4/38

3446 - 30/5.01 - 30

Pre. Trans:

Regarding Nickel-manganese-aluminum contact material.

~~The nickel-manganese-aluminum contact material used for the~~

hydrogenation of paraffin is prepared as follows: To obtain  
30 grams of nickel as catalyst, 125 gr. of nickel nitrate, 25 gr.  
manganese nitrate and 17 gr. aluminum nitrate are dissolved in  
500 cc. of water, brought to the boiling point and precipitated  
as quickly as possible with a solution of 105 gr. of anhydrous  
potassium carbonate in 300 cc. of hot water. The precipitation  
must take place under vigorous stirring to avoid sudden strong  
foaming. Immediately after the precipitation 30 gr. of Nickel-amine  
are added, well stirred, and then the catalyst is washed on a hot  
filter plate 6-times with 500-cc. of hot water. The catalyst is  
then dried at 110 C., pulverised, and reduced in an alumina block  
oven at 450 C. with dry hydrogen. The consumption of hydrogen  
should be 1.5-2.5 liters per gr. of nickel and reduction period  
1-2 hours. The reduced catalyst is allowed to cool in a stream of  
hydrogen. In the cooled state, carbon dioxide can be used as  
protective gas.

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Item 31 (pages 000252-5) Analyses of Catalysts

Holten, 5/23/38

6 catalysts were prepared in the laboratory synthetically from solutions or suspensions. A table shows the amounts of cobalt, thorium oxide and Kieselgur used in the preparation of each of the catalysts. Another table shows the amounts of cobalt, thorium oxide and Kieselgur found on analysis in the catalysts. A third table shows the amounts of free water (determined by means of xylol), combined water, carbon dioxide, total loss on ignition, and Kiesolgur found in the 6 catalysts on analysis. A fourth table gives the composition of the catalysts as to cobalt oxide, thorium oxide, free water, combined water, carbon dioxide, and Kieselgur.

A number of pages are missing at this point but it is assumed that the procedure for determining the amounts of cobalt oxide and thorium oxide and the method of calculation are described in detail.

The determination of total loss on ignition and the Kieselgur content are described and method of calculation explained by means of examples.

It is explained that free water is the amount of water that can be determined by means of xylol loss on ignition is the amount of carbon dioxide and combined water, and Kieselgur equals 100 minus cobalt oxide minus thorium oxide minus free water minus loss on ignition.

1. 2. 3. 4.

Item 12 (page 100235)

Reaction of Miami Gas Under Reduced Pressures

The effect of pressure, temperature and composition  
of the reaction of Miami gas (100 Co, 100 G, 100 L)  
with steam (150) were investigated.

Item 13 (page 100236)

American Oil Co. Study of the Reaction of Miami Gas  
with Steam (150) at Reduced Pressures

1. 2. 3. 4.

1. 2. 3. 4.

Item 14 (page 100237)

American Oil Co. Study of the Reaction of Miami Gas  
with Steam (150) at Reduced Pressures

1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

Experiments with Oil-Catalyzed Cracking

2. 3. 4.

1. 2. 3. 4.

EXPERIMENTS OVER COBALT THORIUM CATALYSTS

(Conducted during the period April 23 to  
May 18, 1935)

1. Long-time Experiments with Co Th Catalysts

Concerning these experiments a report was rendered on May 18, 1935 with special consideration for the formation of gaseous hydrocarbons in comparison to copper containing Co Th catalysts.

2. Comparative Experiments with Co Th Catalysts conducted in S.O. 9 and 6

These experiments are the subject of the report of May 17, 1935.

3. Experiments on Reduction Period

The influence of temperature, hydrogen velocity and reduction time were studied. The experiments were conducted with a quantity of catalyst corresponding to 4g of Cobalt metal (cobalt: Kieselgur = 1:2) in a layer 30 cm. long and were so carried out that the catalyzer in the tube, after a short drying time at 190°C was placed in an oven at 300, 350 or 400°C. The reduction time is thus determined exclusive the heating-up period. The values not underlined in Table I were obtained by observation of the density of the catalyst resulting from reduction; the underlined values were ascertained by experimental determination of the reduction values. The great influence of temperature and hydrogen stream velocity are apparent. Also exhaustive experiments on the activity and stability of the catalyst reduced at 300 and 400°C were undertaken. Low reduction temperatures were perhaps conducive to a high rate of liquid production, while high temperatures effected a quick total reduction with no injurious effect observed, so far.

4. Storage Stability of a reduced Co Th catalyst soaked with oil and paraffin

A soaked catalyst stored in V2A sheet metal cans showed after 30 days almost its original activity. In order to give closer study to the effect of air on the reduced catalyst, some unsoaked catalyst was first put into a Soxhlet thimble in a glass vessel and an air stream of 10 l. per hour supplied while the temperature in the middle of the catalyzer was observed. Reduction was followed by cooling down about 100°C. in one case in a stream of CO<sub>2</sub>, and in the second case in a stream of hydrogen. In both cases, the temperature rose above 300°C and in three runs this occurred within 16 minutes. In a further experiment, where the catalyst was cooled in a CO<sub>2</sub> stream, a maximum temperature of 49°C was reached in ten minutes after which the temperature decreased slowly. Oil-Paraffin-soaked catalyst exhibited by the same treatment only a slight temperature rise; in the case of the CO<sub>2</sub> cooled catalyzer, up to 45° in the case of that with only hydrogen treatment, in one instance up to 70°, in a second instance, after 16 minutes, up to 112° with further rising tendency. Previously, a temperature rise had been surprisingly observed in the hydrogen treatment of a long-stored catalyst.

Soaked Catalyst, subjected to an air treatment without heating to more than 70° (except for a period of 20 hours) showed its original activity as measured by CO/H<sub>2</sub> Conversion.

Experiments have yet to be made to determine the cause of heating when an oil-paraffin soaked catalyst is treated with H<sub>2</sub> at room temperature. Especially should the reduction values of the air treated catalyst be determined.

#### 5. Paraffin Synthesis

An unsoaked catalyst was extracted with benzol after 52 hrs. of operation. 1.8 grams of paraffin, M.P. 84° were found in 12.7 grams of reduced catalyst, equivalent to 15%. After 550 hours of operation or 23 days, 10.4 grams of paraffin, M.P. 86° equivalent to 60%, were obtained.

The first experiment shows that the initial loading of the catalyst itself with 10% high melting point paraffin may be made without affecting the activity.

#### 6. Loadability of copper-containing and copper-free Co Th Catalyst

Table IV, No. 1 shows the normal yield from normal loading of a Co Th Cu catalyst. Under Nos. 2, 3 and 4 a similar catalyst is reported with two, three and five-fold gas thru-put respectively. With the two-fold and three-fold gas thru-put a yield decrease proportional to the thru-put increase results. With the five-fold thru-put the yield falls off drastically.

After five days, loading returned to normal but the normal yield of 140-150 ml/m<sup>3</sup> was not regained. A proportional injury to the catalyst appears to be demonstrated by all three experiments.

Table V shows the loading experiment with cu free Co Th catalyst. Half normal loading produces a slight increase in the yield and improved operation. In this case, the yield of liquid products at one and one-half and at two-fold loading, falls off only a little, in contrast to the copper containing catalyst, except that after 580 hours (24 days) a distinct loss in activity was evident.

Investigations of products from these experiments are in progress. Complete analytical data (Determination of liquid yields, etc.) will be reported after termination of the experiment, simultaneously with data on a second experiment with various catalyst bed depths.

A two-stage experiment, in which the first stage is loaded with the doubled gas thru-put is now being conducted.

#### 7. Co-Ni-Th Catalyst

Table VI shows the good efficiency of this catalyst mixture in that it produces almost the original yield after 400 hours with low operating temperatures and good liquid production. As is to be expected from nickel-containing catalyst, the olefin content of the

liquid products therefrom is less than that obtained from cobalt containing catalyst. Further experiments must be arranged concerning reduction, loadability, tendency toward methane synthesis, etc.

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Oberhausen-Holten May 22, 1935

Table I

Reduction at 3000

Hrs.	4 l/h, H <sub>2</sub>		8 l/h, H <sub>2</sub>		12 l/h, H <sub>2</sub>	
	Reduction Value	Contraction %	Reduction Value	Contraction %	Reduction Value	Contraction %
1	-	9	-	3	-	-
2	-	-	-	4.5	10	1.5
4	5-10	-	30	-	40	-
10	10	-	50	-	50	-
20	60	-	90	-	77	-
70	74	-	79	-	-	-
		Total Hydrogen (l)		Total Hydrogen (l)		Total Hydrogen (l)
		4		8		12
		8		16		24
		12		32		48
		40		80		120
		80		160		240
		280		560		-

20 l/h, H<sub>2</sub>

Reduction value	Contraction	Total Hydrogen (l)
15	2.0	20
25	1.0	40
60	-	80
69	-	200
-	-	-
-	-	-

Table II

Reduction at 3500

Hrs.	4 l/h, H <sub>2</sub>			8 l/h, H <sub>2</sub>			12 l/h, H <sub>2</sub>		
	Reduction Value	Contraction %	Total Hydrogen (l)	Reduction Value	Contraction %	Total Hydrogen (l)	Reduction Value	Contraction %	Total Hydrogen (l)
0.25	-	13	1	-	6.8	2	-	-	3
0.5	-	8	2	-	3	4	-	-	6
1	10	6.5	4	20	3	8	40	3.3	12
2	25	1	8	50	-	16	80	1.5	24
3	30	-	12	70	-	24	90	-	36
4	50	-	16	80	-	32	90	-	48
5	50	-	20	90	-	40	82	-	-
9	70	-	36	90	-	56	-	-	-
45	100	-	180	100	-	360	-	-	-

  

20 l/h, H <sub>2</sub>		
Reduction Value	Contraction %	Total Hydrogen (l)
-	6.7	5
-	1.9	10
65	2.4	20
90	-	40
88	-	60







Table V

Exp. No.	Hours of Operation	Cobalt - Thorium -		Catalyst 50 g.		Normal Gas thruput 12.5 l/h.		CO	H <sub>2</sub>	CH <sub>4</sub>	Carbon Value	N <sub>2</sub>				
		Con- traction %	Oil	Gasoline	Total Liquid Product	Satur- ated Hydro- carbons	Co <sub>2</sub>									
1.	69	12.5	1950	75%	65	67	132	21.9	3.8	0.0	7.4	15.0	23.3	1.58	22.6	
	241	12.5	1950	70%	82	56	138	-	-	-	-	-	-	-	-	-
	481	12.5	1960	69%	83	45	128	19.8	3.2	0.0	15.8	28.7	14.5	1.68	13.0	
	650	12.5	1980	73%	79	44	123	15.1	3.6	0.0	20.0	30.3	19.0	1.6	12.0	
2.	69	6.25	1950	76%	80	57	137	33.3	1.8	0.0	0.2	9.8	31.6	1.72	23.5	
	241	6.25	1950	75%	88	43	131	-	-	-	-	-	-	-	-	-
	481	6.25	1960	73%	90	53	143	34.0	2.4	0.0	2.6	19.5	27.0	1.63	15.5	
	650	6.25	1980	78%	96	50	142	26.3	3.5	0.0	6.4	25.0	21.8	1.75	16.3	
3.	69	18.75	1950	70%	75	65	140	16.5	2.6	0.0	8.4	25.3	26.7	1.96	20.5	
	241	18.75	1950	65%	70	53	123	-	-	-	-	-	-	-	-	-
	481	18.75	1960	63%	70	54	124	15.1	2.8	0.0	20.6	35.0	15.4	1.66	11.1	
	650	18.75	1980	70%	71	55	126	11.6	3.2	0.0	23.2	36.2	15.1	1.51	10.1	
4.	69	23	1950	70%	67	49	116	14.5	3.2	0.1	16.4	27.1	18.5	1.8	20.2	
	241	23	1950	63%	70	54	124	-	-	-	-	-	-	-	-	-
	481	23	1960	64%	57	63	120	10.6	1.3	0.0	24.8	44.3	9.9	1.65	8.5	
	650	23	1980	58%	62	51	113	8.4	2.5	0.0	25.9	42.2	13.0	1.31	8.0	



T 9 H 16

Item 38 (pages 089877-8)

Comparative Experiments with Reactions 9 and 6

Item 39 (pages 089879-782) Exposure of Plant Material by Reaction Water

Laboratory, C.I./H

Glenn Hansen, Holter, 2/28/23

Prof. Martin, Dr. Kitching, Park, Alberta, and Dr. Jung

For the purpose of the number of experimental samples

which were available for in the gasoline plant.

The experiments under consideration had their origin in the  
work done at the University of Alberta at the plant work.

The data examined by the reaction water, which observation was  
into corrosion.

It is interesting to note that water resistant to shale behavior  
toward reaction water at 60 deg. C.

The observations are summarized in a table, the materials  
being listed in increasing order of corrosion stability toward  
reaction water at 60 deg. C., the water being changed daily.

Pure aluminum and the alloys chromium steel (15% chromium,  
Bordeaux and Schmitz), V2A E2 (18% chromium and 8% nickel - Krupp),  
and Coralex (copper, aluminum, iron alloy) are not corroded by

reaction water. Iron is intermediate in its behavior. The less  
resistant materials include: copper steel - Krupp, wrought  
iron, Sidermal - D 15 - Vestag, FK 335 - Krupp, zinc iron, and

Patina - Krupp - Vestag.

Overhulsen-Holten, 2/8/35

Tests lasted 16 days. Results same as above except that it is stated that brass is not dependable under the stated conditions and therefore unreliable.

T. O. M. 46

Item 38 (pages 000283-365)

Works Conference, Ruhrchemie A.-G. Essen, Oct. 3, 1941

The following reports were presented before the Conference:

1. Dr. Pranschke (Brebag), New Experiments on Fine Fractionation. (8 pages)
2. Dr. Mohry (Krupp Treibstoff), Influence of High Sulfur on the Synthesis. (5 pages)
3. Dr. Feisst (Ruhrbenzin), H<sub>2</sub>S Formation in the Synthesis Gas from Sulfate of the Cooling Water in Direct Gas Coolers. (10 pages)

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4. Dr. Dahm (Ruhrbenzin), Development of Medium Pressure Synthesis of Olefins. (6 pages)

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5. Dr. Chue (Hoeschbenzin), Progress in Medium Pressure Synthesis. (16 pages)

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6. Dr. Grimme (Rheinpreussen), CO and H<sub>2</sub> Balance as Aid in Synthesis Control. (9 pages)

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7. Dr. Meier (Brebag), Development of Iron Catalysts. (22 pages)

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8. Dr. Roehn (Ruhrchemie), Increasing the Paraffin Wax Content in the Synthesis Product. (4 pages)

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T O M 46

Item 39 (pages 000365-451)

Conference held in Essen, Jan. 8, 1943.

1. Manufacture of Isopropyl Alcohol and Methyl ethylcarbinol from Gasol by Dr. Grimme (Rheinpreussen) - 9 pages
2. Manufacture of Iso-gasols and Aviation Gasoline from Synthesis Products by Dr. Kolling (Ruhrchemie) - 23 pages
3. The Aromatization of Straight-chain Aliphatic Hydrocarbons from Fischer-Tropsch Synthesis by Dr. Rottig (Ruhrchemie) - 13 pages
4. Preparation of Mixed Diesel Fuels from Synthesis Products and Tar Oils by Dr. Koebel (Rheinpreussen) - 12 pages
5. Recovery of Fatty Acids from the Condensate Water of Pressure Synthesis by Dr. Ohme (Hoesch-Benzin) - 7 pages
6. Recovery and Composition of the Alcohols in the Waste Water of the Active Carbon Unit by Dr. Ohme (Hoesch-Benzin) - 5 pages
7. Preparation of Fatty Acids and Soaps from Products of CO Hydrogenation by Dr. Roelen (Ruhrchemie) - 6 pages.



I O M 76

Work of James JOHNSON (720) Conference of Work 40 years

Conference held in Green, Jan. 20, 1944

- 1. Instruments with Electrical and Mechanical (Brown)
- 2. Brown Instruments in the field (Brown, Bell, G. H. Brown)
- 3. Brown Instruments with High Power (Brown)
- 4. Brown Instruments in the field (Brown, Bell, G. H. Brown)

Conference of the Scientific Institute of the State

Conference of the Scientific Institute of the State

Conference of the Scientific Institute of the State

Conference of the Scientific Institute of the State

Conference of the Scientific Institute of the State, held March 24, 1944

Conference of the Scientific Institute of the State, held March 24, 1944

Conference held in Essen, April 17, 1942

1. Advantages and Disadvantages of the Use of Refining Agents with Higher Porosity than Previously Used - 3 pages
2. Advantages and Disadvantages of the Two Water Recycle Systems present in the Low Pressure Ovens - 1 page
3. Durability of Active Carbon with regard to Guarantees made by Lurgi - 2 pages
4. Corrosion of the End Gas Lines in Low Pressure Synthesis as well as Corrosion at other Points, e.g., Gasometer, etc. - 2 pages
5. Which Method of Catalyst Regeneration is Preferable: Hydrogenation, Extraction or Extraction plus Hydrogenation? - 3 pages

Conference held in Essen, July 31, 1941

1. Experiments with "Roestgur" Catalysts (evidently a type of kieselguhr) - 4 pages
2. Delivery of Finely Divided Gas Purifying Media - 2 pages

Conference held in Oberhausen-Holtien, Nov. 30, 1939

1. Preliminary Purification - 2 pages
2. Final Purification - 3 pages
3. Synthesis:
  - (a) Catalyst Quality - 3 pages
  - (b) Catalyst Regeneration by Extraction and Hydrogenation - 1 page
  - (c) Corrosion - 1 page

Conference held in Holtien on May 5, 1939

1. Catalyst Composition - 2 pages
2. Gas Purification - 2 pages
3. Emptying Catalyst Ovens (time study by various plants) - 4 pages

Conference held in Bergkamen, July 14, 1939

1. Catalyst Problems - 7 pages
2. Experiments with Magnesium Catalyst - 2 pages
3. Gas Purification - 2 pages

Conference held in Holten, April 13, 1939

1. Catalyst Deliveries - 3 page
2. Experimental Catalysts - 2 pages
3. Catalyst Quality - 1 page
4. Yields - 1 page
5. Catalyst Extraction - 1 page
6. Problems of Final Gas Purification - 1 page
7. Corrosion Problems - 1 page

Conference held in Holten, Jan. 25, 1939

1. Tank Fire in Holten and its Causes - 1 page
2. Mixed Catalysts (Thorium-Magnesium) - 2 pages
3. Removal of Catalysts - 1 page
4. Thorium vs. Mixed Catalysts - 2 pages
5. Catalyst Regeneration - 2 pages

Conference held in Holten, Nov. 25, 1938

1. Mixed Catalysts - 7 pages
2. Catalyst Regeneration - 2 pages

Conference held in Holten, Sept. 6, 1938

1. Mixed Catalyst (Th/Mg) - 7 pages
2. Physical Character of Mixed Catalyst - 2 pages
3. Emptying of Ovens - 1 page
4. Regeneration with H<sub>2</sub> or Solvents - 3 pages
5. Paraffin Content of Spent Catalysts
6. Properties of the Products - 1 page
7. Production Data - 1 page
- ~~8. Catalyst Consumption - 1 page~~
9. General - 1 page

Conference held in Holten on July 18, 1938

~~Six pages: Mixed catalyst, regeneration, life, removal from oven.~~

Conference held in Holten, June 17, 1938

- ~~1. Gas Purification - 3 pages~~
2. Synthesis Operation - 10 pages

Conference held in Holten, May 10, 1938

1. Co-ThO<sub>2</sub>-MgO catalyst - 7 pages
2. Experimental Catalysts with Co ratio of 1:1 - 3 pages
- ~~3. General - 5 pages~~

Conference held in Holten, April 6, 1938

Catalyst Delivery and Quality

- (a) Normal Co-ThO<sub>2</sub> Catalysts - 5 pages
- (b) Co-ThO<sub>2</sub>-MgO Catalysts - 6 pages

Conference held in Schwarzheide, Feb. 7, 1938

1. Final Gas Purification at Schwarzheide - 2 pages
2. Catalyst Problems - 5 pages
3. Emptying of Ovens - 2 pages
4. Catalyst Supplies in Feb. 1938 - 1 page

Conference held in Holten, Jan. 7, 1938

1. Chemical Composition of the Catalyst - 1 page
2. Gas Distribution in the Ovens - 5 pages
3. Purity of the Synthesis Gas - 2 pages

~~Conference held in Holten, Aug. 24, 1937~~

1. Preliminary Gas Purification - 1/2 page
2. Final Gas Purification - 1 page
3. Deliveries of Catalysts - 1 page
4. Catalyst Quality - 1 page
5. General Problems - 2 pages
6. Emptying of Ovens - 1 page

Conference held in Berlin, July 30, 1937

1. Preliminary Gas Purification - 1 page
2. Final Gas Purification - 3 pages

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3. Synthesis:
  - (a) Catalyst Quality - 1 page
  - (b) Catalyst Impregnation - 2 pages
  - (c) Oven Emptying - 1 page
  - (d) Catalyst Composition -  $\frac{1}{2}$  page
  - (e) Catalyst Distribution - 1 page

Conference held in Rauxel, July 2, 1937

1. Preliminary Gas Purification - 2 pages
2. Final Gas Purification - 2 pages
3. Ovens - 1 page
4. Catalyst Quality - 3 pages
5. Corrosion Difficulties in Motor Fuel Refining - 1 page

Conference held in Ruhland, May 21, 1937

1. Preliminary Gas Purification - 1 page
2. Final Gas Purification - 2 pages
3. Catalyst Evaluation - 1 page
4. Catalyst Regeneration with  $H_2$  -  $\frac{1}{2}$  page
5. Oven Emptying -  $\frac{1}{2}$  page
6. Motor Fuel Refining Problems
  - (a) Condensers -  $\frac{1}{2}$  page
  - (b) Active Carbon Unit - 2 pages
  - (c) Motor Fuel Quality - 2 pages

Conference held in Holten, April 23, 1937

1. Preliminary Gas Purification - 2 pages
2. Final Gas Purification - 4 pages
3. Catalysts - 5 pages
4. Motor Fuel Refining -  $\frac{1}{2}$  page

T O M 46

Item 41 (pages 000721-765)

Hungarian Plant for Acetylene from Methane

Acetylene desired by Hungary for conversion to acetaldehyde. Starting material gas containing 99-99.25% CH<sub>4</sub>; unit to produce 0.195 ton C<sub>2</sub>H<sub>2</sub> per hr. Thermal processes (1400-1500 deg. C.) were investigated, using varying degree of vacuum (e.g., 76 mm abs.); C<sub>2</sub>H<sub>2</sub> recovered with water wash under 11 atm. pressure. Yield, 40-50 CH<sub>4</sub> conversion to C<sub>2</sub>H<sub>2</sub>. Discussion of explosion danger due to Diacetylene, shock cooling of the hot gases, detailed cost data furnace construction; flow sheets and sketches.

Item 42 (pages 000766-000778)

Toluene and Aircraft Fuel Synthesis (Hungary)

Some of this material is missing. It begins here with a discussion of an active carbon plant for recovery of volatile vapors.

Next is a discussion of a visit to the Ruhrchemie by two Hungarians to study the production of toluene from Hungarian oil via the heptane-methylcyclohexane fraction. The Ruhrchemie investigation was made with the Fischer heptane fraction which is slightly more difficult to aromatize than the heptane-methylcyclohexane. Recycling gave 88% theoretical yield:

<del>86.7%</del>	unrefined toluol
3.9	cracked gas
6.4	light gasoline
6.8	H <sub>2</sub>
2.3	Carbon

~~No details are given as to process used, except mere mention of the Aro-catalyst employed. (See Item 43.)~~

Brief description is given of precision distillation apparatus used for laboratory control.



T O M 46

Item 43 (pages 000779-797)

Plant for the Preparation of C<sub>3</sub> and B<sub>1</sub> Fuels from Hungarian Petroleum Gasoline

By precision distillation of a Hungarian petroleum gasoline it was possible by the Ruhrchemie process to separate components which could be blended to give aviation gasolines of the C<sub>3</sub> and B<sub>1</sub> grade. Distillation and other tests, including engine tests, are given of both products. Tests are also given of motor gasolines, light Diesel oil and a fraction suitable for toluene manufacture resulting from this precision distillation.

Hydrocarbon composition of the Hungarian gasoline is given.

In Part II of this report is a description of process used for preparation of toluol from the heptane-methylcyclohexane fraction of this Hungarian gasoline. It boiled between 98 and 102 deg. D., composition 23% n-heptane, 71% methylcyclohexane, 5% singly branched heptane, 0.8% toluol and 0.2% doubly branched C<sub>8</sub>. With a temperature of 460 deg. C. and a charging rate of 130 cc/l. catalyst/hr. the following were obtained:

92%	wt. liquid yield with 43% vol. of toluol
3	cracked gas
3.5	H <sub>2</sub>
1.6	carbon

In the liquid product, besides unconverted C<sub>7</sub> fraction were also small amounts of C<sub>5</sub> and C<sub>6</sub> hydrocarbons. By recycling 80% toluol was obtained, and by acid treatment 74% refined toluene. The catalyst used contained about 13% wt. chromium oxide, 30.5% alumina and 1.5% alkali. Catalyst regeneration briefly discussed. Flow sheets.

Item 44 (pages 000798-804)

Miscellaneous Flow Sheets

Evidently relate to active carbon unit for light vapor recovery.

Item 45 (pages 000805-7)

Monthly Data from Works of all Licensees

~~Item 46 (pages 000908-921)~~

I. Influence of the Cobalt and Kieselguhr Content on the Efficiency of Synthesis Catalysts (4 pages)

II. Influence of the Amount of Cobalt with Constant Kieselguhr Content and Constant Rate of Flow (3 pages)

III. Influence of the Co-Kieselguhr Ratio with Constant Amount of Co and Constant Rate of Flow (5 pages)

T O H 46

Item 47 (pages 000822-000906)

Treatment of Ruhrchemie and Hoeschbenzin primary product to give the best yields of Airplane Oil. Continuation of work described in Item 52.

Item 48 (pages 000907-000916)

Details of the normal pressure reactors of all the licensees: Ruhrchemie, Rheinpreussen, Brupp, Essener, Winterhall.

T O H 46

Item 49 (pages 000909-000916) Polymer Gasoline

Ruhrchemie Aktiengesellschaft  
Oberhausen-Holtten

June 15, 1942

Re: Manufacture of R<sub>4</sub> and R<sub>5</sub> Aviation Fuels for Berlin

A well fractionated C<sub>4</sub>-C<sub>5</sub> cut from catalytic cracking that had been subjected to polymerization was used as a starting material. The C<sub>4</sub> fraction should be almost C<sub>3</sub>-free, since only a small amount of propylene sharply depresses the overload performance of the polymerization product. A 90% conversion could be applied in polymerization of the C<sub>4</sub> fraction since the degree of polymerization has no great effect on the overload performance. A 60% conversion is applied to the C<sub>5</sub> fraction since an increase in conversion seems to reduce the overload performance curve. A repetition of these experiments indicated no difference in overload capacity between 60% and 90% conversion. Hence momentarily work was concentrated on the clarification of this question. The resulting products were then distilled, the C<sub>4</sub> product up to 165 deg. C., the C<sub>5</sub> product from 50-168 deg. C. These fractions were completely hydrogenated and treated with 0.005% by weight of Stabisol (I.G. Inhibitor). They were shipped to Berlin without TEL addition identified as

R<sub>4</sub>: C<sub>4</sub> polymer

R<sub>5</sub>: C<sub>5</sub> polymer

R<sub>4/5</sub>: Mixture of R<sub>4</sub> & R<sub>5</sub> (1:1)

R<sub>4/5</sub> Product: The gas used had the following composition:

	Vol. %	Wt. %
Normal and iso-butane	9.1	9.7
1- and 2-butylene	51.9	51.6
Iso-butylene	39.0	38.7
Total olefine	90.9	90.2

Of the total (90.9%) butylenes approximately 43% was isobutylene.

The polymerization was carried out in the experimental laboratory (LT) at 60 atmospheres, 130-140 deg. C. and at a weight space velocity of 1:1. The off-gas showed the following composition:

(Page of text missing.)

The C<sub>5</sub> fraction is included in the crude product. This mixture has the following composition:

	Vol. %	Wt. %
Normal and isobutane	1.3	1.1
Butylene-1 and -2	7.5	6.0
Isobutylene	0.5	0.4
Isopentylenes	18.6	
<u>n-pentane</u>	20.5	36.8
<u>n-pentylenes</u>	46.9	
Hexanes and heavier	4.7	5.7
Residual Olefines	73.5	

This corresponds to a volumetric C<sub>5</sub> conversion of 67%, whereas it amounts to only 60% by weight.

The R<sub>4/5</sub> product was a 1:1 mixture of R<sub>4</sub> and R<sub>5</sub> and had the following tests:

	R <sub>4</sub>	R <sub>5</sub>	R <sub>4/5</sub>
Sp. Gr. 20 deg. C.	0.7129	0.7059	0.7095
Refractive Index 20 deg.	1.4014	1.4018	1.4016
Reid V.P.	0.12	0.43	0.29
I-No.	0.0	0.0	0.0
Bomb test			
1. (100 deg. C., 240 mins.)	1.0	1.0	1.0
2. (100 deg. C., 240 mins., 1.2 Pb / Stabisol)	5.8	7.2	6.0
<u>Distillation</u>			
IBP	76 deg.	35	60
BP	173	167	169
10%	104	49	79
50%	114	129	120
95%	150	156	154
Loss	2.0	5.5	4.0
Octane No., Motor	92.4	90.0	91.9
1.2 Pb	103.7	100.5	102.8

T. O. M. 46

Item 50 (pages 000915-000932)

Large Scale Manufacture of Airplane Oil Stabilized by an Inhibitor

Ruhrchemie A.-G.

October 19, 1942

Airplane oil for RLM had following specifications:

1. Visc. at 50 deg. C. about 10 deg. E.
2. Visc. pole height about 1.52
3. Stable to oxidation
4. Pour below -40 deg. C.

(4) could be met by removing in vacuo the lowest boiling constituents  
and replacing them with spindle oil. This also favorably affected  
the viscosity to meet (1).

Phenthiazin was used as oxidation inhibitor. This synthetic  
oil was obtained by the  $AlCl_3$  polymerisation of special cracked  
gasoline cuts.

Experiments on the preparation of phenthiazin are also dis-  
cussed.

P O M 46

Item 51 (pages 000933-957)

Flow Sheets for proposed Japanese Lubricating Oil Plant

(Most of these are illegible.)

T O M 46

Item 52 (pages 000937-000962)

Data on Synthetic Lubricating Oil produced from Cracked Gasoline. Ruhrchemie report of May 5, 1941. Production of motor oil of 1.8 pole height, viscosity at 50 deg. C. 8-15 deg., flash 220 deg., 50% yield. Airplane oil: viscosity 20 deg., pole height 1.8-2, flash 240-250 deg., yield 35% with 15% engine oil. Cracking stocks of 180-300 deg. C. boiling range and from 300 deg. to E.P. should be cracked separately. ~~For motor oil the cracked gasolines obtained are polymerized together,~~ for airplane oil they can be polymerized separately or the lower boiling stock can be omitted.

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The primary product from Fischer-Tropsch synthesis boiling above 250 deg. C. was also used for motor oil manufacture. The paraffin cut was cracked to olefins and the C<sub>4</sub> to C<sub>16</sub> fraction of the cracked gasoline obtained was polymerized with AlCl<sub>3</sub>-olefin complex for 12 hrs.

Detailed account of above process is given: cracking, drying cracked gasoline, dechlorinating unit, filtration of reaction products, vacuum distillation unit, clay treatment, adsorption of HCl vapors.



T O M 46

Item 53 (pages 000963-000981)

Investigation of a cracked product from Lubricating Oil Operation. Ruhrchemie report dated July 1, 1941. Distillation characteristics and hydrocarbon composition of various fractions. Suitability of these fractions for blending to aviation gasoline and motor gasoline.

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Item 54 (pages 000982-000990)

Oxo plant drawings

T O M 46

Item 55 (pages 000991-2) Oxo Synthesis

(Memorandum by Dr. Martin of Ruhrchemie concerning conference with I.G. at Ludwigshafen on April 8, 1943)

(1) The gentlemen showed an apparatus in which olefins from a hydrocarbon synthesis, probably the so-called Michael-Synthesis, are being used, and particularly olefins from C<sub>5</sub> to C<sub>10</sub> naturally mixed with paraffins. The process used is the one worked out by Dr. Reppe using the cobalt salt of fatty acids. The synthesis has now been running two months with best results and it is the opinion that this process will eventually be used commercially.

Dr. Ambros informed us that two pressure vessels, together with the accompanying compressors were available in Ludwigshafen so that the process could be carried out in Ludwigshafen. It was thought that it would be possible to purchase the olefins from us at a specified price and the other components from I.G., who could then prepare the alcohols of the desired purity. The alcohols then would naturally be sold to the commerce in the same manner as the C.F.H. is now being handled.

Another possible way of preparing the desired alcohols is that the Oxo Company in Holten could operate, in accordance with the process of I.G. in Ludwigshafen, with one or two vessels which will eventually be made available. The alcohol-paraffin mixture obtained must then be sent to Ludwigshafen for further processing where it is thought that the mixture could be esterified with phthalic acid and the paraffin separated from the esters.

I am asking Dr. Roelen to determine how high the present olefin content is in the naphtha fraction from C<sub>5</sub> to C<sub>10</sub> (also to C<sub>9</sub>) and

I will advise Dr. Reppe by telephone. Upon receipt of this information he will advise whether he desires 50 kilos of this naphtha as a synthesis charge.

### Propylaldehyde

(2) There has been developed commercially, according to Dr. Reppe, a propylaldehyde synthesis with special solid catalyst, using ethylene, apparently obtained from Holten. The process is carried out in aqueous solution and in such a manner that a 2 to 3% aldehyde solution is continuously obtained. This aldehyde solution is extracted from the reaction vessel and run through a distillation column. The propylaldehyde, as well as the resulting by-products, is steam-distilled. In order to obtain pure aldehyde, the mixture is again distilled.

Up to now the yields that have been obtained are slightly in excess of 70%. The catalyst used is a special cobalt catalyst which is precipitated on such a carrier that: (1) the cobalt does not react with water and lose its activity; and (2) so conditioned that no reaction is obtained between the catalyst carrier and the cobalt metal. At first a silicate carrier was used, but it was found that at 200 deg., in the presence of water, a reaction with the cobalt was obtained. It appears that no one is too clear as to which carrier will actually be used. For this reason, the gentlemen have not concluded their efforts in this direction. We shall accordingly wait for further results, which should be carefully analyzed before we can definitely conclude whether the apparatus at Bombrini should not be so constructed that we can use the process of I.G. in Ludwigshafen without too many changes.

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It has been agreed with Dr. Ambros that in the near future Dr. Roelen and Dr. Landgraf will go to Ludwigshafen to observe their research.

(page 000993-4) Hoesch Product

(Memorandum by Dr. Martin of Ruhrchemie dated April 23, 1942)

At the beginning of this month we obtained from Dr. Schuff of Hoesch 5 liters of a heavy oil resulting from a new synthesis. This oil is supposed to have a high olefin content and we were to establish whether this oil could be used as a charge in the Oxo synthesis. The investigation of this heavy oil resulted in a rather remarkable discovery. That which was determined by Hoesch as olefins actually contained only a small portion of pure olefins, while the major portion consisted of oxygen-containing compounds, as well as some paraffins which were dissolved by the sulfuric-phosphoric acid reagents.

It is desirable to have a single method of analysis. Particularly noteworthy was the high content of aldehydes, as well as ketones. The analysis of such a complex oil is not particularly simple. The work on the separation of the aldehydes and ketones from the Oxo compounds has not been started. Anyway, we obtained a product of around 35% alcohols from the hydrogenation. This high content of oxygen-containing compounds, on the one side, and the low content of true olefins of around 9%, on the other hand, does not offer interesting prospects for this type of heavy oil as a charge in the Oxo synthesis.

These results I have reported to Dr. Ohme through a letter to Dr. Schuff, copy is attached. We have taken great pains to report all the details of our investigation. Apparently, the gentlemen at Hoesch haven't any idea what they have developed. They have apparently fallen into the error that all the sulfuric acid soluble portions (73.5%) of their oil are true olefins.

From this composition I could advise Dr. Ohme almost certainly that here we have a high pressure oil. In answer he advised that it was obtained at 7 atmospheres. This brings up the question as to what the remaining synthesis conditions are. It is logical that acetylene was used as the synthesis charge. The peculiar composition of this heavy oil, as well as its compositions after hydrogenation, makes it almost imperative that we proceed as previously mentioned before Hoesch investigates the composition.

(page 000995) Boric Acid Process

(Memorandum by Dr. Martin concerning discussion with Dr. Ambros in Dusseldorf on February 13, 1942)

For some time I have asked Dr. Ambros to consider which separation processes for alcohols and paraffins are possible when relatively small percentages of an olefin mixture is used in the Oxo reaction, for example, olefin content under 30%. Since the sulfonation of the alcohol-paraffin mixture apparently cannot be considered, for chlorine and sulfur-containing paraffin residues are formed with chloro-sulfonic acid or high concentrations of oleum, and besides, the separation of the sulfonates in and of themselves is not easy, I.G. in Ludwigshafen have undertaken research to separate the alcohols by means of the boric acid esters through distillation.

The most difficulty is encountered in distilling off the residual hydrocarbons from the boric acid esters. It is possible to completely distil off the hydrocarbons from thin layers of the boric acid ester. This process does not appear technically ready to predicate a large scale process thereon.

(page 000996) Butanol from Propylene

(Memorandum by Dr. Martin concerning discussion with Dr. Ambros at Dusseldorf on February 13, 1942)

Ludwigshafen has thoroughly developed this Oxo reaction and established that when a mixture of nine parts of propylene and one part of hexane is reacted continuously it results in a yield of approximately 95%. 60% of the product is made up of a mixture of equal parts of normal and isobutanol. The remainder consists of further condensation products, such as ethylhexanol, which, it is believed, can all be used.

They are now proceeding in Ludwigshafen to construct a plant of about 5 to 6,000 tons per year butanol capacity from the propylene reaction. They are estimating the operation cost, including amortization for 1 kilogram of Oxo product at about 80 pfennigs, and the average cost of butanol between 90 pfennigs and 1 mark.



T O M 46

Item 56 (pages 000997-001006) Kieselguhr

Report relates to the removal of iron from Kieselguhr by different types of treatment. There seems to be some doubt regarding the soundness of the results.

Item 57 (pages 001007-001020)

Catalysts for the Hydrogenation of CO. Ruhrchemie report, dated May 20, 1943. Activation of the cobalt catalyst by means of HgO. Brief discussion also of aldehyde formation by action of CO and H<sub>2</sub> on olefins. Deposition of higher paraffins on cobalt catalyst in F-T synthesis amounts to 100-150% of Co-Th catalyst by weight. Effect of physical characteristics of the kieselguhr carrier on course of the reaction. General discussion of the F-T reaction.

T O M 46

Ruhrchemie A.-G.  
Oberhausen-Holtien  
Abt. HL Tr/Mn.  
November 28, 1941

Item 58 (pages 001021-6)

German Patent Application R-569 covering Cracking with the  
Addition of Low Boiling Hydrocarbons

Against the above-named patent application the German Patent Office has cited U. S. Patent 2,206,055. It is pointed out that this U. S. Patent covers a gas reversion process in which  $C_3$  and  $C_4$  gases are added to a gas oil cracking stock; these added hydrocarbons undergo polymerization and also reaction with cracked fragments of the oil, with resultant formation of gasoline. However, in the patent application in question only  $C_4$ ,  $C_5$ , and  $C_6$  hydrocarbons under the conditions of the operation have no effect whatever on the cracking of the gas oil and are themselves isomerized. If  $C_7$  hydrocarbons are used, there is considerable cracking, since the cracking propensity of this hydrocarbon lies close to that of the higher boiling hydrocarbons.

Two examples are given indicating that the amount of cracking and the nature of the cracked products are practically the same according to method used in this application whether gas oil alone is cracked or whether  $C_4$ ,  $C_5$ , or  $C_6$  hydrocarbons are added but that in the latter case these added hydrocarbons are recovered in practically the same amount but are strongly isomerized. For example, 22 kg. of a Fischer-Tropsch oil boiling between 100 and 400 deg. C., 51 kg. cracking reflux, 95 kg. steam, and 10 kg.  $C_5$  fraction with an olefin content of about 90% and an iso content of about 8% were passed through a reaction vessel filled with 1200 liters cracking catalyst, the temperature of the catalyst being 490 deg. C., the

reaction period 40 minutes. At the end of this time the apparatus was steam blown for one minute and then treated with air for 15 minutes to burn off the carbon. The reaction products were as follows:

	By Weight
Gasoline	6%
C <sub>5</sub> hydrocarbons	38%
C <sub>4</sub>	21%
C <sub>3</sub>	16%
C <sub>1</sub>	4%
C <sub>2</sub> , H <sub>2</sub> , and C	5%

Disregarding the amount of C<sub>5</sub> hydrocarbons added, these yields are as follows:

	By Weight
Gasoline	22%
C <sub>5</sub> hydrocarbons	19%
C <sub>4</sub>	37%
C <sub>3</sub>	21%
C <sub>1</sub> -C <sub>2</sub> / H <sub>2</sub>	5%
Carbon	7%

The above amounts are not different in very great degree from those obtained under similar conditions but without addition of C<sub>5</sub> hydrocarbons.

	By Weight
Gasoline	24%
C <sub>5</sub> hydrocarbons	17%
C <sub>4</sub>	25%
C <sub>3</sub>	22%
C <sub>1</sub> -C <sub>2</sub> / H <sub>2</sub>	5%
Carbon	7%

Thus it is shown that the added C<sub>5</sub> hydrocarbons were recovered in practically the same amount. However, the iso content of the recovered C<sub>5</sub> fraction is now about 60%.

T. O. M. 46

Item 59 (pages 601027-8)

E-433 - Chromium Oxide Catalysts Containing Activator for  
Aromatization

Industrie A-G Oberhausen-Kolten  
135, 14 - 12/11/41

November 26, 1941

Dr. Langfeldt

With reference to the denial of claims 1 and 2 of the above  
application the following statements can be made:

It can not be taken from British Patent 349,444, page 4,  
lines 16 to 18, that chromium oxide-chromium oxide catalysts with  
more than 30% chromium oxide are especially active agents for

aromatization of hydrocarbons.

ably less than 10% of active material. Further, several U.S.P.  
applications containing substantially less than 10% of an activator  
have been refused. Comparative tests by us have indicated, and

have been recently confirmed by a number of other references

(for example, German references of Dr. Gilly) that catalysts with  
high chromium oxide content (about 30-50%) are decidedly better

results in aromatization than those with lesser chromium oxide content.

The statement made in the Patent Office application referred to that

with the utilization of activators the ratio of basic materials

chromium oxide and aluminum oxide must be held as the maximum

can thus be considered as fulfilled in English Patent 349,444. In

fact, in this British patent (page 2, lines 74 to 81) a catalyst

is described which consists of pure chromium oxide and boric acid,

and, according to our experience, such a catalyst is much more

sensitive with regard to regeneration than are the conditions  
with aluminum oxide; however, prolonged tests have shown that  
the first size decrease occurs very rapidly. Our own work has  
further shown that the hydroxyl group has a significant  
effect.

With reference to Table II it is seen from an examination of  
the data that the present data are in general agreement with  
the observations of the literature and that the addition of  
the activating addition of hydrogen and chlorine has been  
shown. On the other hand, the most important observation is  
that the rate of reaction is not affected by the addition of  
hydrogen and chlorine and that the rate of reaction is  
not affected by the addition of hydrogen and chlorine. The  
rate of reaction is not affected by the addition of hydrogen  
and chlorine and that the rate of reaction is not affected  
by the addition of hydrogen and chlorine.

1. With 0.5 mole of hydrogen and 0.5 mole of chlorine
2. With 0.5 mole of hydrogen and 0.5 mole of chlorine
3. With 0.5 mole of hydrogen and 0.5 mole of chlorine

low temperatures by the reaction of hydrogen and chlorine  
and that the rate of reaction is not affected by the  
addition of hydrogen and chlorine. The rate of reaction  
is not affected by the addition of hydrogen and chlorine.  
The rate of reaction is not affected by the addition of  
hydrogen and chlorine. The rate of reaction is not  
affected by the addition of hydrogen and chlorine.

at 400 deg. C. in a nickel catalyst. The rate of  
reaction is not affected by the addition of hydrogen  
and chlorine. The rate of reaction is not affected  
by the addition of hydrogen and chlorine.

surprising that the rate of reaction is not affected  
by the addition of hydrogen and chlorine. The rate of  
reaction is not affected by the addition of hydrogen  
and chlorine. The rate of reaction is not affected  
by the addition of hydrogen and chlorine.

foregoing example) furnished considerably higher yields of aromatics without side reactions occurring to a greater extent. Manganese, in the case of nickel, and thorium in the case of cobalt, possess in the invention in question only the role of stabilizers for the activating additions. Chromium-oxide-aluminum oxide catalysts with an addition of only manganese or thorium oxide did not give a higher aromatic yield in the liquid product.

Since it is seen from the negative ruling of the Patent Office that a limitation to cobalt and nickel as activating substances appears possible without further discussion, at least this part of the application can still be saved.

T O M 46

Item 60 (pages 001029-39) Miscellaneous Additions to Patents

Ruhrbenzin A.-G.

BE II V/WR

8 September 1941

Subject: Patent Application R-513 covering a process for the preparation of high molecular fatty acids

The German Patent Office examiner had cited against the above application German patent 553,038, which covers the decolorizing of montan wax by means of sulfuric acid and alkali bichromate, which are the reagents used in subject application. Evidently, Application R-513 covers the oxidation of carbon monoxide hydrogenation paraffin. Reference is also made to Application R-541, it being understood that the iodine number of the hard paraffin covered in R-541 is 6.6-6.8 and that since no mention of the iodine number of the paraffin covered by R-513 is given, evidently this material is entirely olefin-free. Also the R-513 product is prepared using a CO:H<sub>2</sub> ratio of 1:2.

Patent Application R-514 covering the oxidation of Fischer-Tropsch paraffin; the wax is first chlorinated, then dechlorinated to give olefins which are oxidized with a solution of alkali bichromate in H<sub>2</sub>SO<sub>4</sub> at about 100 deg. C. U.S. 1,110,925 was cited against this application by the Examiner.



Ruhrbenzin A.-G.  
BL II V/Wk

September 9, 1941

Patent Division:

Subject: Patent Application R-541, covering the oxidation of water gas paraffine

For discussion of this application see Patent Application R-513.

Ruhrbenzin A.-G.  
BL II Bkf/Wk

October 6, 1941

Subject: Patent Application R-546 covering a process for the oxidation of synthetic paraffin

Hard paraffin obtained by the catalytic hydrogenation of CO with a melting point of 91 deg. C. was used. 5 kg. of this material was heated to 121 deg. C. and 1.25 liters nitrosyl sulfuric acid (containing about 10.5% NO, specific gravity 1.91 at 15 deg. C.) was slowly added while at the same time 5850 l./hr. ammonia combustion gases with a content of about 8% NO were passed in. The reaction product was separated from the mineral acid, washed several times with water and dried, giving 4546 grams or 91% yield of an oxidation product having the following properties:

Neutralization Number - 101.5

Saponification Number - 105.5

Melting Point - 60.5 deg. C.

Another example is given in which a paraffin of 52 deg. C. melting point was used.

T O M 46

Item 61 (pages 001041-2)

Addition of Acetylene to Synthesis Gas

October 7, 1941

Ruhrchemie A.-G.  
Oberhausen-Holtien  
Abt. HL-Rg./Mm.

Professor Martin, Dr. Hagemann, Director Alberts:

Subject: Experiments on the hydrogenation of CO by the addition of acetylene in the liquid phase under pressure.

The results described in a previous report (August 1, 1941) on CO hydrogenation with acetylene addition in the liquid phase at an operating pressure of 100 atmospheres have been extended by an experiment carried out under practically the same conditions with the exception that the operating pressure during the experiment was held at only 20 atmospheres. The other conditions are briefly:

Average reaction temperature - 100 deg. C.

Water gas plus 18% acetylene

The average conversion was acetylene 85%, CO 20%, H<sub>2</sub> 40%.

In the earlier experiment pentane was used as the liquid medium while in this case heptane was employed. The duration of the experiment was about 100 hours.

The final liquid product was distilled in a small Brunn column with 20 plates, giving the following fractions:

Forerunning - up to 93 deg. C.

Main fraction - 93-100 deg. C.

Residue - Above 100 deg. C.

Examination of these various fractions shows that low pressure in hydrogenation of CO with addition of acetylene in the liquid phase gives no indication of the formation of unsaturated oxygen-containing compounds and that, in contrast to analogous experiments in the gaseous phase, the olefinic portion of the resulting gasoline is considerably decreased.

T O M 46

Item 62 (pages 001043-6) Dubbs Cracking Plant

Ruhrchemie found unsatisfactory an evaluation of their feed stock by UOP who contemplated operation at a pressure of 5 atmospheres and 550 deg. C. It was Ruhrchemie's contention that since a major fraction of the cracked product was to be used in the production of lubricating oil a substantially lower temperature and a longer time would best meet Ruhrchemie's requirements. The installation made by Ruhrchemie provides for operation at 10-12 atmospheres at a maximum temperature of 500 deg. C. with 33% more tubes in the furnace than had been recommended by UOP. The installation was found by test to be capable of operation at the designed capacity of 825 barrels per day while producing liquid products containing about 50% of material suitable for use in lubricants. These results were in substantial agreement with an evaluation later made by UOP in accordance with Ruhrchemie's designed conditions and requirements.

T O M 46

Item 63 (pages 001047-51)

December 22, 1941

Ruhrchemie A.-G.  
Oberhausen-Holtien  
Abt. HL-Spk/Km

Subject: Treatment of a catalytic cracked gasoline with  $BPO_4$  in comparison with the use of Granusil.

In this series of tests for comparing the refining effect of  $BPO_4$  in comparison with that of Granusil (a decolorizing material) an average temperature of 330 deg. C. was maintained, no pressure and a throughput of 500 cc. gasoline per hour. The gasoline was divided into three portions, one of which remained untreated, the second was treated with Granusil, and the third with  $BPO_4$ . It was found that the  $BPO_4$  treatment caused not only a slight polymerization but also some cracking. The attached table gives the characteristics of the untreated and treated products from which the following conclusions can be drawn.

In the case of the non-hydrogenated product there was no difference in the research octane numbers between the two treated gasolines, while the research octane was 10 units lower in the case of the untreated non-hydrogenated product. However, when the three products were hydrogenated, the differences in research octanes were relatively slight and all products showed approximately the same lead response.

In the case of motor octanes there was practically no difference between the hydrogenated and non-hydrogenated products treated with Granusil and  $BPO_4$  and their lead response was also the same, while the untreated gasoline was 7 units lower in the case of the non-

hydrogenated and 4 units in the case of the hydrogenated product.

However, this difference was removed by the addition of lead so that also in this case there is practically no difference between the untreated and the treated products.

The conclusion is drawn that the treatment of catalytic cracked gasoline for the purpose of improving and increasing the yield of aviation gasoline is unsuccessful either with Granusil or with  $\text{BPO}_4$ .

Table 1

Gasoline 50-100 deg. C.	Untreated		Granusil		BPO	
	Non-hydrogenated	Hydrogenated	Non-hydrogenated	Hydrogenated	Non-hydrogenated	Hydrogenated
d <sub>20</sub>	0.6806	0.6628	0.6932	0.6765	0.6879	0.6752
nD <sub>20</sub>	1.3959	1.3762	1.4022	1.3892	1.3996	1.3837
Reid Vapor Pressure	0.55	0.61	0.44	0.38	0.61	0.64
Iodine No.	261.0	0.3	221.3	2.4	240.0	2.9
Research Octane	86.5	66.1	96	70.7	96.1	73.3
Research Octane / 1.2Pb	98.6	91.9	100	92.5	101.5	92.8
Motor Octane	74.3	65.5	81.6	69.5	81.9	70.5
Motor Octane / 1.2Pb	84.3	89.1	86.5	90.7	86.0	91.7
I.B.P.	48 deg.	49	50	44	43	41
E.P.	125 deg.	128	242	225	226	230
T deg.	52 deg.	52	54	50	48	50
	62 deg.	62	66	68	65	67
	95 deg.	100	165	145	180	184

(10%)  
(50%)  
(95%)

T O M 46

Item 64 (pages 001052-1108) Methods of Hydrocarbon Analysis

- pp. 001052-65      A modified method for determining olefins in gasolines and diesel oils by a bromo-metric method (micro method).
- 001065-87      Determination of iodine number for gasolines and diesel oils (micro method).
- 001088-89      Supplement to the paper on a bromo-metric micro iodine number method for gasolines and diesel oils.
- 001090-101      Analytical experiments on the usefulness of the iodo thiocyanogen number method of Kaufmann for the determination of unsaturated hydrocarbons.
- 001102-2b      Determination of iodine number by means of thiocyanogen. Continuation of preceding with math. method of determining I#.
- 001103-7      The use of bromothiocyanogen for the determination of olefins in hydrocarbon mixtures.
- 001108      Supplement to the paper of Sept. 16, 1941 on the usefulness of iodo thiocyanogen and bromothiocyanogen for the determination of the unsaturated hydrocarbons. (See Osl n. Kohle 14 200 (1938)).