

FILM STUDY GROUP

REPORT

T.O.M. REEL NO. 42

Prepared by

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Report on Reel 42 (formerly 10B) of
U.S. Technical Oil Mission Microfilm

This reel reproduces documents taken from the Ruhrchemie A.G., Sterkrade-Holten, Germany. The Ruhrchemie Company was a leader in the field of Fischer-Tropsch synthesis. The film contains much miscellaneous material on this subject and on related hydrocarbon chemistry, but does not include any important single reports. There are many research suggestions and orders to do laboratory work, written mostly by Roelen, which are of interest in indicating the research trends. There are also some reports on analytical methods for products from the synthesis process and the Oxo process.

All material in the film is covered by the following abstracts. Although several detailed abstracts are given for certain analytical material, this in no way indicates that the analytical material is of greater relative importance. The page numbers given are written in pencil in the upper right hand corners of the frames.

Reel 42, Abstracts
Ruhrochemie A.G., Sterkrade-Holten

Bag 3439 continued
Target 30/5.01

Item 10 Page 1 Note suggesting that I.G. has prepared special lubricating oil by reaction of carboxylic acid with Oxo-alcohols (no details).

Holten

Feb. 27, 1943

Page 2 Note on the possible use of various metal carbonyls in Oxo-process.

Holten

Dec. 1, 1941

Page 3 Note on problem of adequate heat removal during Oxo-synthesis.

Holten

Sept., 1941

Pages 4-5 Letter from I.G. discussing status of Oxo-synthesis and requesting samples of highly olefinic material.

Holten

July 1, 1941

Page 6 Note requesting samples of product from Oxo-synthesis boiling below 200°C for "knock" tests.

Holten

Apr. 24, 1939

Item 11 Pages 7-8 Letter from Roelen discussing results of new iron catalyst from Rheinprussen.

Hanover

Sept. 6, 1944

Page 9 Brief discussion of copper-containing iron catalyst for paraffin production.

Holten

May 15, 1942

Page 10 Note on use of synthesis gas feeds comprising two or more parts of H₂ to one part CO with iron catalysts.

Holten

Aug. 15, 1941

Page 11 Summary of conversation between Martin, Heckel and Roelen on current synthesis investigations.

Holten

Aug. 9, 1941

Page 12 General problems connected with iron catalysts.

Holten

June 20, 1941

Item 12 Pages 13-18 Report on possible methods for synthesis gas purification.

Holten

April 22, 1940

Item 13 Pages 19-21 Discussions leading to a two-party and three-party agreement on the Oxo-process, between Ruhrochemie, Henkel and I.G.

Ludwigshafen

Aug. 28, 1940

Pages 22-29 Cost estimates for fatty alcohols (C₁₂-C₁₈) from a proposed 10,000 tons/year Oxo-plant. Equipment and utilities requirements outlined. Flowsheet shown.

Holten

Oct. 28, 1940

Pages 30-33 Discussions between Holten and Ludwigshafen on Oxo-synthesis. Cost estimates, status of investigations, nature of product and analyses (no details). Holten Oct. 30, 1940

Page 34 Possible applications of fatty acids prepared from higher olefins. Holten Sept. 22, 1938

Pages 35-44 Text of the agreement on Oxo-synthesis between Ruhrchemie, Henkel and I.G. Holten Oct. 31, 1940

Pages 44-55 Text of the agreement on Oxo-synthesis between Ruhrchemie and I.G. Holten Oct. 30, 1940

Pages 56 Agreement between Ruhrchemie, Henkel and I.G. on special products. Holten Oct. 31, 1940

Item 14 Pages 57A-B Diagrams indicating possible product utilization from Fischer-Tropsch synthesis plants. Holten

Item 15 Pages 59-70 Volumetric determination of sulfate ion according to W. C. Schroeder (Ind. & Eng. Chem. Anal. Ed. 5, 403-406, 1933). This method, involving direct titration of sulfate ion using tetrahydroxyquinone as an internal indicator, was tested. It was found that the determination is more accurate if the excess of barium chloride is back titrated instead of titrating directly with barium chloride.

Pages 71-77 Determination of small proportions of chloride ion. In this method chloride ion is titrated with standard mercuric nitrate solution using diphenylcarbazone as an indicator. The method has been published in Die Chemie 55, 319, (1942).

Item 16 Pages 81-107 Modified method for the determination of the neutralization and saponification number of gasolines, Diesel oils and lubricating oils. This report describes a semimicro procedure which is claimed to be just as accurate as the micro method but has the advantage of greater speed and reducing the cost per analysis considerably.

Pages 108-120 Determination of Olefins with Phosphorus Pentoxide-Sulfuric Acid (Kattwinkel reagent)

Abstract

A study was made to clarify discrepancies that were encountered with this method when diluents had been used in the determination of olefins in Diesel oils. It is concluded that in the gasoline range with an olefin content up to 60-65% the direct sulfonation as well as sulfonation on a diluted sample gives concordant results. The direct sulfonation procedure is improved by using an acid to gasoline ratio of 4:1 instead of 3:1 as has been used. The higher ratio is applicable to samples of highest olefin concentration. In the diesel oil range the dilution method gives too high results so that it is not applicable for such products. Since the direct sulfonation on samples in the diesel oil range did not show any differences in the results when an acid ratio between 3:1 and 4:1 was used it is contemplated that in the future the olefin determination on all products is made with a 4:1 acid to sample ratio.

Pages 121-129 Determination of Gaseous Paraffins

The material under this heading appears to be of interest and has been translated.

In connection with experiments on polymerization of Ruhrgasol and Fischergasol the problem of the analysis of gaseous paraffin hydrocarbons has been investigated. The methods of separation so far known are all based on fractional distillation, fractional condensation, or absorption with activated charcoal followed by selective desorption. All these methods have disadvantages in that they require expensive apparatus and the time involved in an analysis is quite lengthy.

We investigated the possibility of making this separation by conventional gas analysis methods. The separation of C_3 and C_4 hydrocarbons by means of activated charcoal was not easily made because of the low selectivity. It is known that various liquid absorbents such as silver sulfate-sulfuric acid, fuming sulfuric acid, silver sulfate-fuming sulfuric acid, and others absorb higher paraffins and give rise to errors in analysis. These reagents all absorb propane and butane incompletely; however, we found that a reagent previously proposed for the determination of carbon monoxide (suspension of iodine pentoxide in fuming sulfuric acid) is capable of removing propane and butane rapidly and completely from gases.

According to Dittrich (Z.f. angew. Chem. 43, 979: 1930), carbon monoxide can not be determined in the presence of higher hydrocarbons by means of iodine pentoxide - fuming sulfuric acid because butane, propane, and to a small extent ethane are absorbed. During our investigation another publication by Dittrich appeared (Brennstoffchemie, 17, 245; 1936) on gas analysis methods in which it was mentioned explicitly that I_2O_5 - fuming sulfuric acid could not be used for determining paraffins because the time required for complete absorption is too lengthy. Contrary to this, we found that by selecting the proper I_2O_5 and SO_3 concentrations butane and propane can be absorbed in a relatively short time, and a correction for ethane absorption can be made by noting the constant absorption per timed pass. Consequently, as in the propylene - ethylene separation by means of concentrated sulfuric acid, an extrapolation can be made to zero absorption and the amount of ethane absorbed can be determined graphically or algebraically. In the subsequent combustion analysis most of the ethane and all of the methane, which like the hydrogen have not been removed, are determined. The analysis is illustrated below by an example.

Because of the high viscosity of the solution ordinary pipets cannot be used because gas cannot be readily forced into the narrow openings and capillaries. Therefore, we have used pipets filled with glass beads, as shown in Figure 1, which have also been proposed for carbon monoxide absorption. At 1 is a drain cock, to remove the solution when the analysis has been completed, which is necessary because the iodine pentoxide forms a thick sludge on the glass beads and the solution cannot be agitated. At 2 is an opening for introduction of the glass beads. It is essential that the glass beads completely fill the pipet in order to provide sufficiently intimate contact with the reagent to ensure rapid reaction. The pipet must be packed with beads in such a manner that empty spaces will not form.

In conducting analyses it has been found advisable to allow a two-minute contact time with the liquid in the pipet. Following the absorption in $I_2O_5 - SO_3$ the gas is passed twice into potassium hydroxide solution to remove SO_2 gas. The iodine pentoxide suspension has the following concentration: 10 g. I_2O_5 in 250 g. of 2.5 to 3.0% fuming sulfuric acid.

We have also investigated higher concentrations of fuming sulfuric acid and found that owing to activated absorption ethane is not removed uniformly, but is removed at a higher rate together with butane and propane in the beginning of the analysis. Consequently too much propane and butane and correspondingly too little ethane is found. This error was avoided by using the concentration specified above. The quantity of iodine pentoxide was chosen such that the viscosity of the suspension was not too high. For the preparation of the reagent 10 g. of iodine pentoxide are triturated with 125 g. of 2.5% fuming sulfuric acid (per 100 g./ 46 g. 95% sulfuric acid and 5.4 g. 20% fuming sulfuric acid) in a mortar and the remaining 125 g. of acid added and the mixture shaken for one hour.

In Tables 1 and 2 are summarized the results obtained with this reagent. With mixtures containing the three components methane, ethane, and propane are determined by a single analysis. The agreement with known values is good. If, however, the gas contains butane also, the carbon number of the gas must be determined by a second analysis in order to calculate the propane and butane contents. As may be seen, the agreement with the four component mixture is not as good as with the three component mixture but further work is planned. The accuracy can be increased by determining the density with a gas density balance instead of the carbon number because the density can be determined with considerably greater accuracy than can the carbon number. When using the carbon number a correction factor must be applied due to the different molecular volumes of carbon dioxides, butane, propane, etc. For example:

<u>Found Carbon No.</u>	<u>True Carbon No.</u>
1	1.01
2	1.982
3	2.939
4	3.904

The purity of the gases used in the experiments was as follows:

~~The methane, propane, and butane were obtained from cylinders while the butane was taken from the plant. The Concordia methane contained 99% methane; higher hydrocarbons were absent. The ethane contained 3-4% propane and 7-8% propylene + ethylene. The bulk of the olefins were removed with silver sulfate-sulfuric acid and the rest liquified. For the tests only the portion distilling between $-95^{\circ}C$ and $-85^{\circ}C$ was used so the propane was removed completely. However, the ethane still contained 7 to 8% methane. The propane and butane were used directly. Analysis of the liquified gases gave the following results:~~

Propane

Combustion: 99.2% $C_nH_{2n} + 2$
 C No. found: 2.985
 C No. corrected: 2.925

Analysis with I_2O_5 - Fuming H_2SO_4

C_3H_8	96.0%	Const. factor = 0.0
C_2H_6	2.7%	
CH_4	0.5%	

C No. from analysis: 2.940
 Difference: 0.015

Butane

Combustion: 99.2% $C_nH_{2n} + 2$
 C No. found: 3.938
 C No. corrected: 3.850

Analysis with I_2O_5 - Fuming H_2SO_4

	<u>I</u>	<u>II</u>
C_4H_{10}	85.8	86.0
C_3H_8	11.8	11.8
C_2H_6	0.2	0.4
CH_4	0.8	0.8
C No.	3.855	3.848
Difference:	+0.005	-0.002

The individual gases were blended in various proportions and the mixtures analyzed. For the analysis of an unknown gas mixture the procedure is as follows: The gas is analyzed in the usual manner and the C number determined. One finds, for example, 65% saturated hydrocarbon with corrected C No. of 2.755. A second portion of the sample is analyzed in the usual manner through the carbon monoxide determination and the gas then passed through $I_2O_5 - H_2SO_4$ solution before the H_2 is burned. It is found after 20 passes (each 2 minutes) that 35 ml. have been absorbed by the solution with a constant factor of 0.15 (found 5 times) i.e., $20 \times 0.15 = 3$ ml. ethane have been absorbed. The residual gas is burned over copper oxide and hydrogen and the saturated hydrocarbons, which consist only of methane and ethane, are determined. It has been found for example a C number of 1.833 (corrected) by burning 30 ml. Therefore in 30 ml. there are $0.833 \times 30 = 25.0$ ml. of ethane and consequently 5.0 ml. of methane. Summing up:

Total $C_nH_{2n} + 2$	= 65 ml.	C No. 2.755
of this Propane + Butane	= 32.0 ml.	(35-3)
Ethane	= 28.0 ml.	(25+3)
Methane	= 5.0 ml.	

65 ml. $C_nH_{2n} + 2$	= 179.2 ml. CO_2
-28 ml. C_2H_6	= -56.0 ml. CO_2
- 5 ml. CH_4	= - 5.0 ml. CO_2
32 ml.	= 118.2 ml. CO_2

Residual C No. = 3.69
that is Butane = 22.1 ml. (0.69 x 32)
Propane = 9.9 ml.

Summarizing further:

65.0 ml. $C_nH_{2n} + 2$ C No. 2.755
of which Butane = 22.1 ml.
Propane = 9.9 ml.
Ethane = 28.0 ml.
Methane = 5.0 ml.

If a gas contains less than 15% ethane and methane it is advisable to dilute with nitrogen before the absorption with $I_2O_5 - H_2SO_4$.

The present results are not final and will be supplemented. Analyses should be made with gases of 99% purity so that synthetic mixtures can be prepared with greater accuracy and furthermore there are questions with regard to the solubility of gases in the solution and also questions concerning the stability of the solution, recovery of the iodine, and the mechanism of reaction. The I_2O_5 is consumed rapidly and with aged solutions the rate of absorption is considerably reduced. It is not completely clear as yet whether the aging of the solution can be avoided by the addition of fresh I_2O_5 or SO_3 or how long the solution can be used. Regarding the reaction mechanism, it remains to be explained how butane and propane react with I_2O_5 ; the gases are absorbed without formation of an equivalent amount of CO_2 . They are probably sulfonated with intermediate olefin formation; as oxidation product water and free iodine should then be formed. This question is important for the recovery of the solution.

Summary

A method is described for the determination of gaseous paraffins in the usual gas analysis. A suspension of I_2O_5 in fuming H_2SO_4 absorbs butane and propane completely in a relatively short time; ethane is absorbed so slowly that an absorption factor can be determined while methane and hydrogen are not attacked.

Oxo Products Analysis, Methods and Data

In connection with the Oxo-process, i.e., the production of higher alcohols and other oxygen-containing materials by the addition of CO and H_2 to olefins, interesting analytical information is presented which has been either abstracted or translated.

Table 1 Analysis of Propane, Ethane, Methane Mixtures

<u>Determination</u>	1	2	3	4	5	
C ₃ H ₈	Present, ml.	28.8	9.6	67.2	85.0	48.0
	Found, ml.	29.1	9.9	67.2	84.8	48.2
	Diff., ml.	+0.3	+3	0	-0.2	+0.2
C ₂ H ₆	Present, ml.	55.0	69.9	25.2	11.3	37.4
	Found, ml.	54.2	69.7	24.7	11.3	37.3
	Diff., ml.	-0.8	-0.2	-0.5	0	-0.1
CH ₄	Present, ml.	5.5	7.0	2.7	1.3	3.9
	Found, ml.	5.0	6.8	3.1	1.1	3.5
	Diff., ml.	-0.5	-0.2	+0.4	-0.2	-0.4
C No.	Present	2.26	2.031	2.675	2.858	2.496
	Found	2.27	2.034	2.670	2.861	2.503
	Diff.	+0.01	+0.003	-0.005	+0.003	+0.007
Const. Factor for C ₂ H ₆	0.30	0.433	0.0	0.0	0.2	
No. of Passes Required to Reach Const. Factor	7	4	10	18	11	

Table 2 Analysis of Butane, Propane, Ethane, Methane Mixtures

<u>Determination</u>	1	2	3	
C ₄ H ₁₀	Present, ml.	33.2	27.8	25.5
	Found, ml.	32.1	29.7	23.6
	Diff., ml.	-1.1	+1.9	-1.9
C ₃ H ₈	Present, ml.	33.7	39.1	32.4
	Found, ml.	34.8	36.5	34.9
	Diff., ml.	+1.1	-2.6	+2.5
C ₂ H ₆	Present, ml.	25.6	25.6	8.8
	Found, ml.	27.9	24.5	6.6
	Diff., ml.	+2.3	-1.1	-2.2
CH ₄	Present, ml.	3.3	3.3	31.2
	Found, ml.	1.3	4.8	30.8
	Diff., ml.	-2.0	+1.5	-0.4
C No.	Present	3.015	2.952	2.531
	Found	3.020	2.956	2.535
	Diff.	+0.005	+0.004	+0.004
Const. Factor for C ₂ H ₆	0.175	0.15	0.0	
No. of Passes Required to Reach Const. Factor	5	6	10	

Item 18 Pages 153-155 New method for determining double bond number
(communication from Ruhrchemie 12/4/42). The determination of the double bond number in organic molecules is based on the fact that the ethylene bond is capable of addition reactions. So far mainly the addition of hydrogen, halogen, and sulfuric acid has been used for the quantitative determination of the double bond. Although the hydrogenation method gives accurate values with pure compounds using a suitable catalyst, the two other methods may give results which may be useful for technical purposes but are unsatisfactory on a scientific basis. The uncertainty of results obtained by the determination of the iodine number is indicated by the fact that it is necessary to report also the procedure that has been used. Moreover, the numerous methods that have been worked out for determining the iodine number are a criterion of the dissatisfaction of the methods used.

The main reason of the frequent discrepancies lies in the fact that so far it has not been possible to determine the end point of the halogen addition so that substitution is prevented. The conventional methods for determining the iodine number prescribe a definite reaction time which gives accurate results as long as olefins are present which exhibit the same rate of reaction in the halogen addition. We have therefore investigated the interaction of ozone and olefins with the intention to use the ozonides, which for the first time had been studied by Harries, for the analysis. The addition of ozone to the double bond is a strongly exothermic reaction which, for example, in the case of fumaric acid ethyl ester liberates 115 Kal. (Briner) while water shows a heat of reaction of only 6.8 Kal.

For this reason and in order to avoid oxidation of the saturated hydrocarbons, the ozonization was carried out at temperatures of -50°C to -70°C . Moreover, under these conditions the end point of the ozonization can be recognized; at these low temperatures the excess of ozone dissolves with a blue color in the saturated hydrocarbons. It was found that with the appearance of the blue color no double bond could be identified in the reaction mixture with bromine water. Also, under these conditions no indication of an oxidation of the saturated hydrocarbons could be noticed. Even the three double bonds in benzol are not attacked under these conditions.

The method consists in weighing a certain amount of the olefin to be analyzed into a suitable vessel and then passing ozone through the solution until it begins to turn blue. From the weight increase after ozone has been passed through the solution the iodine number is calculated according to:

$$\frac{\text{weight increase} \cdot 5.288 \cdot 100}{\text{weight of sample}}$$

We have designated the iodine number as Ozon iodine number (O-I-Z). The new method has been tested with different hydrocarbons and the results are shown in Table 3.

Procedure for determining Ozon iodine number

1-2 g. hydrocarbon is accurately weighed in a Kali-apparatus (translator's comment: this is a small absorption bulb shaped like the Milligan absorber which is used for absorbing CO₂ in carbon and hydrogen in combustion analysis) diluted with 10 to 20 ml. diluent (nonane purified with Kattwinkel reagent), weighed again and treated with ozone until beginning blue coloration (Ozon concentration 6%, velocity 10-15 l. per hour). During the introduction of ozone the vessel is cooled with dry ice. The absorption vessel is dried and allowed to stand for 15 minutes in a dessicator and reweighed. From the difference in weight the O.I.Z. is calculated according to the above formula.

Table 3 Comparison of Results Obtained by Various Methods

No.	C No.	Ozone Iodine No.	Oxo-Synthesis	Cortese Iodine No.	Soluble in Kattwinkel Reagent
136	9	54.1	54.8	59.2	67.0
137	10	50.0	56.3	52.5	61.0
132	11	47.5	49.0	55.5	50.0
133	12	47.6	44.0	54.3	54.0
135	13	45.0	44.0	47.0	48.0
138	14	24.0	29.4	35.6	32.0
139	15	26.6	29.9	40.6	35.0

Pages 156-158 Method for the determination of terminal olefinic bond. For many purposes, particularly in polymerization of low boiling olefins to lubricating oils and for the Oxo-synthesis, it is of importance to have olefins containing as many as possible terminal bonds. A chemical method for determining the terminal bonds has so far not been known. In the ozonization of olefins a method has been found which had frequently been used for determining the constitution of natural substances. The applicability of this method has been investigated. It consists in the ~~addition of ozone to the double bond and splitting the ozonides by inter-~~ addition with water in aldehydes and acids. The cleavage of the molecule takes place where formerly the double bond was located. In this way by determining the carbon number of the formed fragments conclusions as to

the location of the double bond may be drawn. Disadvantages of this method are the inhomogeneity of the products formed and the fact that the reactions do not proceed quantitatively. In the literature are described cleavages which gave only about 20 per cent yield. A considerable improvement is offered by the method by Asinger consisting in the oxidative cleavage of the Ozonides by means of silver oxide. By this method only acids are formed as final products and a good yield is obtained. Asinger, however, worked only with materials which yielded the higher fatty acid while in our case for the determination of olefins in the terminal bond particularly the lower members are of importance.

The principle of the determination of olefins with terminal bonds consists in treating the olefin with ozone until the olefins have reacted completely, oxidative cleavage of the ozonide, and quantitative determination of the formed formic acid. In order to obtain useful results various requirements have to be fulfilled. Firstly, the end-point of the completed addition of ozone has to be established accurately in order to avoid oxidation of saturated hydrocarbons that may be present. The latter requirement could be met by working at low temperatures. At low temperatures the excess of ozone is dissolved in the hydrocarbon with a blue color which thus indicates the end point of the ozone addition. In order to avoid losses of formic acid and formaldehyde the vessel was equipped with a reflux condenser. To determine the formic acid the procedure by Asinger was modified and improved. In the examination of various olefins having presumably terminal olefinic bonds it was found that not all could be considered terminal as had been assumed. The shift of a terminal olefinic bond toward the middle of the molecule may mean that the molecule was energized, a condition which easily could be created by various reactions during the preparation of the materials. So, for example, a sample of hexene-1 obtained from a known chemical firm showed a content of terminal olefin of only 11 per cent. It was therefore tried to prepare nonen-1 by means of the Grignard reaction from hexyl bromide and allyl bromide. In this way, olefins were obtained which had terminal olefin bonds between 90 and 100 per cent. Whether these discrepancies were caused by errors in the determination or by a shift of the double bonds to a certain extent, could not be decided. Several olefins prepared in the laboratory and obtained from other sources were analyzed in order to test the method. The results are shown in Table 4. The terminal olefinic bond is reported as iodine number of terminal olefin and designated as terminal iodine No. E-J-2, and is calculated according to the following equation:

$$\frac{\text{Amount formic acid} \cdot 5.52 \cdot 100}{\text{Weight of sample}}$$

Procedure

Approximately 2-3 g. of the olefin are weighed accurately and diluted with 15-20 ml. solvent (purified with Kattwinkel reagent) and placed in a separatory funnel equipped with a ground joint. The funnel is inserted in a glass tube having a ground joint and being connected to

the ozone generator. Now, from below a stream of ozon (ozon content 6%) is introduced at such a rate that with the stopcock open the reaction liquid in the funnel does not drain (rate 10-15 l. per hour). The neck of funnel is connected to a vent tube which leads to a Meyer ten bulb absorption tube containing 50 ml. of water to absorb volatile reaction products. Around the funnel is placed a mantle which is filled with dry ice to cool the reaction liquid. Ozon is introduced until the solution begins to turn blue. The separatory funnel is then inserted in a 2-neck reaction flask equipped with ground joints to hold also a reflux condenser. The reaction flask is immersed in a boiling water bath and the ozonides are added slowly, drop by drop, to a suspension of silver oxide in 10 per cent NaOH and allowed to stand for 1/2 hour. The solvent is distilled off by exchanging the reflux condenser with an ordinary descending condenser. Then the absorber solution from the 10-bulb absorption tube is added to the flask and the contents heated for another 30 minutes. After cooling the solution is acidified with HCl in order to separate the higher fatty acids and also to precipitate any silver that has gone in solution. In the filtered solution the formic acid is then determined by the calomel method and from the value found is calculated the E.J.Z (terminal iodine number).

Table 4 Olefin Content and Terminal Olefinic Bonds
in Synthetic Hydrocarbons of Various Origin

Name	Origin	Determination of Iodine Numbers		Determination of Terminal Olefinic Bonds		
		According to Cortese	By Ozone	Terminal Iodine No.	% Terminal Olefin According to Cortese	% Terminal Olefin by Ozone
Nonene	Grignard	194	187	165	85.1	88.3
Allyl-bromide	Essen	193	198	171	88.6	86.4
Nonene	Grignard	180	159	148	82.2	93.0
2,5-methyl octene	Grignard	186	176	150	80.7	88.4
C ₁₅ Hydrocarbon	Henckel	123	97	104	84.7	100
Octene	I.G.	209	207	118	56.5	57.0
Dodecene	I.G.	148	151	38	25.7	25.2

Minutes

Pages 164-168 On the discussion of the Analysis of Products of the Oxo process held at Ludwigshafen, December 7, 1942.

Abstract

Present at the meeting were representatives from Ludwigshafen, Oxogesellschaft, Henkel, Ruhrchemie, Leuna, and Oppau. On hand of a compilation of analytical results obtained on four cooperative samples by the various laboratories the following points were discussed.

Olefins: Primary oil C_{11/12} and C₁₇. The molecular weight had been determined cryoscopically in benzol, dioxane and glacial acetic acid, the latter being used to prevent association of any alcohols present. Since the alcohol content is small, benzol as solvent is recommended. For the determination of the carbonyl number only the method by Stillmann and Réed should be considered. The time of boiling should be 1/4 hour and instead of bromophenol blue as indicator also methyl orange can be used. The calculation has to be made as mg./one gram.

The hydroxyl number had been determined either in open vessels or sealed tubes without indicating essential differences in the results. The sample size should be sufficiently large but at least 4/5 of the used acetic acid anhydride should be back-titrated. Reference is made to the method by Kaufman (Fette and Seifen 1939, p. 518), which in cases of dispute should be the referee method.

For the determination of the amount soluble in phosphorpentoxide sulfuric acid (S.P.L.) according to Kattwinkel the procedure by Buechner using the butyrometer tube has been found satisfactory. This procedure, developed at Leuna, circumvents the use of rubber stoppers which are objectionable. The ratio olefin to phosphorpentoxide - sulfuric acid should be at least 1:3.

For the determination of olefins, Ruhrchemie proposes the bromine number according to Cortese in a specially designed flask. Henkel had unfavorable experience with this method. Leuna emphasizes the advantage of the simple procedure by Kaufman which requires a relatively short time for bromine addition and uses arsenious acid for the back titration, thus eliminating the use of iodine.

Decision. The iodine number of primary oils is made according to Kaufman using arsenious acid for back-titrating the excess of bromine.

Follows a report on a new procedure of determining the ozone iodine number. This method is not thought to replace the method by Kaufman but is to be used for determining the constitution, in particular the position of the double bond.

In regard to molecular weight determination the agreement of the results obtained by different laboratories is still unsatisfactory which is probably caused by the tendency of association. Leuna proposes to acetylate the alcohol in acetic acid anhydride, to expel the excess of acetic acid anhydride in a current of air, and to determine the molecular weight of the remaining ester cryoscopically in benzol.

Decision. All laboratories will check the molecular weight determination after conversion to the acetic acid ester and determine the molecular weight of the original alcohol by freezing point depression in naphthalene.

Determination of the non-alcoholic portion. This determination cannot be made by the Kattwinkel method. Likewise, other procedures have failed. It is agreed to use a sulfonation method which has the advantage to simulate the plant operation.

From the determination of hydroxyl number the molecular weight of the alcohols and the alcohol content cannot be calculated accurately. However, it can be calculated from the difference from 100 and the non-alcohol content. For the determination of the molecular weight of the alcohols the sulfonates, after removal of the unsulfonated residue, can be hydrolyzed and the alcohols obtained in pure form.

For the determination of the degree of branching, the procedure using antimony pentachloride has not been too successful. It was found of importance to use freshly distilled $SbCl_5$.

Miscellaneous. The method for determining terminal olefinic bonds using ozonition and subsequent cleavage of the ozonides with silver oxide will be communicated in the near future.

Pages 169-174. Analytical methods agreed upon at meeting, December 7, 1942.

1) Solidification point. 50 g. of sample contained in a test tube are melted by immersion in a bath $10-15^\circ C$ above the expected solidification point. For complete drying, 2 g. of Drierite are added to the melt by means of a thermometer. The test tube is then inserted in another test tube to serve as an air jacket and the assembly immersed in a bath whose temperature is about $5^\circ C$ below the expected solidification point. After supercooling the melt by about $2^\circ C$, it is seeded and the thermometer moved slowly up and down observing the temperature rise until it reaches its maximum; this temperature is reported as solidification point.

2) Density. The density is determined in the conventional manner with the pycnometer; in case of olefins at $20^\circ C$ and in case of alcohols at $50^\circ C$; vacuum correction need not be applied.

3) Molecular Weight. This determination is made by the conventional method of freezing point depression. ~~As the solvent for the olefins benzol is to be used, however for the purpose of comparison also acetic acid anhydride is to be used.~~ For the cryoscopic molecular weight determination of the alcohols naphthalene as a solvent should be tested.

Moreover, it is suggested to convert the alcohol with acetic acid anhydride in the ester, to remove the excess acetic acid anhydride and formed acetic acid by means of an air current, and to determine the molecular weight of the remaining ester cryoscopically, using benzol as the solvents and to calculate herefrom the molecular weight of the alcohol.

- 4) Acid number. Conventional method.
- 5) Saponification number. Conventional method.
- 6) Ester number. Calculated from saponification number minus acid number.

Hydroxyl number. The acetylation reagent is prepared by diluting 25 g. of acetic acid anhydride in a 100 ml. volumetric flask with pure dry pyridine and filling to the mark. Since the reagent discolors on standing exposed to light it is recommended to prepare it freshly. Depending on the expected hydroxyl number the following sample weights should be used:

20 g.	with a hydroxyl number up to 14 mg. KOH/g.
10 g.	" " " " " " 14-28 mg. KOH/g.
5 g.	" " " " " " 28-56 " " "
2 g.	" " " " " " 56-140 " " "
1 g.	" " " " " " 140-280" " "
0.75 g.	" " " " " " 280-370" " "
0.6 g.	" " " " " " 370-460" " "

Procedure. The sample is weighed in a round bottom flask to which by means of a ground joint an ascending tube can be attached, and exactly 5 ml. of acetylation reagent are added. The reaction mixture with the tube in place is heated for one hour on the steam bath and after cooling one ml. of water is added through the tube. If the solution becomes turbid, a little pyridine is added and heated again for ten minutes. After cooling 5 ml. of previously neutralized ethyl alcohol is added through the tube and the solution titrated with 0.5 n alcoholic potassium hydroxide using phenol phthalein as an indicator. In the same manner a blank is made. If a gram sample consumes b ml. 0.5 n caustic and the blank consumes c ml. 0.5 n caustic, the hydroxyl number is:

$$\text{OH number} = \frac{c-b}{a} \cdot 28.05 + \text{acid number mg. KOH/g.}$$

8) Carbonyl number. The reagent is prepared by dissolving 40 g. hydroxylamine hydrochloride in 80 ml. water, adding 800 ml. ethyl alcohol and with stirring 600 ml. of 0.5 n. alcoholic potassium hydroxide. To this solution indicator solution is added and filtered. The indicator solution is prepared by triturating 0.1 g. bromophenol blue with 3 ml. of 0.05 n NaOH and diluting with water to 25 ml. (methyl orange can also be used as an indicator).

Ten grams of the sample are gently refluxed on the steam bath with 75 ml. of the reagent and after cooling titrated with 0.5 n hydrochloric acid. In the same manner a blank is made. If for a g. sample b ml. of 0.5 n HCl are consumed and c ml. 0.5 n HCl for the blank the carbonyl number equals:

$$\text{Carbonyl number} = \frac{c-b}{a} \cdot 28.05 \text{ mg. KOH/g.}$$

9) Iodine number. Solutions required: a) Bromine solution; 120 g. anhydrous sodium bromide are dissolved in one l. pure methanol and 5.2 ml. elementary bromine are added. This solution is close to 0.2 n and almost stable.

b) 0.1 n. sodium arsenite solution: 5 g. arsenous oxide (As_2O_3) are dissolved with 2 ml. 35% sodium hydroxide and water by boiling, after cooling neutralized with 1 n H_2SO_4 against litmus paper, 20 g. sodium bicarbonate added and made up to one liter with water. The solution is standardized with 0.1 n iodine solution to be exactly 0.1 n (standardization may also be made in acid solution with 0.1 n bromide-bromate solution using indigo carmine or methyl orange).

c) 0.2 per cent aqueous indigo carmine or methyl orange solution.

Depending on the iodine number a sample weight of 0.4 to 1 g. of the olefin is weighed in an Erlenmeyer and dissolved in 25 ml. of an equal volume mixture of methanol and carbon tetrachloride. From a burette methanolic bromine solution is added, while agitating the flask, until the solution becomes yellow following which about one half the volume of bromine solution consumed to this point is added and the stoppered flask allowed to stand for ten minutes. Then a volume of 0.1 n arsenite solution, equal to that of the added 0.2 n bromine solution is added and after mixing, indigo carmine or methyl orange indicator is added and the solution titrated with 0.2 n methanolic bromine solution to colorless. For the standardization of the bromine solution 25 ml. are added to 25 ml. methanol - carbon tetrachloride mixture and the solution allowed to stand in the stoppered flask for ten minutes. Then 50 ml. of 0.1 n arsenite solution is added, mixed and titrated with the same indicator as used with the sample to colorless. It should be noted that in the titration of the blank as well that of the sample, addition of the bromine solution toward the end point should be made slowly and dropwise.

If in the titration of a gram sample in total (inclusive the final titration) b ml. of 0.2 n bromine solution have been consumed, and c ml. of 0.1 n. sodium arsenite solution and if according to the blank d ml. of the approximately 0.2 n bromine solution are equivalent to 25 ml. of 0.1 n arsenite solution, then the iodine number:

$$\text{Iodine number} = \frac{50 \cdot b}{5d} - \frac{c}{a} \times 1.269 \text{ g. I/100 g.}$$

For the determination of the very low iodine number of alcohols a larger sample weight 2-5 g. is used, otherwise the procedure is the same.

10) Phosphorpentoxide - sulfuric acid soluble; PSL in olefins.
In the conventional vessel or in the butyrometer tube, developed at Herseburg, an appropriate quantity is measured and carefully at least 3 times the quantity of Kattwinkel reagent added and mixed with cooling in ice water. The mixture is then centrifuged and the volume of the insoluble layer recorded. The difference, volume of sample minus insoluble represents the PSL which is expressed in volume per cent. In order to obtain a measure of the olefin content the amount of alcohol, carbonyl compound, and ester corresponding to the OH, CO, and saponification numbers respectively have to be deducted from the PSL. Knowing the molecular weight of the olefins these amounts can be calculated from the respective characterization numbers.

11) Non-alcohol portion in aliphatic alcohols. The aliphatic alcohol is converted to the acid alkyl sulfuric acid ester by interaction in dry ether solution with chlorosulfonic acid and removal of ether and formed hydrochloric acid by vacuum. The residue is neutralized with caustic, dissolved in 50 per cent alcohol, and the unsulfonated portion extracted with petroleum ether; after distilling off the petroleum ether the residue is weighed. Since the aliphatic alcohols are not converted quantitatively to the sulfuric acid ester a portion of the alcohol remains in the unsulfonated residue, the hydroxyl number in the residue from the distillation is determined and the amount of alcohol corresponding to this is deducted.

50 g. of the anhydrous aliphatic alcohol¹⁾ whose hydroxyl number H has been determined are placed in a 3-neck flask having a separatory funnel, stirrer, and thermometer, 300 ml. of ether, dried over sodium, are added and the flask cooled in ice water. When the temperature has dropped to 10°C, then $H \times 0.12$ g. (H = OH number) chlorosulfonic are added slowly from the separatory funnel (within 5-10 minutes) so that the temperature of the reaction mixture does not exceed 15°C, and the separatory funnel is rinsed with a small portion of ether. The reaction flask is immersed in a water bath of 25°C and stirring continued for 1/2 hour. After this the separatory funnel is replaced by a connection to a water jet filter pump to remove ether and hydrogen chloride.

- 1) If the alcohol is not free of water, dilute 60 g. with 200 ml. of petroleum ether (b.p. 30-60°C), dry overnight with calcined sodium sulfate, filter and distill off the ether. Remove the last traces of ether by means of vacuum and passing a current of dry air at 60°C.

For the neutralization of the formed aliphatic alkyl sulfonic acid the contents of the flask is poured slowly with stirring in a mixture of 150 g. ice and $H \times 0.16$ g. 35 per cent NaOH, and the flask rinsed quantitatively with ether; the solution should be alkaline to phenolphthalein. The neutralized solution is diluted with an equal volume of 95 per cent ethyl alcohol and, if necessary, more 50 per cent alcohol is added until complete solution. The solution is extracted three times with 100 ml. portions of petroleum ether. The combined ether extracts are washed twice with 100 ml. portions of 50 per cent alcohol and twice with 100 ml. portions of water, then dried with calcined sodium sulfate and after filtration and rinsing with petroleum ether transferred to a distillation flask and the petroleum ether distilled off using a water bath. To remove the last traces of ether vacuum is applied. The residue is weighed and its hydroxyl number is determined. If a grams fatty alcohol with the hydroxyl number H was used and b grams residue with the hydroxyl number Z was found then the alcohol contained

$$\left(1 - \frac{Z}{H}\right) \cdot \frac{b}{a} \cdot 100\% \text{ non-alcoholic portion}$$

Pages 175-178 Determination of Hydrocarbons in fatty alcohols, particularly in Lorols (FC-Lorol and Kokoslorol). This is a communication from Bohme, Fettchemie, describing a procedure in which the fatty alcohols by reaction with a mixture 1:2 of anhydrous potassium hydroxide - calcium oxide are first converted at 100°C to the alcoholates and then oxidized at 250-280° to the fatty acid salts. Hydrocarbons present are thereby distilled off and collected in a receiver and weighed. The distillate may be checked, by determining the hydroxyl number, for loss of alcohol during the reaction. Also, by determining the carbonyl number; it can be ascertained whether ketone formation has taken place.

Pages 204-206 Analysis of Products of the Oxo contract. This is a communication from I.G. Farben giving results of cooperative test samples and comments on the agreed analytical procedures.

I. Olefins

1) Olefin determination by means of halogen addition. The procedures by Kaufmann for determining the iodine number as well as those by Hanus and Winkler and also the rhodan (thiocyanogen) and jodrhodan (thiocyanogeniodide) are suitable and results are in agreement. The bromometric method of Kaufmann is recommended because of its simplicity and its advantage of using arsenous acid for backtitrating excess of bromine.

2) Olefin determination by hydrogenation. Results by this method did not agree too well and therefore no recommendations are made.

3) Phosphorpentoxide - sulfuric acid method (Kattwinkel). Even though alcohols, esters, and carbonyl compounds are absorbed and corrections are necessary the method is useful, being rapid.

4) OH, CO, and Saponification number. No comments.

6) Determination of degree of branching. It was necessary to further modify the method of Schaarschmidt modified by Leithe in order to eliminate some error. In only paraffin mixtures the determination can be made within an error of ± 5 units; however, olefins cannot be analyzed directly. The procedure can be changed for analyzing paraffin olefin mixtures by hydrogenating the mixture and determining the degree of branching of the whole sample. In a second sample the residue after treatment with Kattwinkel reagent is analyzed. Prerequisite is that the paraffin - olefin mixture does not contain hydrocarbons less than C_{10} because they are absorbed partly by Kattwinkel reagent and, furthermore, that during hydrogenation no constitutional changes take place.

II. Alcohols.

- 1) Determination of hydroxyl number. No comments
- 2) Determination of carbonyl number. The oxime method using hydroxylamine hydrochloride fails. However, the method by Stillmann and Reed by reacting in the heat with free hydroxylamine is suitable.
- 3) Acid, saponification, and ester numbers. No comment.
- 4) Iodine number. As in the case of the olefins also here the method by Kaufmann is recommended.
- 5) Determination of neutral oil (non-alcohol portion). The combination of the methods proposed by Ludwigshafen and Henkel has been found satisfactory and is recommended.
- 6) Degree of branching. The method as used for paraffin - olefin mixture is not applicable. The possibility of converting the alcohols to paraffins is considered.

Pages 224-225 Directions for preparation of sulfonate pastes from oxo alcohols. Communication from Henkel & Company.

100 g. of Oxo alcohol, together with 150 ml. of dry ether, are placed in a sulfonation flask of 750 ml. capacity, which is equipped with thermometer, stirrer, separatory funnel, and vent. With alcohols or mixtures which are liquid below $20^{\circ}C$, the flask is cooled at the beginning of the sulfonation in ice water; with alcohols of higher melting point, only after some of the chlorsulfonic acid has been added, cooling is applied in order to prevent solidification. With good stirring slowly 1.05 moles chlorsulfonic acid (hydroxyl number of the alcohol times 0.218 g. chlorsulfonic acid) are added slowly. The temperature of the reaction mixture at the beginning of the sulfonation should be between 10 and $15^{\circ}C$ and can increase towards the end to $25^{\circ}C$. After all the chlorsulfonic acid has been added, stirring is continued for one-half hour. During this after-stirring the flask is connected to a water jet pump and evacuated, first very carefully and later to 15 mm. to remove the ether and hydrogen hydrochloride.

For the neutralization of the acid ester 1.15 moles NaOH in the form of 35 per cent NaOH (hydroxyl number times 0.254 g. NaOH) and 150 g. ice are placed in a one liter beaker and the ester is slowly stirred in at 20-25°C. After all has been added the alkalinity, if necessary, has to be adjusted to phenolphthalein. To determine the unsulfonated portion in this paste the following procedure is used:

Isolation of the unsulfonated portion. 100 g. of the paste are diluted with 250 g. water and mixed thoroughly in a separatory funnel with 400 ml. ether. If the phases do not separate a few ml. of saturated sodium sulfate solution are added. It may also be helpful to add a few ml. of methanol. The sulfonate solution is then extracted three times each with 200 ml. ether.

The collected ether extracts are washed four times with 200 ml. each of water to remove any sulfonate. A small emulsion layer that may form can easily be removed by adding a few ml. of saturated sulfate solution. The ether extract is dried over sodium sulfate and the ether distilled off. For this a 500 ml. round bottom flask is used which is equipped with a simple Hempel column. The flask is heated in a water bath at 60°C and the ether is added by means of a separatory funnel.

After the ether has been distilled off, the flask is placed in a water bath at 30°C and evacuated (15 mm. Hg.) for 10 minutes. The ether free residue is weighed.

Pages 255-261 Analysis of olefinic heavy oils and pure alcohols used in the Oxo-synthesis according to status of August, 1941.
Communication from Oberhausen-Holteln, August 19, 1941.

I. Starting Oils

A. Olefin content. Experience: Not all olefins have the same rate of addition in the Oxo-synthesis. Therefore not any of the methods for determining olefins is generally applicable because olefins that have reacted in the analytical procedure may not react in the Oxo-synthesis.

Therefore, in a questionable case the amount of utilizable olefins cannot be evaluated by an olefin analysis. In these cases small scale runs of the Oxo-synthesis have to give the information as to the amounts of olefins capable of addition.

Status: It has been found that for synthetic oils, delivered at present and provided for the future, the iodine - thiocyanogen number gives the correct value for the olefins capable of addition. This method is recommended in the form proposed by Kaufmann. The same values are found by determining the sulfuric acid - phosphorpentoxide (Kattwinkel reagent) soluble before and after hydrogenation. The original Kattwinkel method has been improved considerably so that now an analysis can be made in a very short time and with very small samples (Butyrometer method).

For the small scale Oxo-synthesis a suitable apparatus has been developed which makes it possible to process 10-20 ml. of the oil in a short time. This apparatus can also be used for the hydrogenation of the sample to be used in the sulfuric acid - phosphorpentoxide soluble test.

B. Molecule size of olefins. Experience: Determination of molecular weights did not give in all cases the correct molecular magnitude of the olefins but only average values which tell nothing about distribution. In the presence of alcohols not even the average values are anywhere correct.

In order to determine the distribution, a fractional distillation of the olefinic oil has to be made with a subsequent group analysis (iodine number, etc.) of the single fractions

Status: For the fractionation various apparatuses have been used and an agreement on a standardized apparatus seems advisable.

C. Other constituents. Experience: Products interfering with the Oxo-synthesis have not been encountered in our primary products. The analysis is concerned merely with the oxygen containing compounds, particularly the alcohols.

Status: The commonly used and generally known methods are applicable for:

- 1) Determination of OH number;
- 2) determination of CO number;
- 3) determination of acid and saponification number.

D. Structure of olefines. Experience: Depending on the condition of the synthesis the olefines have either straight chains or are branched in unknown amounts and manner. Analytical methods to determine the changes in structure are so far not known.

The only possibility to evaluate the structure of the initial oils is the small scale Oxo-synthesis and the preparation and analysis of the single alcohols.

Status: ~~Details have not been worked out as yet except consideration of investigational work.~~

II. Finished Products: Pure Alcohols

A. Nature of finished products. As finished products of the new Oxo-plant only pure alcohols should result. For accounting the following applies:

- 1) For the present no agreements seem to be required for hydrocarbon containing crude alcohols.

2) The pure alcohols are obtained as the products of a careful fractionation. From this the molecular magnitude is known which can be evaluated in the analytical examination.

B. Determination of quantity of alcohol. Experience: The determination of OH number is sufficient. Secondary alcohols, as experience has shown, are not contained in the pure distillates.

C. Other constituents. Experience: As secondary products can occur:

1) Hydrocarbons, originating from primary synthesis because of imperfect distillation.

2) Primary formed oxygen containing products, for example alcohols, because of imperfect fractionation.

3) Aldehydes which have not been hydrogenated.

4) Hydrocarbons, originating from splitting off of water and from hydrogenation of alcohols.

5) Higher molecular oxygen containing products from the Oxo-synthesis (heavy oils, for example, double molecular secondary alcohols, esters, acids, etc.)

Experience has shown that the amount of primary formed alcohols is negligible if the plant is run under the right conditions.

Non-hydrogenated aldehydes are practically not encountered and can easily be detected by the CO number.

However the quantity of hydrocarbons reaches measurable value. They can easily be determined as residue from the sulfuric acid - phosphorpentoxide soluble test.

The heavy oils, mentioned above, are present in the pure alcohols in only small proportions if the plant is run under the right conditions. The analysis can be made in a number of ways.

a) Heavy oils have a low OH number, high refractive index, and very high saponification numbers. An estimate can be made from the drop of the OH number, the increase in refractive index, density, and saponification number.

b) Determination of the absolute amount is possible by making a careful fractional vacuum distillation and measuring the residue.

Status: 1) OH number.

2) CO number.

3) Hydrocarbons by the sulfuric acid - phosphorpentoxide soluble test.

- 4) Refractive index.
- 5) Density.
- 6) Neutralization and saponification number.
- 7) Fractional vacuum distillation.

D. Molecular weight of the alcohols. Experience: When the plant is working properly the technical fractional distillation separates clean fractions. With the exception of C₁₈ol all other alcohols are obtained in pairs. The proportion of the two alcohols in a mixture can be obtained from the OH number (after deduction of the non-alcoholic portion) the determination of the molecular weight is less accurate.

Errors can occur if, because of imperfect fractionation, fractions overlap. In this case only fractional distillation with subsequent determination of the OH number of the fractions can give the desired information.

Status: 1) OH number.

2) Molecular weight according to Beckmann, cryoscopically in 10% glacial acetic acid solutions; limit of error $\pm 5\%$.

3) Fractional vacuum distillation.

Structure of the alcohols. Experience: It has been found that the single synthesized pure alcohols can be separated in their isomers by a sharp fractionation. The latter can then be characterized by physical and chemical means.

Other methods which circumvent the fractional distillation, for example, optical methods are not considered for practical purposes.

For the preparation of single alcohols the hydrocarbon distillation had been carried out in such a way that the forerun and the intermediate fractions, which contain isomeric olefins, had been separated. However, in the provided pair-wise processing the intermediate fraction is used in the synthesis. In this way additional isomeric alcohols are formed whose boiling range lies in the region of the next lower molecular alcohols.

This fact makes more difficult the determination of the structure of the pair-wise obtained alcohols from vacuum distillation. Status details have not been worked out.

F. Color and metal content. Experience: The products are colorless under normal conditions, Disturbances may cause light coloration probably owing to metal content.

III. Summary

Initial Oils

- A. Analyses to be made regularly:
- 1) Engler distillation
 - 2) a) Iodine-thiocyanogen number
b) Soluble in Kattwinkel reagent before and after hydrogenation
 - 3) OH number
 - 4) Neutralization and saponification number
 - 5) CO number
- B. For accurate characterization.
- 1) Fine fractionation: determination of iodine - thiocyanogen number in the single fractions.
 - 2) Oxosynthesis on small scale up to the alcohols and determination of quantity and properties

Finished Products

- A. Analyses to be made regularly:
- 1) OH number
 - 2) CO number
 - 3) Neutralization and saponification number
 - 4) Kattwinkel reagent soluble
 - 5) Density
 - 6) Refractive index
- B. For characterization: Fractional vacuum distillation and determination by analyses 1-6.

Pages 264-267 CO number and iodine - thiocyanogen number.
Communication from Ruhrchemie, May 7, 1941

Abstract

For clarification of some statements by Dr. Roelen (the previous communication is one of them but not that referred to) it is said that the term "iodine-thiocyanogen number" is wrong and misleading. In the method that is used for determining olefins pure thiocyanogen is used which has quite different properties than the iodine - thiocyanogen solution. Follows a polemic to the extent that the writer doubts the applicability of the thiocyanogen method. In regard to CO number determinations it is pointed out that one hour heating does not seem necessary and may lead in certain cases to erroneous results because of catalytic decomposition of the hydroxylamine through traces of metals.

Pages 268-272 Methods for the analysis of Oxo-products used
by I.G. Ludwigshafen. June 13, 1940

Item 19 Pages 273-285 Methods for the determination of the normal paraffins in the gasoline, middle oil and wax fractions. Removing iso-paraffins by reaction with $SbCl_5$. Oppau, August 2, 1940

Item 20 Page 286 Analysis of gasoline and diesel oil fractions from recycle operation using iron catalyst. Information from I.G. Holten, May 23, 1939

Page 288 Analysis of "Ausgangs und Endgase" from I.G. gas recycle process. Ludwigshafen, March 20, 1939.

Page 290 Analysis of liquid product from I.G. gas recycle process. March 13, 1939

Page 292 Description of I.G. gas recycle process. Operating conditions: temperature, over $300^\circ C$; pressure, 20 atmospheres; feed, $CO:H_2$ mole ratio 4:5; total CO reacted after second stage, 91.5%; life of iron catalyst, 9 weeks; gas hourly space velocity (inerts included) 300. Yields: oil, 99 g./ $m^3 CO+H_2$; alcohol, 14 g./ $m^3 CO+H_2$; C_2-C_4 , 47 g./ $m^3 CO+H_2$. Holten, January 10, 1939

Page 297 Description of I.G. oil recycle process. Operating conditions: catalyst, fused iron containing Mn, Ti and Si; temperature, $350^\circ C$; pressure, 20-100 atm., feed, water gas; oil recycle ratio, 50. Yield: oil, 113 g./ $m^3 CO+H_2$; alcohol, 9 g./ $m^3 CO+H_2$; C_2-C_5 , 25 g./ $m^3 CO+H_2$. Holten, January 13, 1939

Page 302 I.G. oil recycle process at 100 atmospheres. Discussion of problems connected with Winkler generator, methane splitting and sulfur removal. Holten, January 16, 1939

Page 307 Letter of transmittal of various cobalt catalysts from Ruhrchemie to Ludwigshafen. January 10, 1939

Page 309 Report of gas recycle process by Michael, the oil recycle process by Ludwig, wax synthesis, methane splitting, and synthesis gas feed purification. General information. Holten, January 6, 1939

Item 21 Page 324 The patent rights on hydrocarbon synthesis held by I.H.P. and I.G. Abstracts of patents given. November 30, 1938

Item 22 Pages 340-369 Experimental data and brief reports on an investigation of Fe-CaO-Cu-kieselguhr catalyst for synthesis at 10 atms. and $200-220^\circ C$. Water gas at $200-230^\circ C$, and atmospheric pressure is used for catalyst reduction. Work under supervision of Roelen. Rees, September to December, 1944

Pages 370-372 Status of synthesis with iron catalysts. General information. Holten, June 13, 1944

Pages 373-425 Summary of synthesis experiments No. 786 to 657. Testing various catalyst preparations comprising 100 Fe, 5-20 Cu, 10 CaO, 30-50 kieselguhr, with either soda or potassia precipitation, and usually impregnated with definite amounts of potassia.

Holten, January to August, 1944

Item 23 Pages 426-427 Recovery of cobalt from spent catalysts.
Holten, October 20, 1939

Pages 428-432 Discussion of economics of extracting waxes from spent catalyst before recovery of the cobalt.

Holten, December 16, 1940

Pages 433-435 Discussion of various means by which the performance of cobalt catalyst may be improved, i.e., catalyst preparation, pretreatment and synthesis gas feeds.

Dortmund, October 15, 1941

Pages 436-441 Availability and distribution of an improved type of cobalt catalysts made by Ruhrchemie. Discussion with licensees.

Essen, March 24, 1941

Pages 442-448 Discussion between Ruhrchemie and licensees on problems connected with cobalt catalyst synthesis including (1) utilization of improved catalyst prepared from "Rostgur", (2) actual monthly catalyst requirements, (3) difficulty of Ruhrchemie in meeting catalyst particle range specification, (4) estimated increased costs resulting in working up spent catalysts containing waxes and other impurities, (5) use of feed purification catalysts during the first half of 1941.

Bochum, February 4, 1941.

Pages 449-451 Number of synthesis reactors in use by licensees. Cobalt and thorium stock situation in 1940.

Holten, April, 1940

Page 452 Note of thorium and cobalt losses in catalyst preparation.

Holten, July 29, 1938

Pages 453-454 Cobalt catalyst reduction costs.

Holten, July 1, 1941

Item 24 Pages 456-457 Discussion on characteristics of various kieselguhrs.

March 3, 1944

~~Page 458 Specifications for "Oluhgur" and "Rostgur".~~

~~Holten, February 24, 1943~~

Pages 459-460 Use of "Rostgur" in the preparation of catalysts.

Schwarzherde, February 28, 1941

~~Pages 461-468 Discussion between Ruhrchemie and licensees on kieselguhr supplies.~~

~~Holten, May 7, 1940~~

Pages 469-470 Report on quality of kieselguhr.
Holtten, August 19, 1939

Pages 471-474 Report on the examination of a sample of kieselguhr, including microscopic, elutriation, and filterability analysis.
Holtten, August 14, 1939

Pages 475-476 Report on the effect of time of calcination (995°C) on the amount of soluble iron in kieselguhr. Münster, July 13, 1939

Pages 477-480 Letter discussing difficulty in maintaining kieselguhr quality specifications
June 23, 1939

Pages 491-493 Relation between per cent loss on ignition and per cent acid soluble matter in kieselguhrs calcined at various temperatures.
Münster, June 1, 1939

Page 484 Note on the purification of kieselguhr by water washing.
Münster, May 13, 1939

Pages 485-499 Miscellaneous notes on kieselguhr. General information on impurities, analyses, etc.

Pages 500-505 Description of kieselguhr-120 and kieselguhr purification
April 19, 1939

Pages 504-508 Kieselguhr reclamation. March 20, 1939

Pages 509-510 Kieselguhr reclamation. March 7, 1939

Pages 511-513 Note on increased sand in kieselguhr samples.
August 23, 1938

Pages 514-517 Kieselguhr supplies. July 30, 1938

Item 25 (Thorium Recovery) Page 518 Scheme for thorium recovery.
October 27, 1941

Page 518 Brief letter on thorium recovery program.
Holtten, February, 1939

Pages 520-522 Thorium recovery at Bragbag, giving procedure, apparatus, yields and material balances. January 20, 1939

Pages 523-527 Thorium recovery at Schwerzbeide. Procedure, apparatus, and cost estimates given. December 19, 1938

Pages 528-532 Holtten process for recovery of thorium. Flowsheet and costs given. Holtten, October 22, 1938

Pages 533-537 Discussion between Auer-gesellschaft, Bragbag and Ruhrbenzin on thorium recovery.

Pages 538-541 Results of a large scale operation for recovery of thorium by the sulfate process. Molten, July 27, 1938.

Pages 542-543 Thorium recovery using a mixture of sodium and potassium sulfates. Molten, July 16, 1939

Pages 544-548 Thorium recovery, giving balances and operating data for 1 year period. May 31, 1938

Item 26 Pages 548-555 Summary of feed purification data from Ruhrchemie licensees. Molten, June 27, 1941

Item 27 Research suggestions (Author, Roelen). General Synthesis.

Page 557 Improving high melting wax yields. May 4, 1939

Page 558 Suggestion to determine octane number of low boiling product from the Oxo-process. April 24, 1939

Pages 559-560 Miscellaneous procedural suggestions.

Page 561 Regeneration of cobalt with high H_2 flow at high pressures. July 2, 1938

Page 562 Production of low boiling olefins with cobalt catalysts operating at high pressures and temperatures. October 15, 1938

Page 564 Suggestion to study the influence of recycle operation (500 to 1000 atm. pressure) on reaction of water gas with ethylene. November 18, 1938

Page 566 Synthesis at pressures over 500 atm. December 12, 1938

Page 567 Recycle operation to produce low boiling hydrocarbons. January 11, 1939

Pages 568-569 Influence of catalyst composition on wax production. January 11, 1939

Page 570 Lubricating oil improvement. February 11, 1939

Page 571 High pressure synthesis February 17, 1939

Pages 572-573 Program to study means of improving wax yields. March 13, 1939

- Page 574 Lubricating oil. March 24, 1939
- Page 575 Improving wax yields. July 22, 1939
- Page 576 Alcohol prepared from cracked gasolines. July 20, 1939
- Page 577 Iron catalysts. August 14, 1939
- Page 578 Synthesis program for men under Roelen during months of August and September.
- Page 579 Synthesis at high pressure. December 11, 1940
- Pages 580-581 Effect of synthesis gas composition on olefinicity of product. September 4, 1941
- Page 582 Influence of cobalt catalyst density on wax retention. March 25, 1937
- Page 584 Life studies on four different cobalt catalysts. May 30, 1937
- Page 585 Influence of catalyst composition on wax. November 11, 1937
- Pages 586-588 Program to study synthesis mechanism. Addition of olefins (especially ethylene), alcohols, ketones, etc. to synthesis gas. December 11, 1937
- Page 589 Addition of NH_3 to synthesis gas. November 19, 1937
- Page 594 Production of olefins. Co catalysts. October 27, 1938
- Pages 595-596 Results with 90 Fe:10 Ca catalyst. February 6, 1939
- Pages 596b-596c Miscellaneous notes on iron catalysts. May 22, 1942
- Page 597 Gasol production - cobalt catalyst. March 1, 1939

- Page 598 Note on improving wax yields. February 17, 1939
- Pages 599-600 Study of reaction mechanism with Co catalyst, reduction of alcohols to hydrocarbons. February 17, 1939
- Pages 601-603 Program to study process variables to improve wax yields. March 4, 1939
- Pages 604-605 Program to study catalysts to improve wax yields. March 13, 1939
- Page 606 Removal of MgO from Co catalyst to attempt to reduce aldehyde polymerization. March 9, 1939
- Page 607 Effect of inerts in synthesis gas. June 24, 1939
- Pages 608-610 Program for the study of various Fe/Ca/kieselguhr catalysts. June 22, 1939
- Page 611 Use of alcohols in solvent extraction of catalyst. June 24, 1939
- Page 612 Recycle operation with iron catalyst. August 14, 1939
- Page 613 Catalyst study program for improved wax yields. August 19, 1939
- Page 617 Multistage process for regeneration of cobalt catalyst with H₂. October 23, 1939
- Pages 618-621 Suggested program to study conditions to improve high boiling olefin yields with Fe catalysts. January 4, 1940
- Page 623 Note on use of iron catalysts in feed purification. April 18, 1942
- Pages 624-625 Notes on iron synthesis catalysts. May 22, 1942
- Pages 626-629 Suggestions on synthesis reactor improvements. July 16, 1942
- Pages 630-631 General comments on improving olefin yields in cobalt catalyst synthesis. October 30, 1942
- Page 632 Suggestion for further investigation of aromatic formation with iron catalysts. April 22, 1943
- Pages 633-634 Notes on iron catalysts. July 12, 1944
- Page 638 Use of alcohols in solvent extraction of cobalt catalysts. July 21, 1939

- Page 640 Lubricating oils containing oxygenated compounds.
June 13, 1941
- Page 641 Hydrogenation of polymer from Oxo-process with copper chromite catalyst to produce alcohols.
July 8, 1941
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- Page 643 Suggestion to determine extent of chain branching in hydrocarbon products.
October 2, 1939
- Page 644 Presence of colloidal cobalt in product.
February 27, 1940
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- Item 28 Research Suggestions - Oxo-process (Author, Roelen).
- Page 650 Separation of alcohols from neutral oil in the diesel oil range.
June 3, 1939
-
- Page 651 Suggestion to determine the point of attachment of CO to propylene in Oxo-synthesis.
October 15, 1938
- Mechanism of alcohol synthesis through the hydrogenation of aldehydes.
October 28, 1938
- Page 652 Note of losses of cobalt during synthesis.
October 15, 1938
- Pages 653-654 Program for oxidation of aldehydes.
November 15, 1938
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- Page 655 Production of low boiling olefins by adding CO₂ to synthesis gas.
November 25, 1938
- Page 656 Note on high pressure synthesis.
November 21, 1938
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- Page 657 Fatty acid recovery.
November 13, 1938
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- Pages 658-659 Uses for product from reaction of CO:H₂ with high boiling olefins.
December 9, 1938
- Page 670 Side reactions in Oxo-process.
December 30, 1938
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- Page 671 Suggestion to study differences between temperature requirements for continuous and discontinuous Oxo-synthesis.
December 30, 1938
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- Page 672 Note to study mechanism of ketone formation.
December 30, 1938
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- Page 673 Note on oxidizing alcohols to fatty acids.
December 30, 1938
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- Pages 674-675 Program to study the preparation of fatty acids.
December 13, 1938
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- Page 679 Possible substitution of nickel or iron catalysts for cobalt.
January 3, 1939

- Page 680 Purification of high boiling aldehydes by distillation.
February 8, 1939
- Page 681 Possible synthesis of aldehydes and ketones by reacting
 $\text{CO} + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. February 7, 1939
- Pages 682-684 Discussion on mechanism of ketone and acid
formation in reaction $\text{CO} + \text{H}_2 + \text{C}_2\text{H}_4$. February 6, 1939
- Page 685 Production of fatty acids from olefins.
January 30, 1939
- Page 686 Note on possible application of petroleum fractions
to Oxo-process. January 30, 1939
- Page 687 Olefin condensation. $\text{CO} + \text{olefin}$ in presence of
 NH_3 . January 30, 1939
- Page 688 Addition of water gas to AlCl_3 polymerized olefins.
January 30, 1939
- Page 689 Discussion of problems in separating products from
Oxo-reaction using ethylene. January 17, 1939
- Page 690 Purification of high boiling aldehydes by bisulfite
formation. January 17, 1939
- Page 691 Recycle operation with C_2H_4 + water gas.
January 11, 1939
- Pages 692-694 Addition of water gas to propylene.
February 17, 1939
- Page 695 Air oxidation of Oxo-product. February 13, 1939
- Page 696 Proposed mechanism for reaction between water gas
and C_3H_6 . March 9, 1939
- Page 698 Brief note on effect of adding Ni to Co catalysts.
March 17, 1939
- Pages 699-702 Possible reactions involving aldehydic products.
March, 1939
- Page 705 Suggestion to add ethylene oxide to water gas.
- Pages 708-710 Research program for pilot plant study of Oxo-process.
A flow sheet for a continuous reactor is given. February, 1940
- Page 711 Suggested use for "Dickol" high-boiling oxygenated
product from Oxo-process. April 12, 1940
- Page 712 Suggested use for aldol condensation products.
April 10, 1940

- Pages 713-714 Addition of butadiene to water gas. June 14, 1940
- Page 714 Suggested use of metals not in iron group as catalysts for the Oxo-synthesis.
- Page 715 Proposed program for Oxo-synthesis. September 9, 1940
- Page 716 Use of cracked diesel oil for aldehyde production.
August 8, 1940
- Pages 717-718 Suggested catalyst treatment in aldehyde synthesis.
July 7, 1940
- Page 719 Program for study of lubricating oils from Oxo-process.
December 9, 1940
- Page 720 Suggested means for facilitating catalyst filtration.
December 9, 1940
- Pages 721-722 Possible method for preparing aldehydes from alcohols.
August 8, 1939
- Page 723 Production of higher alcohols from wax by chlorination.
August 18, 1939
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- Page 724 Ester formation from alcohols. August 18, 1939
- Page 725 Oxo-synthesis with iron catalysts. January 22, 1940
- Page 726 New catalysts for oxo-synthesis. November 13, 1941
- Pages 727-728 Study of various products from Oxo-synthesis.
December 4, 1939
- Page 729 Preparation of ethers. November 29, 1939
- Page 730 Preparation of esters. November 6, 1939
- Page 731 Study of aldol condensation. February 29, 1940
- Page 732 Preparation of aldehydes. February 5, 1940
- Page 732 Suggested means to avoid polymer formation in Oxo-synthesis.
January 23, 1940
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- Page 733 Aldol condensation. December 12, 1940
- Page 734 Preparation of acetal. November 21, 1940
- Page 735 Preparation of aldehydes. November 14, 1940
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- Page 739 Hydrogenation of aldol condensate with Cu/Cr catalysts.
November 11, 1941

Page 740 Suggestion to use metal carbonyls in reaction with olefins, H_2 and CO . December 22, 1941

Page 741 Proposed use of acetals as cooling mediums. May 6, 1942

Page 742 Use of CO_2 to decompose dissolved metal carbonyls. February 6, 1942

Pages 743-744 Possible preparation and uses for unsaturated aldehydes. May 5, 1942

Page 745 Preparation of high molecular weight acetals. May 21, 1942

Page 746 Determining the extent of double-bond shift during Oxo-synthesis October 15, 1942

Pages 747-748 Preparation of aldols July 24, 1942

Page 749 Use of olefins from iron catalysts for Oxo-process. February 1, 1940

Pages 750-751 Suggested oxidation of aldehydes under pressure. August 12, 1940

Page 752 Attempt to prepare more highly branched alcohols. November 1, 1941

Pages 753-754 Use of acetylene in Oxo-process. January 11, 1941

Page 755 Desirability of excluding CO_2 from feed in Oxo-synthesis. June 9, 1941

Page 756 Suggestion to use higher concentrations of H_2 in Oxo-synthesis. June 6, 1941

Page 757 Testing effect of low temperature and low CO concentration in Oxo-synthesis July 2, 1941

Page 758 Note on testing alkali-free cobalt and iron catalysts. September 22, 1941

Page 759 Determination of partial pressure of CO needed for Oxo-synthesis. November 24, 1941

Pages 760-761 Suggestions for apparatus for liquid phase Oxo-synthesis. January 22, 1942

Page 762 Various suggestions on more efficient utilization of feed gases. January 4, 1940

- Pages 763-764 Possible direct synthesis of acids from CO,
H₂O and olefins. December 4, 1939
- Pages 765-766 Possible uses for Oxo-products. December 29, 1939
- Page 767 Esterification of alcohols using Co catalysts.
November 6, 1939
- Page 768 Testing other metals that form carbonyls in Oxo-
synthesis. December 6, 1940
- Pages 769-770 Reactions of alcohols over Ni catalyst.
January 14, 1941
- Page 771 Production of fatty acids from alcohols.
January 6, 1941
- Page 772 Testing efficiency of hydrogen treatment in removing
high boiling oxygen containing compounds from catalyst.
December 14, 1940
- Pages 773-775 Production of fatty acids from alcohols.
December 10, 1940
- Pages 776-779 Various reactions of aldehydes and alcohols.
January 15, 1941
- Page 780 Preparation of acids from aldols using Ni catalysts.
January 21, 1941
- Page 781 Preparation of fatty acids from alcohols by alkali
fusion. January 20, 1941
- Pages 782-783 Possible catalytic alkali fusion.
February 14, 1941
- Pages 784-786 Use of Cu/Cr catalyst for aldehyde hydrogenation.
November 17, 1941
- Page 787 Suggestion to use butindiol in feed for Oxo-synthesis.
June 30, 1941
- Page 788 Suggested studies for new lubricating oils.
June 13, 1941
- Page 789 Suggested study of the effect of operating variables
on cobalt carbonyl concentration in raw aldehyde. June 13, 1941
- Page 790 Use of mixture of Co and Cu/Cr catalysts in Oxo-
synthesis. November 17, 1941
- Page 792 Fatty acid synthesis. March 21, 1942
- Page 793 Study of cobalt carbonyl formation. December 2, 1941

Item 29 Research Suggestions - Paraffin Oxidation

Pages 797-809. Various suggestions on preparation of fatty acids by paraffin oxidation. July 31, 1940

Page 810 Preparation of detergents by sulfonation of raw fatty acids. August 5, 1940

Pages 812-813 Separation of high and low molecular weight acids. February 3, 1942

Pages 814-816 Investigation of the properties of fatty acids from various sources. January 6, 1941

Item 30 Research Suggestions - Catalysts

Pages 825-858. Miscellaneous ideas recorded by Roelen in 1937-1938 on cobalt synthesis catalysts. They deal in general with minor changes in promoter, concentration, etc.

Page 858 Suggestion to study the effect of synthesis gas pressure on hydrocarbon desorption from catalyst. October 15, 1938

Pages 859-862 Effects of various treatments on catalyst activity. October 15, 1938

Pages 863-870 Various notes on effect of purity of raw materials for cobalt catalyst preparation.

Page 872 Discussing a study of the sensitiveness of magnesia promoted catalyst to mechanical agitation. August 21, 1939

Page 873 Study of effect of heat treatment on catalysts of high cobalt content. August 21, 1939

Pages 874-876 Regeneration studies. June 20, 1939

Item 31 Research Suggestions - Kieselguhr

Pages 878-880 Study to determine difference between fresh and regenerated kieselguhrs. August 25, 1937

Pages 881-890 Various suggestions for purification of kieselguhrs. October 8, 1942

Page 891 Specifications of kieselguhr for cobalt and iron catalysts. June 18, 1941

Item 32 Research Suggestions - Diesel Oil (Author - Roelen)

Page 894 Use of nitrate esters of C₁₀-C₂₀ alcohols from Oxo-synthesis as diesel oil additives. December 8, 1941

Pages 896-898 Various means of extracting alcohols from diesel oil range. June 30, 1939

Pages 899-907 Numerous suggestions on improvement of diesel oils by means associated with the Oxo- or Synol processes.

Item 33 Research Suggestions - Methane (Author - Roelen)

Pages 909-926 Numerous suggestions on the enrichment of town gas by the methanization of town gas with Ni and Ni-Fe containing catalysts. Ideas deal mainly with catalyst improvement. Written between 1939-1943.

Item 34 Research Suggestions - Dehydrogenation

Page 927 Dehydrogenation and cracking of diesel oil with iron catalysts in presence of steam. May 1, 1941

Pages 928-929 Dehydrogenation with elementary sulfur as hydrogen acceptor. June 1, 1941

Item 35 Methanol Synthesis - Holten

Page 930 Note on a zinc oxide containing catalyst that was active for methanol synthesis. March 3, 1943

Item 36 Water gas generation

Pages 931-933 Attempts to find catalyst active at low temperatures. Holten, 1941-1942

Item 37 Liquid Phase Synthesis

Pages 934-935 Cracking of high boiling paraffins in liquid phase synthesis. Holten, January 10, 1942

Page 936 Suggestion to observe extent of catalyst oxidation by product water in liquid phase synthesis. Holten, July 17, 1939

Pages 937-940 Program to study operating variables and catalysts in liquid phase synthesis. Holten, June 28, 1939

Item 38 Isomerization

Pages 941-942 Suggestion to study octane number improvement as result of an $AlCl_3$ treatment of a hydrogenated synthetic gasoline. May, 1939

Item 39 Cracking Paraffin Waxes

Pages 943-944 Suggestion to thermally crack under mild conditions high melting waxes to lower their melting point from about 90-100°C to about 50°C. Holten, February, 1939

Item 40 Synthesis Gas Purification

Pages 945-947 Miscellaneous notes. Holten, 1937-1941

- Item 41 Oxidation of high molecular weight alcohols
Pages 948-959 Survey of patent literature. September, 1939
- Item 42 Drying Oils
Pages 950-961 Program for the preparation of drying oils and resins from aldehydes obtained in Oxo- and Synol processes.
Holten, January 25, 1943
Pages 962-963 Brief notes on drying oils. June 6, 1941
- Item 43 Organo-metallic compounds
Pages 964-965 Proposed program to study the reaction of Na etc. with hydrocarbons.
Holten, July 1, 1942
- Item 44 Pages 966-969 Report on discrepancies in cobalt balance in plant scale synthesis reactors.
Holten, April 3, 1944
- Item 45 Page 970 Suggestion to study C₁₂ alcohols prepared from C₁₁ olefins.
Holten, September 3, 1941
- ~~Item 46 Page 971 Suggestion to dehydrate product from Fe synthesis.
Holten, August 12, 1940~~
- Pages 972-976 Proposed study of the dehydration of alcohols with zinc chloride.
Holten, January 20, 1941
- Item 47 Pages 977-978 Suggestions on hydrocarbon chlorination.
Holten, October 23, 1939
- Item 48 Pages 979-980 Suggestion to study dehydrogenation and cracking of wax at high pressures in presence of CO and with Fe or Co catalysts.
Holten, October 23, 1939
- Item 49 Page 981 "Dickol" from Oxo-process as a diesel oil additive.
Holten, May 18, 1940
- Item 50 Pages 982-983 Flowsheet for separation of coke oven gas constituents
June 11, 1942
- ~~Item 51 Pages 984-1002 Scheme for the determination of the progress of synthesis based on analysis of the exit gases. Holten, November 17, 1943~~
- Item 52 Pages 1003-1004 Iron catalyst synthesis program for maximum production of middle oil fraction.
Holten, November 17, 1943
- ~~Item 53 Pages 1005-1007 Statement on iron catalysts for methanization.
Holten, October 3, 1941~~
- Item 54 Pages 1008-1016 Two reports on the Ruhrchemie process of acetylene production from methane.
Holten, February 22, 1939

Item 55 Pages 1017-1020 Quarterly report for April, May and June.
Gives effect on production at Holten of air attack of June 16-17, 1944.
Holten, July 8, 1944

Pages 1021-1036 Quarterly production reports for Holten from
January, 1943, to March 31, 1944.

Item 56 Pages 1037-1040 Report on preparation of Cr/Al₂O₃ aromatization
catalyst on pilot plant scale. Holten, January 10, 1944

Item 57 Pages 1042-1043 Report on preparation of polymerization catalyst
(H₃PO₄/SiO₂) Holten, January 18, 1944

Page 1044 Flowsheets for preparation and regeneration of Cr/Al₂O₃
aromatization catalyst. January 7, 1943

Item 58 Pages 1044-1051 Patent references. Lists and brief abstracts
of patents covering a wide range of subjects taken out in Germany, Denmark,
Sweden and Switzerland. Holten, February 15, 1945

Item 59 Pages 1052-1053 Brief report with flowsheet on methanization
of town-gas. Holten, October 7, 1941

Item 60 Pages 1054-1055 Summary of data from synthesis with iron
catalysts (no catalyst description). Holten, November 17, 1941

Item 61 Pages 1056-1061 General report on synthesis with cobalt
catalysts, giving yields and costs data. Holten, January 16, 1937

Item 62 Pages 1062-1081 Report on continuous dechlorination process
using zinc. Extensive operating data given. Holten, July 17, 1944

Item 63 Pages 1082-1095 Flowsheet for preparation of nickel catalyst.
Holten, January 20, 1945

Item 64 Pages 1096-2000 Drawings for town gas.
Holten, November 4, 1942

Item 65 Pages 1083-1088 Rough sketches for Oxo-plant. Costs of
construction. Holten, May 2, 1941

Item 66 Pages 1089-1095 The Lurgi process for coupling the methanization
of "treibgas" and the production of liquid products. July 14, 1942

Item 67 Pages 2009-2010 Summary of status of "Paranol" process at
Holten. Holten, November 28, 1944

Items 68-71 Pages 2011-2022 Charts giving cost data for lubricating oil,
paraffin wax, synthesis, and synthesis gas production at Holten.
1939-1941

Item 72 Page 2022 Brief summary of utility requirements for 200-250 t/mo. Oxo-plant. Holten, December 10, 1944

Item 73 Pages 2023-2025 Note on ethylene oxide plant. Power requirements. October 26, 1944

Item 74 Page 2026 Purification of gasoline with $ZnCl_2$. Product analysis.

Item 75 Page 2027 Production data at Holten, 1942-1944. Holten, January 9, 1945

Item 76 Pages 2028-2037 Report on $AlCl_3$ polymerization of cracked gasoline to lubricating oil. Holten, January 9, 1945

Item 77 Pages 2038-2039 Production of methanization catalyst. No details. January 8, 1945

Item 78 Pages 2040-2043 Report on extent of CO decomposition over organic sulfur removal catalyst. Holten, January 31, 1945

Item 79 Page 2044 Synthesis yields and steel requirements for a 1000,000 m^3 /day synthesis gas plant. Holten, August 7, 1944

Item 80 Pages 2045-2057 Comparison of catalytic cracking of gas oils from F.T. synthesis and from petroleum. Holten, May 12, 1943

Pages 2058-2064 Catalytic cracking of two gas oils. A comparison of products is given. Holten, December 11, 1944

Item 81 Pages 2065-2072 Polymerization of cracked gasoline to oil in a two-stage process. November 25, 1944

Item 82 Pages 2072-2080 Polymerization of cracked gasoline in a seven-stage process. December 19, 1944

Item 83 Pages 2081-2085 Effect of iron in $AlCl_3$ on the polymerization of cracked gasoline. December 16, 1944

Item 84 Page 2086 Octane number of gasoline containing 1-3% water. Little effect was observed. September 19, 1944

Item 85 Pages 2087-2093 Labor requirements for aromatization catalyst manufacturing. Holten, September 15, 1944

Item 86 Pages 2094-2095 Program for nitration studies. Holten, September 19, 1944

Figure I- ABSORPTION PIPET FOR PROPANE-BUTANE

ABSORBENT I_2O_5 - FUMING H_2SO_4

