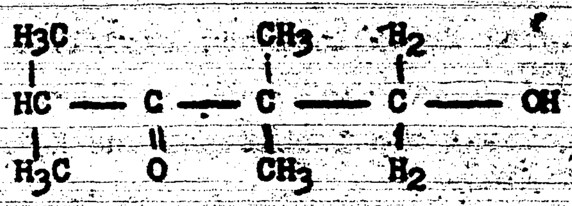
2. Details (Cont'd.)



$$(H_3C)_2HC-\overset{\displaystyle O}{\overset{\|}{C}}-C(CH_3)_2-CH_2-OH$$

The isolated methylol "isobutyron" is then hydrogenated over a copper chromite catalyst at 200 atmospheres and a temperature of 180 to 200° C.

The product is purified by a fractional distillation in which methanol is removed from the top of the column, pure isobutanol is taken off as side steam, and the high boiling residues are taken off at the sump.

About 400 tons per month of isobutanol are obtained from 500 tons of "isobutyron". This is a yield of about 62% of the theoretical.

The isobutylalcohol is dehydrated over alumina to isobutylene at 330 to 360° C. The best temperature gives 95% conversion and the operation is once through. No recycle is required. The alumina has a 3 - 4 month life.

Isobutylene was used for iso-octane production and as feed stock for oppanol (polyisobutylene).

While the isobutysynthesis was of importance during the war for the production of iso-octane, it was claimed that the process was equally of peacetime value as a producer of isobutylenes for appanol and particularly for the higher alcohols boiling from 180 to 250° C. This fraction was used for the production of the "Zornol" (synthetic lubricants).

3. List of References.

(1) Schedule "Aus dem Isobutylöl isolierte Verbindungen".

(2) "Efrfahrungs austausch uber Roh isobutylöl Destillation", by Hanisch, 25 January 1944.

(3) Flow sheet: "Isobutylöl destillation".

(4) "Unterteilung der gesteh-kosten fur die Roh-isobutylöl Produkte", 19 Oppau, 27 November 1935.

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3. List of References (Cont'd.)

(5) "Methanol und Isobutylöl destillation", 1939/1940
by Dr. W. Weber 1939.

(6) "Verfahren zur Herstellung von Isobutanol aus K-Fraktion",
Leuna, 30 November 1943.

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION VI

LOW PRESSURE METHANOL SYNTHESIS

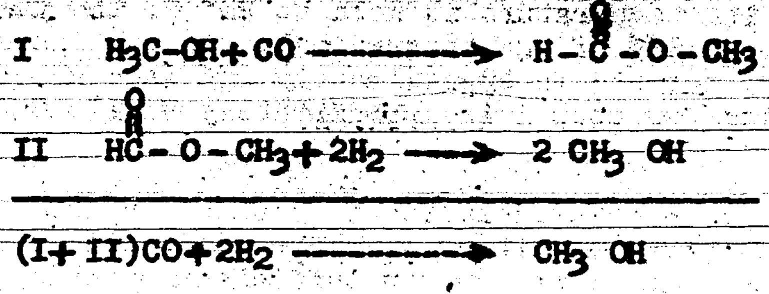
SUMMARY

The attached report covers the development of a new synthesis of methanol which is carried out at 30 atmospheres as compared with the usual operation at 250 atmospheres. The work was carried out on a laboratory scale and had resulted in the assembly of a pilot plant at the Degussa laboratory at Wolfgang near Hanau.

In view of the large saving in equipment and operation this synthesis, if carried through to commercial realization, may be of great interest to the producers of methanol in the United States.

1. Low Pressure Methanol Synthesis.

The following information on the synthesis of methanol, by utilization of pressures not in excess of 30 atmospheres, was obtained during an interrogation of Dr. Brendlein of the Deutsche Gold-und Silber Scheideanstalt (Degussa) at the Wolfgang bei Hanau plant of the company. This synthesis uses as raw materials carbon monoxide and hydrogen. In this respect it is similar to the commonly used high pressure synthesis of methanol. The net reactions involved are shown in the following equations:



$$\text{I}\quad H_3C{-}OH + CO \longrightarrow H{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3$$

$$\text{II}\quad H\overset{O}{\overset{\|}{C}}{-}O{-}CH_3 + 2H_2 \longrightarrow 2\,CH_3OH$$

$$\text{(I+II)}\quad CO + 2H_2 \longrightarrow CH_3OH$$

The catalyst for reaction I is sodium methylate dissolved in methanol, the catalyst for the second reaction is a typical hydrogenation catalyst described by Adkins, made up of copper, chromium and barium oxide. From the above set of equations it can be seen that although two molecules of

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1. Low Pressure Methanol Synthesis (Cont'd.)

methanol are formed, one is recycled for reaction I and one is product so that the result is the combination of one molecule of carbon monoxide and two of hydrogen to give one methanol. Overall yields of 95% to methanol are claimed for the process.

Enclosed with this description are four reports which give in detail the experimental findings of this work. Report (a) gives the results of experimental batch processes; (b) confirms the findings of (a) and although other alcohols such as ethanol and butanol can be used in the synthesis in place of methanol, methanol is selected as the optimum reaction medium; (c) discusses methods of continuous operation with both counter-current and parallel flow of raw material through the reaction vessels; (d) describes the hydrogenation step (II) of the synthesis. In addition there are also enclosed two charts of which one shows in scheme the arrangement of the experimental equipment and the other shows in detail, the equipment and arrangement for a proposed plant to produce 28 tons per month of methyl formate or its equivalent of 15 tons of methanol.

2. Details.

Reaction I above is conducted as follows for a batch process:

Sodium metal, 5.8 grams, is dissolved in 100 grams of methanol; this makes approximately a 13% solution of sodium methylate. The solution is charged to an autoclave and air is removed by displacement with carbon monoxide, and then a pressure of 30 atmospheres is produced by feeding carbon monoxide. The temperature is raised to 80° C and as the carbon monoxide reacts the pressure is maintained at 30 atmospheres by feeding carbon monoxide. The temperature is held at 80° C. The yield of methyl formate in this step is about 38% of the theoretical. In continuous operation the yield of methyl formate is approximately 25% (see Report (C) above). The heat of reaction for step I is approximately 9 kilo Cal/mol. of methanol.

It is essential in this operation that the reactants be free of water and carbon dioxide, as either of these react with the catalyst as indicated below, so that if present in sufficient quantity, they will preclude the desired reaction:

(a) $CH_3ONa + H_2O \longrightarrow NaOH + CH_3OH$

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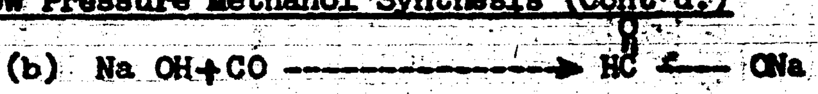
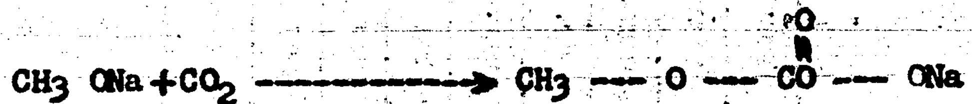
TABLE I

Ester Fed.	Pressure Atm.	Temp. C°	Catalyst Load M/l/h	Ester fed g/h	Length of Expt., hours	% of Ester converted based on Ester fed	Yield of Methanol in % theoretical based on Formic acid
Ethyl Formate	30	210	3.68	41.0	7.0	90.5	85
Methyl Formate	30	215	4.74	42.6	5.75	97.8	58.4
Methyl Formate	30	200	5.42	48.8	7.1	97.7	62.9
Methyl Formate	30	200	4.34	39.0	8.0	96.3	66.2
Methyl Formate	30	180	4.41	39.8	7.75	96.3	83.5
Methyl Formate	30	160	4.34	39.0	7.5	97.4	94.5
Methyl Formate	30	160	13.43	121	7.1	95.7	95.5
Butyl Formate	30	208	2.65	42	7.0	87.6	80
Butyl Formate	30	200	2.94	44.7	7	92.8	90

1. Low Pressure Methanol Synthesis (Cont'd.)

(b) 

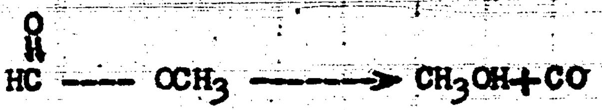
$$\text{Na OH} + CO \longrightarrow H\overset{\overset{O}{\|}}{C} \longleftarrow ONa$$

(c) 

$$CH_3\ ONa + CO_2 \longrightarrow CH_3 - O - \overset{\overset{O}{\|}}{C}O - ONa$$

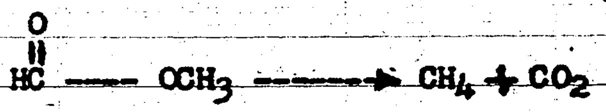
The presence of hydrogen in the carbon monoxide used in this step tends to decrease the yield of methyl formate. It is not essential, however, that the hydrogen be removed completely, because experiments with acceptable yields have been made with carbon monoxide containing 30 volume percent hydrogen.

The crude product from the addition of carbon monoxide to methanol is separated from the catalyst salts by distillation of methanol and methyl formate and is then hydrogenated. The apparatus used in the hydrogenation was a silver plated tube of 175 cc volume containing 150 cc of Adkins catalyst of copper-chromium-barium oxide. The tube was 40 cm. in length. Thermocouples were placed along the tube. The temperature in this step is closely controlled between 175 and 185° Centigrade. Higher temperatures give rise to two side reactions, one of which decreases the yield of methanol but does not decrease the efficiency in that the products are methanol and carbon monoxide which can be recycled in a large installation. This reaction is indicated as follows:



$$H\overset{\overset{O}{\|}}{C} - OCH_3 \longrightarrow CH_3OH + CO$$

The second reaction, which results from too high a hydrogenation temperature, not only decreases the yield but also decreases the efficiency in that the products are not adaptable to further utilization.



$$H\overset{\overset{O}{\|}}{C} - OCH_3 \longrightarrow CH_4 + CO_2$$

The yields obtainable in the hydrogenation step are indicated in the following table taken from Enclosure (A) mentioned above.

The products of the hydrogenation are separated by fractional distallation. The distillation is not complicated in that the products boil at widely different temperatures, methyl formate 31.8° C, and methanol 64.7° C. No azeotropes are formed in the fractionation.

3. List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

(1) Four sections (I to IV) of report:
"Mitteldruck Methanol Synthese/Zweistufen Verfahren" -
by Dr. Brendlein, Date 16 November 1942
17 March 1943
21 October 1943
18 November 1943

(2) One drwg: Flowsheet "Methanolsynthese"

(3) One drwg: Degussa 16159 "Schema Versuchsanlage M2"

(4) "Methylformiat aus CH_3OH and CO" by Dr. Pohl, 14 February 1944.

(5) "Betriebsbeschriebung zur Herstellung von 28 Moto Methylformiate", by Dr. Brendlein, 8 June 1943.

(6) "Mitteldrucksynthese in Vergleich Zum Hochdruckverfahren der I.G." - by Dr. Brendlein, 4 December 1943.

(7) One Letter by Prof. Dr. O. Fuchs re: Methanol Synthesis addressed to Dr. Brundi, 15 May 1943.

(8) One Folder: File on Patent Application by Degussa: "Verfahren zur Herstellung von aliphatischen Estern"

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION VII

THE OXO-SYNTHESIS

SUMMARY

The attached report covers the development of a new synthesis of higher boiling alcohols by reacting olefines with CO and H_2 over cobalt catalyst at 150 atm. The development was carried through laboratory and pilot plant stage and resulted in the erection of one 10,000 ton/year plant by Ruhrchemie AG at Holten.

Contents.

SECTION VII

THE OXO-SYNTHESIS

1. General Introduction. (see ref. VII/1 and VII/2 at the end of this section).

Oxo-synthesis is a process for the production of alcohols by the reaction of olefines with one molecule each of CO and H_2 and subsequent hydrogenation of the resulting aldehyde.

The process was developed independently by Ruhrchemie and I.G. Farben. During the war these companies arrived at an agreement whereby they would pool their information, but up to this time only one commercial plant has been erected (by "Oxogesellschaft"m.b.H. at Holten). The unit was never started and thus no actual plant performance data are available. All information given below is based on large scale pilot plant operation and laboratory work.

The Ruhrchemie plant is based on a batch type operation, while I.G. Leuna had developed a continuous sump-phase type process. It is felt that the I.G. process is ready to be put into commercial practice and is superior to RCH. The main improvement consists in the continuous operation and somewhat higher output per catalyst volume.

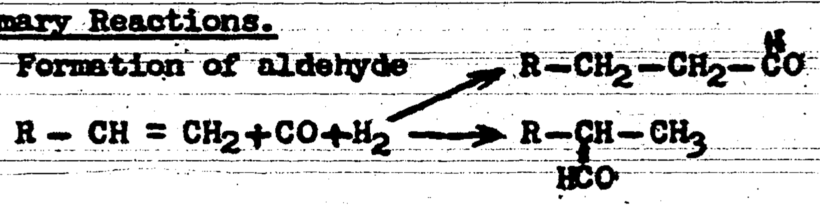
The principles involved and their practical application are described below:

2. Chemistry of the Oxo-Synthesis. (See ref. VII/3, VII/5 to VII/7 at end of this sect.)

The following reactions occur when olefines are contacted with $CO-H_2$ mixtures over certain catalyst:

(a) Primary Reactions.

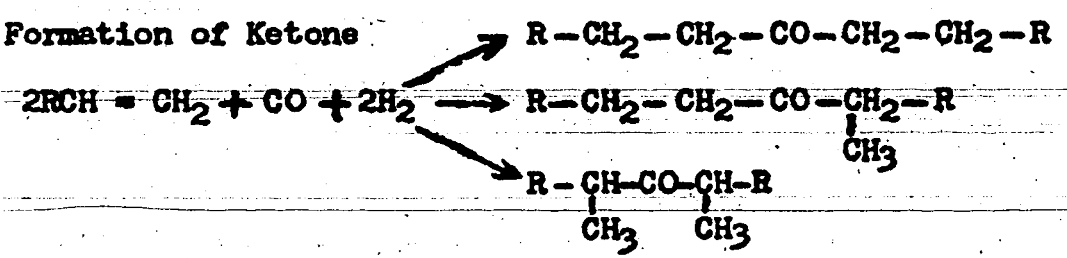
(1) Formation of aldehyde



$$R-CH=CH_2+CO+H_2 \longrightarrow R-CH_2-CH_2-\overset{H}{C}O$$

$$R-CH=CH_2+CO+H_2 \longrightarrow R-\underset{HCO}{\underset{|}{C}H}-CH_3$$

(2) Formation of Ketone



$$2RCH=CH_2+CO+2H_2 \longrightarrow R-CH_2-CH_2-CO-CH_2-CH_2-R$$

$$2RCH=CH_2+CO+2H_2 \longrightarrow R-CH_2-CH_2-CO-\underset{CH_3}{\underset{|}{C}H_2}-R$$

$$2RCH=CH_2+CO+2H_2 \longrightarrow R-\underset{CH_3}{\underset{|}{C}H}-CO-\underset{CH_3}{\underset{|}{C}H}-R$$

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2. Chemistry of the Oxo-Synthesis (Cont'd.)

(b) Secondary Reactions.

(1) Formation of acid: analogous to 1a. using H_2O instead of H_2.

(2) Formation of paraffin: hydrogenation of olefine feed (does not occur under synthesis conditions).

(3) Formation of carbonyl: from catalyst and CO.

A great deal of work has been done to study these reactions and some of the results are listed below:

Pure olefines of different types were subjected to the Oxo reaction and the products separated and each chemical individual analysed in detail.
For example: pure 2 methylpentene - 1 (Isohexane)
pure dodecylene - 1
pure cyclohexene
were reacted with $CO + H_2$. The catalyst was removed and the CO-carbonyl decomposed by washing with 5% H_2SO_4. The products were then analyzed. (Note: that this is only the first step of the oxo-synthesis). The aldehydes are not easily analyzed since they are highly reactive. It is known that more alcohols are usually formed in the oxo synthesis than would be expected from the analytical determination of the aldehydes after the first step.

(c) Products from 2 Methylpentene - 1

45% of product boiling below 200° C (760 mm.) identified in this fraction were:

3 methyl hexylaldehyde (main product)
3 methyl hexylol
3 methyl capronic acid

In the higher boiling fraction the following products could be found:

2, 8 dimetheyl-undecanone - 6
Higher ester of 2-methylcapronic acid.

These products correspond exactly to the basic reactions listed at the beginning of this chapter.

2. Chemistry of the Oxo-Synthesis (c)(Cont'd.)

In parallel fashion cyclohexene was treated and the following identified in the products:

hexahydro - benzaldehyde
dimer of " "
trimer of " "
hexahydro benzyl alcohol
hexahydro benzoic acid - hexahydro benzyl - ester.

The compounds charged to Oxosynthesis, particularly those obtained from F.T. type operations are known to be substantially terminal olefines. Yet it was found that some of the products could have been formed only if a double bond shift had preceded the formation of the aldehyde. This effect was studied and the results are summarized below:

Again n-dodecylene - 1 was used as starting material, and subjected to Oxo synthesis. But the reaction was carried through to the alcohol. In order then to establish the structure of the alcohols, they were first carefully dehydrated and the olefine was next split by oxidation and treatment with Ag_2O. The resulting acids were checked for their chain length and thus the branching was determined, which could only be an effect of a shift of the double bond of the n-dodecylene - 1 feed during the Oxo-reaction.

These tests proved, that from terminal normal olefines the oxosynthesis yields branched alcohols, in particular 2-alkyl alcohols, whereby the yield decreases with increasing length of the sidechain.

It was finally possible to prove that cobalt carbonyl was the catalyst responsible for the double bond shift. Dodecylene - 1 was treated at 150 to 200° C and 200 atm. of CO and with Co-thoria catalyst and all isomer dodecylenes were found in almost equimolecular ratio.

Fe-carbonyl showed a similar effect, but not the same activity, as only 40 to 45% of the dodecylene - 1 was isomerized. Nickel however, had no effect at all. These findings are interesting because the three named metals catalyze the Oxo reaction in about the same extent as they isomerize the double bond.

The shift of the double bond was made the subject of a patent application by I.G. Farben. (See reference VII/9 at end of this section). The disclosure involves the treatment of olefine hydrocarbons with

2. Chemistry of the Oxo-Synthesis (c)(Cont'd.)

metalcarbonyl (particularly cobalt-carbonyl) at 70 atm. CO pressure and at 150° C for two hours with 3% catalyst in the feed as an example. The process should serve to raise the octane number of the hydrocarbon. (Note: that similar tests were carried out on synololefines, which were to be used as feed stock for the Oxo-synthesis). The olefines were found to be at least 90% straight chained.

The Synololefines, on the other hand, are not necessarily all terminal olefines. These facts seem to constitute the proof that the Synol reaction (for alcohols) does not consist in an Oxo type synthesis carried out on initially formed olefines. If such were the case, the synol alcohols would have to contain about 50% α-substituted alcohols, which they do not. Much rather it is possible that they (synol olefines) are the result of a dehydration of the primarily formed terminal alcohol, followed by a shift of the double bond.

That Fe has a tendency to shift the double bond, was seen from the analysis of a Synol fraction (undecylene: 73°- 78° C at 10 mm. Hg.) which had been synthesized over the standard iron catalyst:

Undecylene	D1	D2	D3	D4	D5	D6
Mol. %	60	27	2	1	0	

This compares as follows with the distribution of the double bond, obtained from n-dedecylene-1 by treatment with $Co(CO)_4$

Dodecylene	D1	D2	D3	D4	D5	D6
Mol. %	8.1	27.2	23.0	18.1	13.3	10.3

3. Olefines for the Oxo Reaction.

The following materials were considered as feed for the oxo-synthesis:

Olefines from Fischer oil (Kreislauf operation)
" " Cracked Fischer wax
" " Fe catalyst F.T. operation
" " Synol operation
" " Various cracked mineral oils
" " Shale oils
" " Hydrogenation products.

It appears that the reaction is applicable in principle to all mono-olefines independent of origin. The limitations probably arise from the

3. Olefines for the Oxo Reaction (Cont'd.)

impurities contained in the olefines, such as aromatics, gums, or catalyst poisons. It is for this reason, that synthetic olefines are preferred, but good results were obtained from mineral oil olefines in spite of their sulphur content. The temperature required for the synthesis is somewhat higher and the sulphur content is a drawback in the hydrogenation stage, unless it is carried out quite independently over sulphide catalysts.

Olefines containing charging stocks from different synthesis operations were studied extensively, to evaluate their use for the oxo reaction. The following products were tested:

	Catalyst used in synthesis
Ruhrchemie, primary synthesis olefines	Cobalt
Ruhrchemie, thermally cracked wax	Cobalt
Synol olefines	Iron
Michael (I.G. "Schaumfahrweise") olefines	Iron
Lurgi olefines	Iron

The conclusions were as follows:

(1) In all cases over 95% of the olefines are converted

(2) The cobalt products are more uniform and contain only olefines, paraffins, and alcohols.

(3) The Fe-products contain sizeable amounts of acids, esters, aldehydes, etc., and are rendered more uniform by oxo operation (due to the hydrogenation).

(4) The total alcohol concentration in the final product is lower in the cobalt produced olefines and reaches a maximum in the synol product.

(5) The usefulness of the alcohols for detergents is less in the case of iron synthesis, since the chain length is somewhat shorter.

In order to compare the different synthesis fractions for the oxo-synthesis, the following table has been prepared: (See attached sheet)

Special Feed Stocks:

It was attempted to apply the oxo reaction on other compounds containing double bonds, with the following results:

3. Olefines for the Oxo Reaction. Special Feed Stocks (Cont'd.)

Tetra methylautadiene:	Reaction only with one double bond
Dimethylhexadiene:	Only 40% of expected product; rest is hydrogenated at one double bond, while other reacts according to Oxo reaction.
Allylalcohol:	Reaction products very complex. No detailed analysis available.

4. Catalyst for Oxosynthesis.

The catalyst is identical with the standard cobalt Fischer-Tropsch catalyst. It is applied as a slurry in the liquid feed. Usually in concentration of 3% wt. catalyst based on olefine in the feed. At the end of the operation the catalyst if filtered from the reactants through a ceramic disc or thimble and returned for further use. About 100 batches can be processed with one catalyst charge.

The catalyst contained cobalt, thoria, kiesleguhr in the customary ratio 100—1.5—200 (weight %). It did not contain magnesia, because it was found that MgO encouraged condensation of aldehydes. The catalyst had an apparent density of 0.3 to 0.35. Thus 10 kg. of oil contained about one liter of the catalyst. RCH used batch operation and carefully avoided all pumping of the slurry. The liquid was removed from one vessel to another by gas displacement. In the continous operation used by I.G. it was found that the kieselguhr caused considerable trouble due to abrasion in the pump valves. Attempts to replace the kieselguhr with talcum failed.

One of the main problems in the process is the formation of cobalt carbonyl. (Its effect on the double bond has already been described). I.G. Leuna developed a cobalt- copper catalyst, which gave only a fraction of the carbonyl (less than 10 milligram/liter). The copper has a stabilizing effect on the cobalt. This catalyst was satisfactory for the 1st stage (aldehyde formation) but did not hydrogenate well.

The activity of the standard catalyst for the 2nd stage (hydrogenation) is considerably diminished by the presence of even small quantities of CO in the hydrogen. This sensitivity becomes more pronounced with the age of the catalyst. The installation of a "Methanizer" was therefore considered to remove this residual - CO from the H_2-cycle in the 2nd stage.

TABLE II CONTENT OF OLEFINES AND OXYGENATED COMPOUNDS OF VARIOUS SYNTHESIS PRODUCTS

Fraction °C.	Number of Carbon Atoms	"Kreislauf" middle oil		RCH therm. crack-wax		Synol "Benzin-Fahrweise"		Synol Alcohol Operation		Michael Synthesis Product		Lurgi Synthesis Product	
		ole-fine	Oxygtd Compds	Ole-fine	Oxygtd Compds	Ole-fine	Oxygtd Compds	Ole-fine	Oxygtd Compds	Ole-fine	Oxygtd Compds	Ole-fine	Oxygtd Compds
105-175	8-10	42	16	80	0	-	-	17	65	-	-	-	-
175-218	11-12	41	10	80	0	46	20	18	68	46	36	52	7
218-255	13-14	33	9	75	0	47	21	16	68	48	25	55	5
255-290	15-16	28	9	50	0	43	21	16	68	45	12	50	4
290-320	17-18	20	11	40	0	42	20	18	69	40	14	45	7
320-260	—	15	5	-	-	45	18	17	59	32	20	-	-

All values are weight %

Note: that the Oxygenated compounds include alcohols, aldehydes, acids and esters. For detail breakdown, see attached German report.

See also Reference VII/5 at end of this section.

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4. Catalyst for Oxo-Synthesis (Cont'd.)

Another modification of the continuous process had been developed by I.G. Farben at Ludwigshafen. (See also reference VII/17 at end of this section). In this process cobalt acetate is contacted with fatty acids (from Oxo-alcohols) in an autoclave to yield the cobaltsalt of the fatty acid. (The free acetic acid is condensed).

Thus the cobalt is introduced in solution into the feed to give a 0.02 - 0.05% Co concentration. This mixture is charged to the reactor where it passes over a solid cobalt catalyst bed (Co on pumice). The mixture is finally freed from the cobalt in a special smaller reactor, which is filled with plain pumice. Hydrogen is added here and the reduced cobalt deposited on the pumice. After several months the final reactor must be purged of cobalt. This is done by CO, which forms carbonyl; the carbonyl is again dissolved in oil and returned to the feed.

This process does not require any filtration step. The gas streams of the process must be continuously checked for Co carbonyl. It is necessary to control its decomposition, or if possible, direct it to a part of the plant where it does no harm. In general, it is scrubbed out in a wash column using the olefine feed as sponge. Cobalt deposition throughout the plant due to Co carbonyl has been a considerable problem in the continuous process.

The catalyst, as any F.T. catalyst, must be reduced. In the particular case of the oxo-synthesis, where a slurry is used instead of a solid bed, the pelleting of the catalyst is unnecessary. This however, calls for some special arrangement to reduce the catalyst. It could be pelleted, reduced, and again broken up, but the I.G. engineers proposed reduction in "fluid phase". In a patent application dated 9 July 1942, the use of a funnel shaped vessel was disclosed for the reduction of catalyst powder, (See reference VII/8 at end of this section) where the reducing gas would keep the dust in motion. A filter or other means could be used to remove the catalyst from the gas stream which was recycled through the catalyst.

5. Operating Conditions.

(a) RCH Batch Process.

The total olefine feed ($C_{11}+$) boiling from (175 to 303° C) is first fractionated into narrow cuts. This is necessary for the subsequent

5. Operating Conditions (a)(Cont'd.)

separation of the products into the neutral oil and the alcohols. The latter, having been lengthened in their chain by one carbon atom, boil 20 to 30° C above the corresponding olefine. All distillations in the oxo plant must be done carefully and the different unavoidable intermediate fractions are either rerun or discarded. If this rule is not followed the final alcohol product is contaminated with undesirable products.

The C_{11}-C_{17} feed is fractionated into the following four fractions:

$C_{11}C_{12}$	175 - 218°	45%
$C_{13}C_{14}$	218 - 245°	25%
$C_{15}C_{16}$	245 - 280°	20%
C_{17}+	280 - 305°	10%

(The feed is obtained from LP and MP cobalt synthesis and thermal cracking of "Gatsch".)

The fractionation was carried out under atmosphere pressure for the first two cuts and under 100 - 150 mm. Hg. vacuum for the last two. "Kittel" columns were used, with 10:1 reflux ratio. They were chosen because they were considered to give less pressure drop through the tower and thus allowed a bottom temperature several degrees below that required by ordinary bubble towers.

All four fractions were treated alike in the oxo plant as follows:

A known volume of feed was mixed with 3.0 - 3.5% by weight of the catalyst. The slurry was pressured into the tubular reactor and watergas ($CO:H_2 = 1:1$, purified) introduced at 150 atm. The reaction is exothermic by 45 kg. cal/kg. of olefine. The heat of reaction is removed by the cooling coil. In addition the pressure may serve as a means to control the heat release. (By lowering the pressure the reaction is slowed down).

The gas is pumped through the reactor in a closed recycle. As the reaction proceeds and gas is used up, the pressure drops. New gas is added and the reaction is complete when no further drop in pressure occurs.

Throughout the reaction a temperature between 125 and 140° C is maintained, depending on the type of feedstock. The temperature may be raised towards the end of the reaction to encourage decomposition of the

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5. Operating Conditions (a)(Cont'd.)

carbonyl. The watergas is then released and the entire batch including the catalyst is pressured into the (2nd stage) hydrogenation chamber. The olefines are converted 100% in the "aldehyde" stage. 87 - 95% go to aldehyde, yielding about 100% wt. of alcohol based on olefine fed. The rest goes to ketone and aldol, but the latter are largely broken up in the hydrogenation to give additional alcohol.

The hydrogenation is also exothermic by about 30 - 35 kg/cal kg/mol. hydrogen reacted. The operation is carried out in analogous fahion to the aldehyde step. Pure hydrogen is admitted at 150 atm. The H_2 is recycled until no further pressure drop occurs. The temperature is held at 180° C. At the end of the reaction the H_2 is released and the product withdrawn. The catalyst if filtered through a ceramic thimble.

Before final distillation the product is caustic washed to remove the acids formed in the process. The distillation is carried out in batch columns. Care is to be taken that the kettle temperatures do not exceed 180 to 200° C (about 5 mm. Hg. is required in the higher fractions). Aluminum was used in the construction of the coolers and receivers of the fractionating system (See also reference VII/15 at end of section).

The distillation of the two lower boiling feed fractions ($C_{11,12}$ and $C_{13,14}$) is carried out in one column each. The "neutral" oil and the alcohol are taken overhead in succession. The two higher boiling feed fractions ($C_{15,16}$ and C_{17}) are distilled in two towers each. The neutral oil is removed first and the alcohols in the second tower. The heavy polymers from all four fractions are charged to a common evaporator. Refractive index measurements are used in the distillation to control the overhead cut points. The difference in b.p. between alcohol and paraffin is 1.39 to 1.42.

The gas requirements for oxo-synthesis are given as follows: (they are substantially the same for all types of operation)
Basis 10,000 ton/year of alcohol:

	Watergas	Exit gas 1st stage
CO_2	6.8%	12.9%
CO	38.0%	27.3%
H_2	49.0%	48.1%
CH_4	0.2%	0.4%
N_2	6.0%	11.3%

5. Operating Conditions (a)(Cont'd.)

	Watergas	Exit gas 1st stage
	5,145,000 m^3/year	2,715,000 m^3/year *
	Hydrogen	Exit gas 2nd stage
H_2	90%	85%
N_2	10%	15%
	3,633,000 m^3/year	2,418,000 m^3/year *

* This is on once through basis. (See also reference VII/25 at end of section.)

(b) I.G. Leuna.

The I.G. Leuna type of operation was continuous. It might be pointed out that RCH would probably also have gone over to a continuous operation in the near future. The fresh feed is used to pick up the catalyst from the ceramic filter and is charged to a mixer, where fresh additional catalyst can be added. The slurry is then picked up by the h.p. feed pump and pumped through a preheater in the reactor proper. Watergas is recycled through the reactor at 150 atm. Cooling tubes in the reactor are used to remove the heat of reaction. The slurry is next withdrawn and the pressure released in a gas separater. The gas is passed through a scrubber, where cobalt-carbonyl is removed by washing with fresh olefine feed. The slurry from the gas separator is fed to the hydrogenation system, which is an exact duplicate of the one described above. Pure hydrogen is used instead of watergas. The slurry from the final gas separator is filtered and the filtrate caustic washed, before refractionation.

Details of the operation may be taken from the attached documents.

(c) I.G. Ludwigshafen.

The system was described in the paragraph on catalyst. It is in principle identical with the Leuna system except for the handling of the catalyst.

6. Operating Costs.

The cost of the HP section of the plant is approximately 35.RM/1 yearly ton alcohol. This however does not include the gas preparation,

6. Operating Costs. (Cont'd.)

compression plant and the utilities.

The labor requirement for a 15,000 ton/year unit were given as 50 men/shift (based on batch operation). This includes all operating and maintainance labor.

The Utilities are given below:
Basis: 15,000 ton/year alcohol from $C_{11} - C_{17}$ with 30% olefine content in feed.

Heating Requirement:

Distillation	320,000 kg cal/hr
Gas preheater 1st stage	13,500 "
" " 2nd stage	16,500 "
Methanizer	31,000 "
Losses	40,000 "
	421,000 kg cal/hr

Cooling Requirement:

Synthesis, 1st stage	100,000 kg cal/hr
" 2nd stage	52,500 "
Product cooler, 1st stage	120,000 "
" " 2nd stage	150,000 "
Final cooler	90,000 "
Gas cooler	60,000 "
	572,500 kg cal/hr

Power Requirement: 100 KWH

The operating cost was given based on 1 Kg. alcohol (for 15,000 ton/year plant).

Power	0.04 RM/kg alcohol
Labor	0.03 "
Laboratory	0.01 "
Materials	0.01 "
Feedgas	0.03 "
Amortization	0.06 "
	0.18 RM/kg alcohol

At Ruhrchemie the cost of the olefine in the feed was calculated at 0.43 RM/kg. Thus the price of the final product would be 0.60-0.65 RM/kg Alcohol.

7. Conclusions.

The oxo-synthesis is the second of three major different processes for the production of high boiling alcohols. The great effort put into its commercial realization is due to the shortage of all kinds of soaps and detergents in Germany. Another important use for the product would have been its application in lubricating esters.

The development of the process may lead to continuous operation and possibly better control of the synthesis, such as suppression or closely controlled shift of the double bond to give clearly defined α-substituted alcohols of predetermined branching.

8. List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

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3. "Die Konstitutionder Oxo Alkohole" - by Dr. Asinger, Berg, April 1943.
4. "Anwendung der Oxo-Reaktion auf Mineralöl" - by Dr. Gemassmer, April 1943.
5. "Untersuchung olefinscher CO-H_2 produkte in Oxosynthese" - by Dr. Gemassmer, Berg, 3 November 1943.
6. "Konstitution von Oxo und Synolalkoholen" - by Dr. Asinger, Berg, 21 August 1942.
7. "Uber Reaktionsprodukte des Oxo Verfahrens" - by Eckhardt, 25 February 1942.
8. I.G. Patent Application; 9 July 1942 "Verfahren zur Reduktion staubförmiger Katalysatoren"
9. I.G. Patent Application; 11 September 1942 "Verfahren zur Verschiebung der Doppelbindung"
10. "Wassergas und H_2 Bedarf der Oxo Synthese" letter by Dr. Landgraf 17 December 1942.
11. Memorandum on Oxo-meeting, 10 February by Dr. Wilke, Herold.
12. "Oxo Verfahren" - 29 March 1943, letter I.G. to RCH.
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14. "Erfahrungen uber Korrosion, etc., im Hochdruckterl der Oxo Anlage, Leuna" - by Gemassmer, Berg, 25 September 1943.

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17. Memorandum on meeting of I.G. and RCH, 7 and 8 January 1943.
18. "Schema des Oxo - Riegel Verfahrens von Ludwigshafen" - by Mauthner, Gemassmer, 28 January 1943.
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20. One drwg. Merseburg M3463-16 "Fliesschemen für 50,000 Jato Oxo-Verfahren"
21. One drwg. "Schema d. Kontinuierlichen Fahrweise des Oxo-prozesses, Stand vom 1 May 1942."

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22. "Gesichtspunkte zum Bau hener Oxo Aulagen" - by Wenzel 30 March 1942.
23. Memorandum to Meeting 28 March 1942 by Metzger.
24. Memorandum to Meeting "Planung des Oxo-Verfahren" - by Gemassmer 11 May 1940.
25. Memo Re: "Energieverbrauch, etc. für Oxo-Aulage" - by Gemassmer, Mauthner, 7 July 1943.
26. "Die Herstellung Höberer Alkohole aus Olefinen" - by Grimme, Campen, (Rheinpreussen) 6 December 1943.

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BERICHT

über den Stand der Arbeiten auf dem Gebiete des Forschungsauftrages "Weiterentwicklung der Benzinsynthese aus Kohlenoxyd und Wasserstoff, insbesondere in Richtung einer direkten Synthese von Isoparaffinen (SS 6132 - 9798 / 42)."

im Dezember 1942.

Geheim!!

Über die direkte Synthese von Isoparaffinen aus Kohlenoxyd und Wasserstoff.

Anläss[illegible] vom Untersuchungen über das Verhalten verschiedener Oxyde als Ka[illegible]atoren der Umsetzungen von Kohlenoxyd und Wasserstoff zu Kohle[illegible]erstoffen und sauerstoffhaltigen organischen Verbindungen wurde gefunden, dass Katalysatoren auf Basis von Thorium eine Synthese von verzweigten Kohlenwasserstoffen in hervorragender Weise ermöglichen.

Das Verfahren erfordert ein Arbeiten bei erhöhten Drucken, wobei der optimale Druckbereich von der Art des Katalysators bestimmt wird. Die Thoriumkatalysatoren nehmen als Einstoffkatalysatoren eine Sonderstellung ein, weil mit ihrer Hilfe schon bei verhältnismässig niedrigen Drucken (beispielsweise bei 30 at) verzweigte Kohlenwasserstoffe in grösseren Mengen erhalten wurden. Deshalb, und weil auf Grund der bisherigen Arbeiten allein die Thoriumkatalysatoren eine einigermassen abschliessende Beurteilung zulassen, beschränkt sich der vorliegende erste Bericht auf diese Katalysatoren.

Allgemeines.

Als Ausgangsgas der Synthese wurde i.a. Wassergas mit einem Kohlenoxyd-Wasserstoff-Verhältnis 1 : 1 bis 1,2 : 1 verwendet. Ein derartiges Gasgemisch entsprach unter den optimalen Synthesebedingungen dem Verbrauch an den beiden Komponenten.

Es wurde auch eine Reihe von Versuchen ausgeführt, die als Ausgangsstoffe Dimethyläther und Wasserstoff verwendeten. Diese Versuche, die in der Hauptsache zur Klärung des Reaktionsmechanismus durchgeführt wurden, sind in dem vorliegenden Bericht nicht enthalten.

Die Durchführung der Synthese erfolgte in kohlenoxydfesten Druckrohren, und zwar zum Teil in mit Kupfer ausgekleideten unlegierten Stahlrohren und zum Teil in nicht ausgekleideten legierten Stahlrohren, wie solchen aus V_2A - oder Sicromalstahl.

Die lichte Weite der Reaktionsrohre betrug i.a. 15 mm, es konnten aber auch Rohre mit einer lichten Weite von 25 mm ohne bemerkenswerte Schädigung des Umsatzes verwertet werden.

Der Gasdurchsatz wurde durch Messung des expandierten Endgases und der aus den Stickstoffwerten errechneten Kontraktion bestimmt. Im allgemeinen wurde (auf Grund von Untersuchungen über den Einfluss der Strömungsgeschwindigkeit) mit einer Endgasmenge von 10 Litern je 28 g Thoriumkatalysator und Stunde gearbeitet. Dies entspricht beispielsweise bei einer 50%-igen Kontraktion 20 Litern Ausgangsgas je 28 g

Katalysator und Stunde. Da das Kontaktvolumen von 28 g Thoriumkatalysator ungefähr 15 ccm beträgt, ist die Raumzeitausbeute unter diesen Verhältnissen ungefähr 10 mal grösser als bei der Normaldrucksynthese.

Von den anfallenden Reaktionsprodukten, die aus dem Endgas durch Kühlung bzw. mit A-Kohle entfernt wurden, wurde die Zusammensetzung der Gasolkohlenwasserstoffe stets durch Tieftemperaturdestillation und die der flüssigen Kohlenwasserstoffe durch Feindestillation (i.a. der hydrierten Produkte) untersucht. Von charakteristischen Versuchen wurden von den einzelnen Fraktionen der flüssigen Kohlenwasserstoffe Brechungsexponent, Dichte, Jod-Rhodanzahl, Anilinpunkt u.a.m. bestimmt. Die anfallenden Benzine wurden ausserdem nach geeigneter Destillation und Einstellung des Dampfdruckes in rohem und hydriertem Zustand mit und ohne Zusatz von Bleitetraäthyl in einem I.G.-Prüfmotor nach der Motor-Methode auf ihre Klopffestigkeit untersucht.

Der Thoriumkatalysator.

Die besten Thoriumkatalysatoren wurden durch Fällung aus Thoriumsalzlösungen, zumeist durch Fällung des basischen Carbonats mit Soda aus Nitratlösungen hergestellt. Der frischgefällte Kontakt wurde i.a. bis zur Alkalifreiheit gewaschen, da geringe Menge an Alkali die Aktivität des Thoriumkatalysators herabsetzen und damit eine Erhöhung der Reaktionstemperatur notwendig machen. Nach dem Waschen wurde der Kontakt zunächst bei 110° getrocknet, dann gekörnt und schliesslich bei 300 bis 400° im Luftstrom gesintert. Dann wurde der Kontakt in die teils schräg und teils senkrecht angeordneten Kontaktrohre gefüllt.

Die Lebensdauer der Thoriumkatalysatoren war unter den Bedingungen der Isosynthese eine sehr grosse. Es konnte monatelang ohne nennenswerte Veränderung der Aktivität der Kontakte gearbeitet werden. Katalysatoren, bei welchen nach langer Betriebsdauer, infolge einer Bildung von Kohlenstoff ein Steigen des inneren Widerstandes beobachtet wurde, konnten durch eine Luftbehandlung bei Synthesetemperatur wieder in den ursprünglichen Zustand versetzt werden.

Die Thoriumkatalysatoren sind unempfindlich gegen Schwefelverbindungen. Mit Schwefelwasserstoff oder Schwefelkohlenstoff vorbehandelte Kontakte geben [illegible] wie mit Ammoniumsulfid gefällte normalen Umsatz.

Die [illegible]

Die Art der [illegible] anfallenden [illegible] produkte [illegible] des Katalysators [illegible] haltsdauer der Gase im Kontaktraum, die Aufarbeitung von Kohlenoxyd und Wasserstoff in mehreren Stufen, das Material der Reaktionsrohre u.s.w. in weiten Grenzen variiert werden.

<u>Blatt - 1 -</u> der als Anlage beigefügten Tafeln zeigt die Zusammensetzung der Reaktionsprodukte in Abhängigkeit von der Synthesetemperatur bei einem Druck von 150 at und einer Strömungsgeschwindigkeit der Gase, entsprechend 10 Litern Endgas je 28 g Kontakt und Stunde.

Die Menge der anfallenden Alkohole und anderen sauerstoffhaltigen organischen Verbindungen, die bei niedrigen Temperaturen, insbesonders unterhalb 375° vorherrschen, nimmt mit steigender Temperatur schnell ab. Im Gebiet von 375 bis 425° entstehen vorwiegend flüssige verzweigte aliphatische Kohlenwasserstoffe. Mit steigender Temperatur nimmt die Menge der nebenher anfallenden Naphthene allmählich zu. Ihr Anteil an den flüssigen Produkten ist bei 375° noch nicht beträchtlich, er erreicht aber bei 450 bis 460° 50%. Bei Synthesetemperaturen von 450 bis 500° konnten in den höhersiedenden Fraktionen der anfallenden flüssigen Kohlenwasserstoffe auch Aromaten nachgewiesen werden.

Die Menge der gasförmigen Reaktionsprodukte steigt von weniger als 10% bei 375° auf 50% der Reaktionsprodukte bei 440°. Isobutan ist unter den einzelnen Kohlenwasserstoffen das in grössten Mengen anfallende Produkt. Bei 450 bis 460° bestehen ein Drittel der gesamten Reaktionsprodukte aus diesem Kohlenwasserstoff.

Unverzweigte aliphatische Kohlenwasserstoffe entstehen nur in völlig untergeordneter Masse. Normalbutan fiel i.a. in Mengen von etwa 10% des Isobutans an (0,5 bis 3 der Gesamtprodukte). Die Menge des Normalpentans betrug nurmehr 1% der flüssigen Kohlenwasserstoffe.

<u>Blatt - 2 -</u> bringt Ausbeuten an Benzin und Gasol beim Arbeiten in einer Stufe unter verschiedenen Versuchsbedingungen, insbesonders bei verschiedenen Drucken und bei Verwendung von verschiedenem Material für die Reaktionsrohre. Mit Ausnahme des letzten Versuches wurden alle bei 450° ausgeführt.

Bei Atmosphärendruck war kein Umsatz festzustellen, bei 6 at ein sehr geringer. Bei 30 at wurden bei 22%-igem Umsatz des Kohlenoxyds 5,1 g C_3 + n-C_4 Kohlenwasserstoffe, 5,4 g iso-C_4 - Kohlenwasserstoffe und 16,1 g flüssige Kohlenwasserstoffe je Ncbm inertfreies Ausgangsgas gebildet. Mit steigendem Druck nahm die Menge der in einem Arbeitsgang anfallenden Produkte zu. Sie erreichte bei 500 at 46,5 g iso-C_4-Kohlenwasserstoffe und 40,5 g Benzin + Öl. Bei Verwendung von V_2A-Rohren waren die Ausbeuten an flüssigen Kohlenwasserstoffen grösser als bei entsprechenden Drucken bei Verwendung von mit Kupfer ausgekleideten Reaktionsrohren.

(5)

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<u>Blatt - 3 -</u> bringt den Einfluss des Druckes auf die bei einer Synthese von 450° in einer Stufe erzielten Ausbeuten graphisch. Die Ausbeuten an flüssigen Kohlenwasserstoffen und an Gasol nehmen mit steigendem Druck und damit zusammenhängend mit dem mit steigender Aufenthaltsdauer der Gase am Kontakt steigenden Kohlenoxydumsatz zu. Dieser kann mit steigenden Drucken erhöht werden, weil die Gefahr einer Kohlenstoffbildung mit steigenden Drucken immer geringer wird.

Bei niedrigen Drucken, beispielsweise 50 bis 100 at, könnte beim Arbeiten in mehreren Stufen ein ähnlicher Umsatz erzielt werden, wie er bei hohen Drucken, beispielsweise bei 300 bis 500 at, in einer Stufe möglich ist. Hieraus ergibt sich, dass die notwendige Kontaktmenge umso geringer ist, je höher der Arbeitsdruck gewählt wird.

<u>Blatt - 4-</u> bringt eine typische Gasoldestillation eines bei einem Druck von 150 at und einer Temperatur von 450° ausgeführten Versuches. (Th 101 a). Die Hauptfraktion ist das bei - 12° siedende Isobutan. Isobuten, auf dessen Vorhandensein die zwischen -10 und + 5° siedenden Anteile durch Behandlung mit 64%-iger Schwefelsäure stets untersucht wurden, war bei diesem Versuch nicht entstanden.

<u>Blatt - 5 -</u> zeigt das Ergebnis einer zu demselben Versuch (Th 101 a, 150 at, 450°) gehörenden Destillation der flüssigen hydrierten Kohlenwasserstoffe. In <u>Blatt - 6 -</u> sind Brechungsexponent, Dichte, Anilinpunkt und spez. Dispersion der bei dieser Destillation angefallenen einzelnen Fraktionen zusammengestellt. <u>Blatt - 7 -</u> bringt das Ergebnis der Untersuchung der bei diesem Versuch entstandenen flüssigen Kohlenwasserstoffe. Der Versuch entspricht dem nach Blatt - 1 - bei 450° erzielten Ergebnis. Er liegt im Gebiet einer stark hervortretenden Naphthenbildung (ca. 43% der flüssigen Kohlenwasserstoffe). Normalparaffine waren nur in sehr geringen Menge entstanden. Etwa 1% der flüssigen Kohlenwasserstoffe bestand aus n-Pentan. Dagegen bestanden fast 12% aus dem bei 28° siedenden iso-Pentan. Verhältnismässig grosse Mengen bestanden aus 2 - Methylpentan (13,6%) und wahrscheinlich aus 2,4 - und 2,2-Dimethylpentan. Bei den höheren Fraktionen ergibt sich aus den in Blatt 6 - zusammengestellten Zahlen ein ungefähres Bild der Zusammensetzung der Kohlenwasserstoffe.

<u>Blatt - 8 -, - 9 - und - 10 -</u> zeigen analoge Ergebnisse für den bei 150 at und 375° durchgeführten Versuch Th 101 b. Die Produkte dieses Versuches unterscheiden sich von den bei 450° durchgeführten vor allem durch einen wesentlich geringeren Naphthengehalt, und durch einen erhöhten Gehalt an verzweigten aliphatischen Kohlenwasserstoffen. (Vgl. Blatt -1).

<u>Blatt 11 -</u> bringt eine Zusammenstellung einer Reihe von Klopffestigkeitsmessungen nach der Motor-Methode.

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Die ersten sieben Benzinproben sind vor ihrer Untersuchung mit 30%-iger Chlorcalciumlösung gewaschen worden. Die Oktanzahlen liegen bei 78 bis 80 und zwar ziemlich unabhängig von den Siedegrenzen (vgl. Versuchs-Nr. 3, 4 und 5). Ein nicht gewaschenes Rohprodukt ergab eine Oktanzahl von 84,5 (Versuch 13).

Die Proben 8, 9 und 10 wurden vor Bestimmung der Oktanzahlen an einem Nickelkontakt hydriert. Die Oktanzahlen dieser Produkte liegen zwischen 83 und 85,7.

Das bei 150 at und 450° erhaltene und vor der Klopffestigkeitsbestimmung hydrierte Benzin (11) hatte nach Zusatz von 0,08 Vol.% Bleitetraäthyl die Oktanzahl 95, das bei 150 at und 370° entstandene Benzin (12) 89,6.

Schluss.

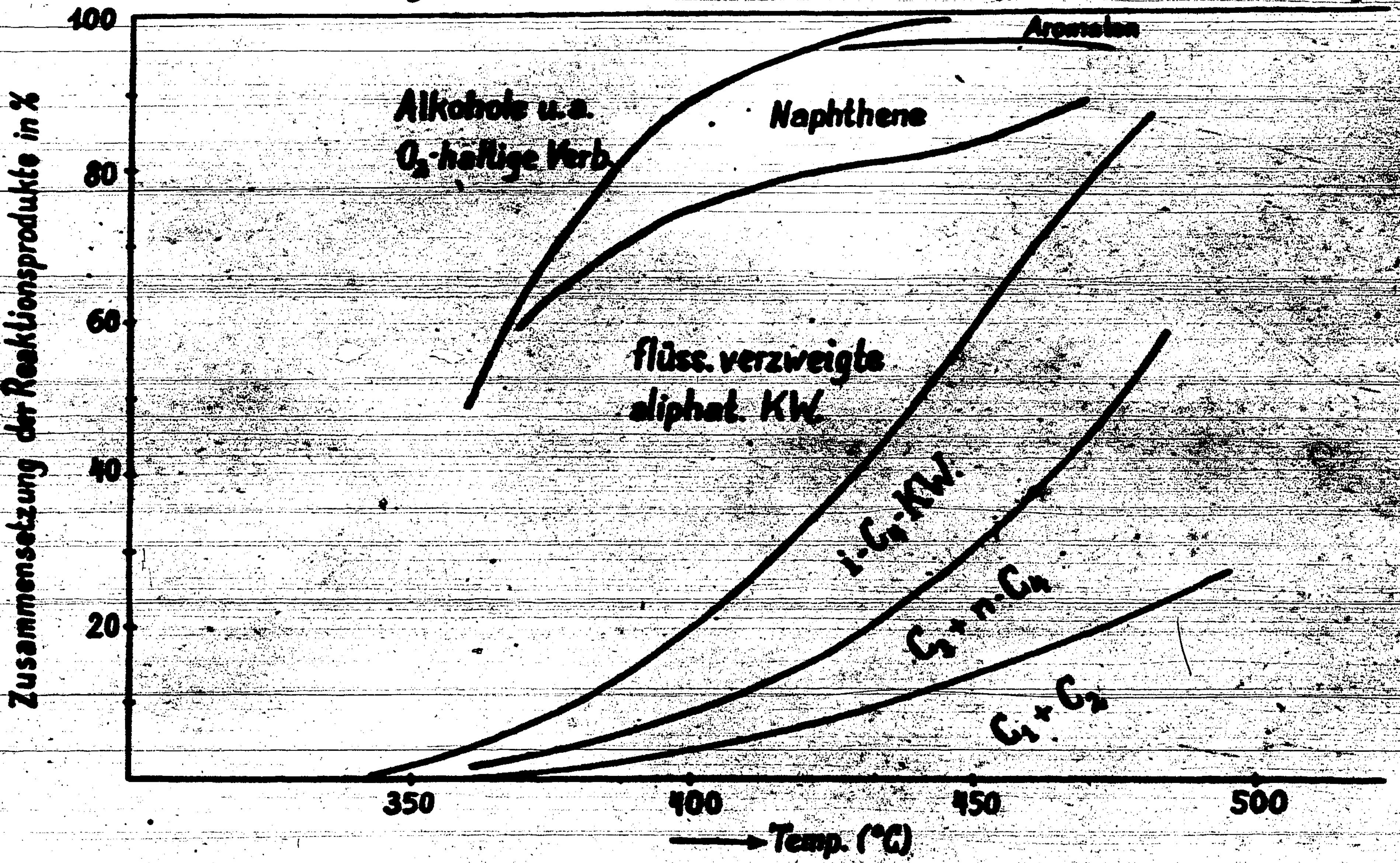
Bei der Isosynthese an Thoriumkatalysatoren konnten beim Arbeiten in einer Stufe an Casöl, Benzin und Öl bis zu 110 g je Ncbm inertfreies Ausgangsgas erhalten werden. Beim Arbeiten in zwei oder mehreren Stufen dürfte es möglich sein, die Ausbeuten weiter zu erhöhen.

Die Zusammensetzung der Reaktionsprodukte konnte durch die Wahl der Synthesebedingungen in weiten Grenzen variiert werden. So konnten beispielsweise die Ausbeuten an Isobutan von etwa 5 g je Ncbm, beim Arbeiten auf Höchstausbeuten an flüssigen Produkten, bis auf 50 g je Ncbm, bei Inkaufnahme entsprechend geringerer Ausbeuten an flüssigen Kohlenwasserstoffen, gesteigert werden. Bei genauerer Kenntnis des Einflusses der Zusammensetzung des Katalysators wird es möglich sein, in noch erhöhterem Masse die Bildung bestimmter erwünschter Kohlenwasserstoffe zu begünstigen.

Die Oktanzahlen der bei der Synthese anfallenden Benzine betrugen nach einer Hydrierung und Zusatz von 0,08 Vol.% Bleitetraäthyl bis zu 95. Wird das nebenher anfallende Isobutan für die Herstellung von Alkylierungsbenzin verwendet, dann dürfte das Gemisch der beiden Benzine ohne weiteres auf Oktanzahlen von 100 und darüber gebracht werden können.

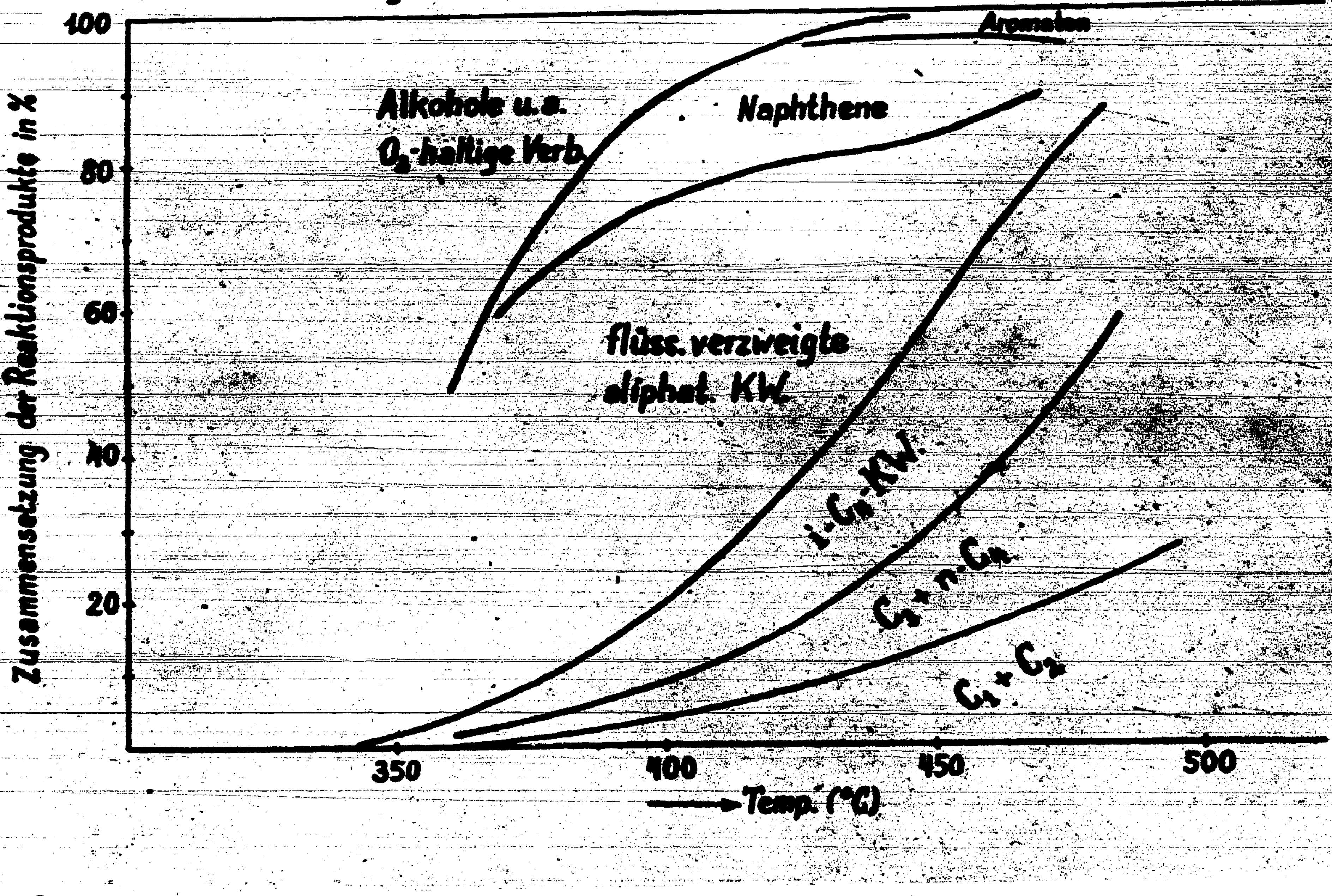
Isosynthese (150 at)

Zusammensetzung der Reaktionsprodukte in Abhängigkeit von der Temperatur.



Isosynthese (150 at)

Zusammensetzung der Reaktionsprodukte in Abhängigkeit von der Temperatur.



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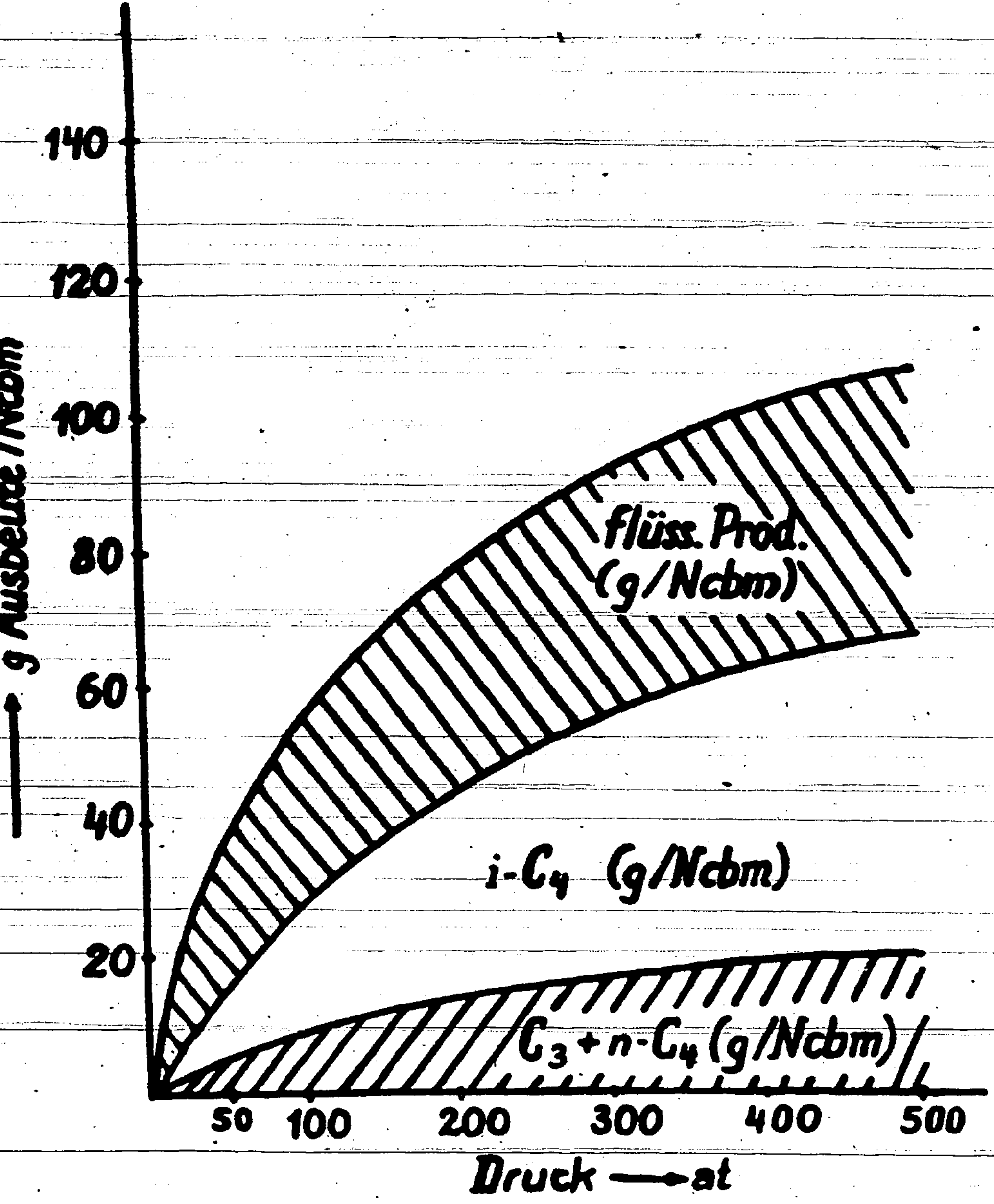
Blatt 1.

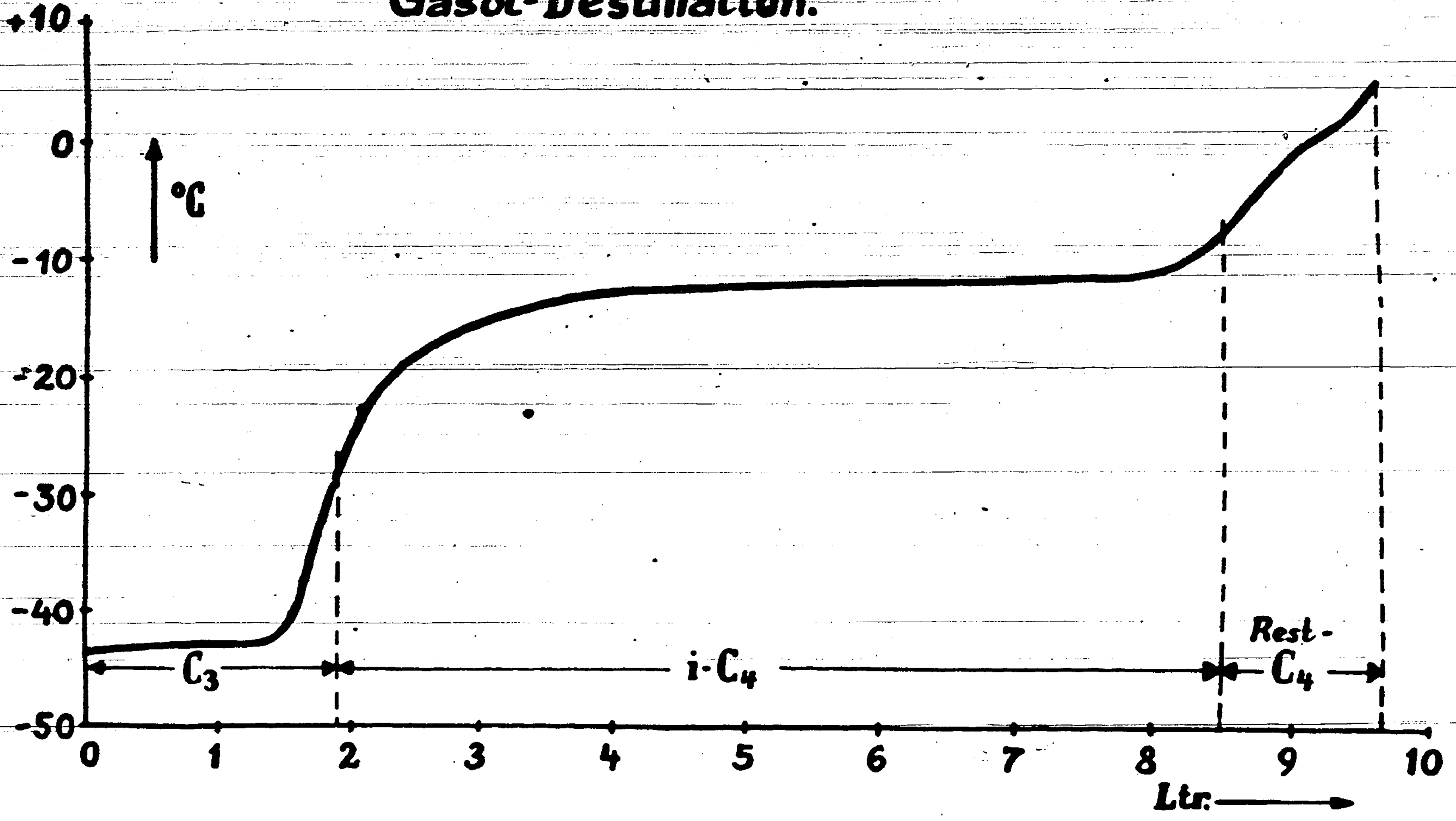
Ausbeuten an Benzin und Gasol unter verschiedenen Versuchsbedingungen.

Versuchs-Nr.	Druck at	Temperatur °C	Material des Reaktionsrohres	Ausbeuten in g/Ncbm inertfr.Gas C_3+n-C_4	 i-C_4	 Benzin + Öl
Th 51	0	450	Cu	-	-	-
Th 134	6	450	Cu	-	-	Spuren
Th 151	30	450	Cu	5,1	5,4	16,1
Th 101	150	450	Cu	9,1	30,0	29,7
Th 153	150	450	Cu	11,4	21,7	31.3
Th 143	300	450	Cu	20,4	41,6	37,4
Th 147	500	450	Cu	16,0	46,5	40,5
Th 139	30	450	V_2A	10,7	10,7	22,6
Th 154	150	430	V_2A	7,2	13,7	56,6

Isosynthese (450°)
Einfluss des Druckes auf die Ausbeute in einer Stufe.



Gasol-Destillation.



Blatt 4.

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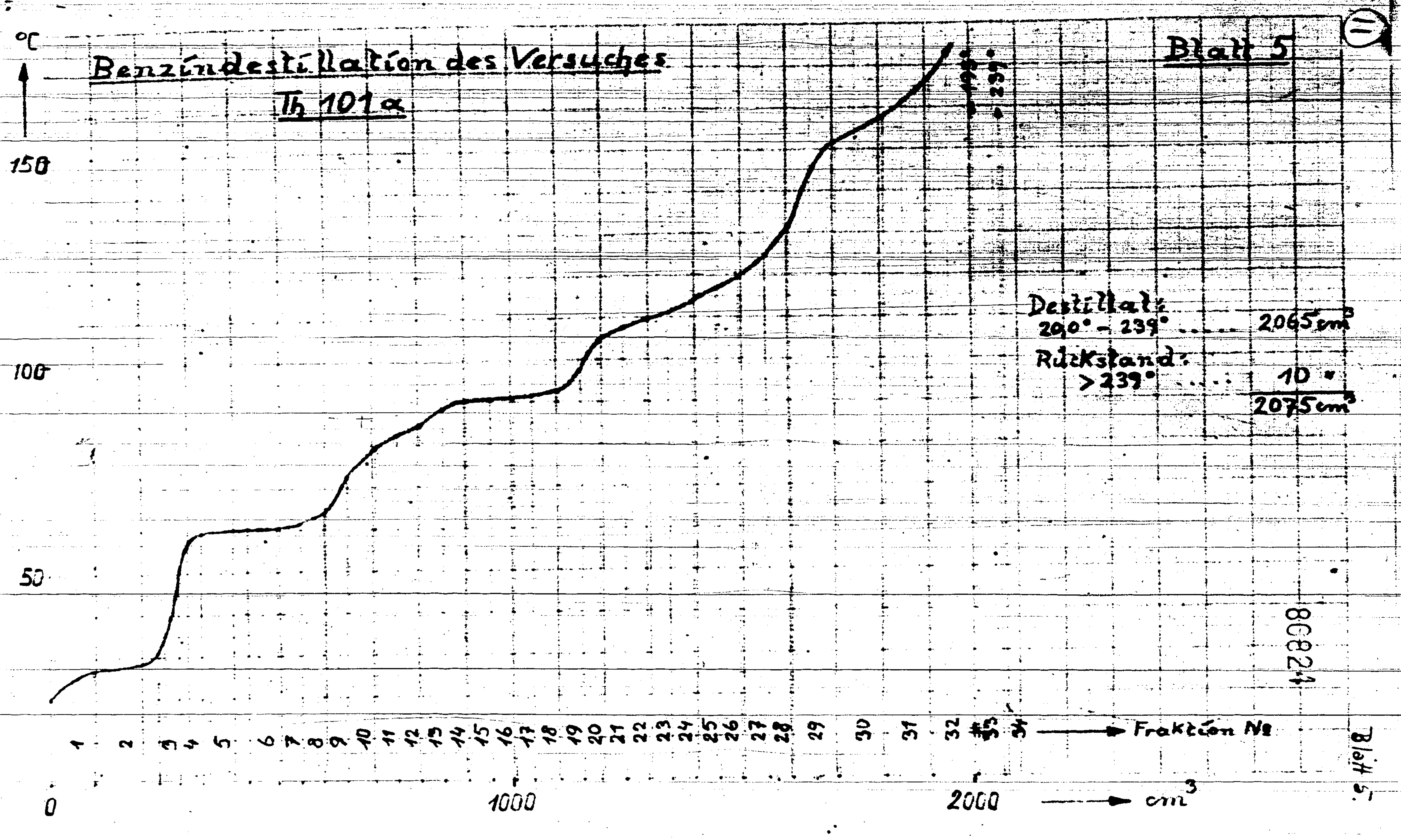
Blatt 5

Benzindestillation des Versuches Th 101a



Destillat:
20,0° - 239° ...... 2065 cm³
Rückstand:
>239° ...... 10 "
2075 cm³

Blatt - 2 -

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Unter[illegible]chung [illegible] Fraktionen d[illegible] [illegible] Versuch [illegible] 111 a.

Nr.	[illegible]	n 20	d 20	[illegible]	[illegible]	[illegible]
1	20,0-26,9	-	-	-	-	[illegible]
2	26,9-30,[illegible]	1,3543	-	-	-	14[illegible]
3	30,9-47,8	1,3[illegible]80	o,[illegible]	-	-	[illegible]
4	50,5-5[illegible],4	1,3720	o,65[illegible]	-	-	[illegible]
5	5[illegible],4-60,3	1,373o	o,6[illegible]5	-	-	1oo
6	6o,3-60,8	1,373o	o,[illegible]5	-	-	[illegible]
7	6o,8-61,4	1,3735	o,[illegible]5	-	-	[illegible]
8	61,9-[illegible]	1,3757	o,[illegible]	-	-	[illegible]
9	[illegible]-72,6	1,3849	o,[illegible]	-	-	[illegible]
1o	72,6-77,[illegible]	1,3220	o,[illegible]	[illegible]	[illegible]	[illegible]
11	77,7-82,[illegible]	1,[illegible]877	o,[illegible]	[illegible],2	[illegible]	5o
12	82,3-84,[illegible]	1,3[illegible]9	o,[illegible]3o	71,[illegible]	[illegible]	[illegible]
13	84,3-88,[illegible]	1,3917	o,[illegible]	[illegible]	-	[illegible]
14	88,[illegible]-90,3	1,3979	o,71[illegible]	[illegible],8	-	[illegible]
15	9o,3-[illegible]	1,4008	o,721o	[illegible]	-	[illegible]
16	9o,8-91,o	1,4017	o,[illegible]	[illegible]	[illegible]	[illegible]
17	91,o-91,[illegible]	1,4022	o,72[illegible]	[illegible],4	[illegible],1	4o
18	91,4-92,7	1,4031	o,72[illegible]	[illegible]	-	[illegible]
19	[illegible],7-97,[illegible]	1,407[illegible]	o,7367	[illegible]	-	[illegible]
2o	98,o-1o4,[illegible]	1,415o	o,7[illegible]oo	[illegible]	-	[illegible]
21	1o4,[illegible]-107,[illegible]	1,413o	o,7[illegible]oo	[illegible],9	1o[illegible]	[illegible]
22	1o7,7-1o9,5	1,415o	o,[illegible]oo	[illegible]	[illegible],7	[illegible]
23	1o9,5-11[illegible]	1,412o	o,7[illegible]	[illegible],1	[illegible]	[illegible]
24	11[illegible]	1,[illegible]18	o,[illegible]	[illegible]	[illegible]	[illegible]
25	11[illegible]-117,[illegible]	1,411[illegible]	o,7[illegible]o7	[illegible],8	[illegible]	[illegible]
26	117,o-119,[illegible]	1,[illegible]	o,[illegible]	[illegible]	7,[illegible]	[illegible]
27	119,[illegible]	1,[illegible]	o,[illegible]	[illegible]	[illegible]	[illegible]
28	1[illegible]	1,[illegible]	o,[illegible]o	[illegible]	[illegible]	[illegible]
29	14[illegible] -1[illegible]	1,442o	o,[illegible]o	[illegible]	[illegible]	[illegible]
3o	15[illegible] -1[illegible]	1,444[illegible]	o,7[illegible]	[illegible]	[illegible]	[illegible]
31	1[illegible] -1[illegible]7	1,[illegible]	o,[illegible]	[illegible]	[illegible]	[illegible]
32	1[illegible]7 -2[illegible]	1,[illegible]	o,[illegible]	[illegible]	[illegible]	1oo
33	1[illegible] -[illegible]	1,[illegible]	o,[illegible]	1,[illegible]	[illegible]	[illegible]
34	[illegible]	-	-	-	-	10

13

80826

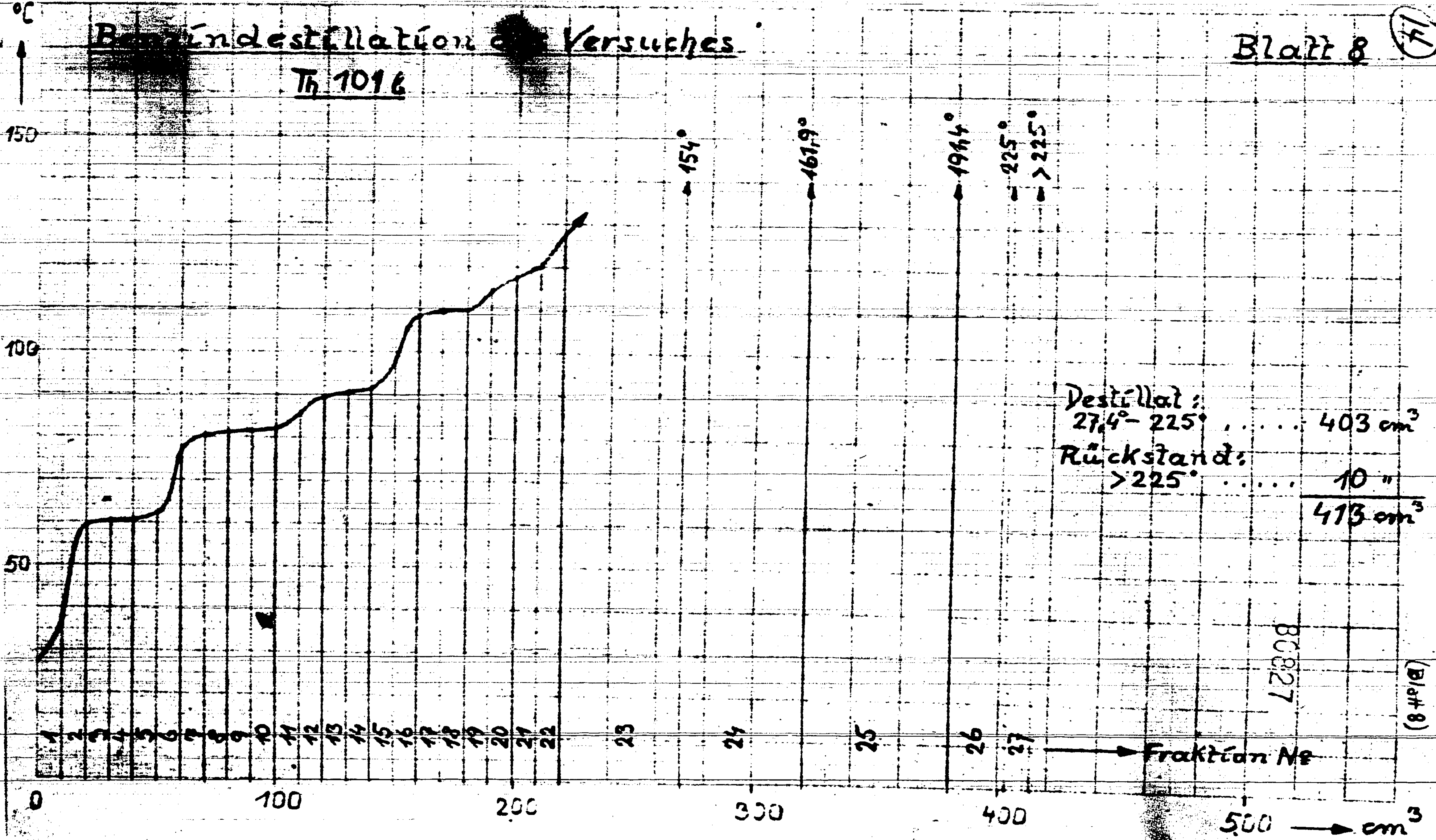
Blatt - 7 -

Unter den flüssigen Reaktionsprodukten des Versuches Th 1o1 a identifizierte Kohlenwasserstoffe.

Siedebereich °C	Verbindung	Vol% vom flüssigen Reaktionsprodukt
2o,o - 33,o	2-Methylbutan	11,8
33,o -47,8	n-Pentan	~1,o
	2,2-Dimethylbutan	<o,2
	unbestimmte Verbindung	~o,3
47,8 - 64,o	2-Methylpentan	13,6
	unbestimmte Verbindung	1,7
64,o - 8[illegible],5	~23 Vol.% Naphthene	2,9
	~77 Vol.% Paraffine	9,6
	(In dieser Fraktion sind grössere Anteile von 2,4-Dimethylpentan und 2,2-Dimethylpentan wahrscheinlich vorhanden).	
8[illegible],5 - 98,o	1,3-Dimethylcyclopentan	[illegible],4
	2-Methylhexan	[illegible],1
98,o -114,o	~[illegible] Vol.% Naphthene	7,[illegible]
	~[illegible] Vol.% Paraffin	[illegible],7
114,o -131,3	~76 Vol.% Naphthene	7,7
	~[illegible] Vol.% Paraffine	[illegible],4
131,3 -239	Naphthene, Aromaten, Paraffine.	2[illegible],[illegible]
239	Rückstand ([illegible])	o,5

Blatt 8 (7)

Benzindestillation des Versuches Th 1016



Destillat:
27,4°–225° ..... 403 cm³
Rückstand:
>225° ..... 10 "
413 cm³

⑮

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Blatt - 9 -

Untersuchung der einzelnen Fraktionen des flüssigen Reaktionsproduktes von Versuch Th 1o1 b

Nr.	Sp.	n_d^{2o}	d_4^{2o}	A.P.	spez. Disp.	ccm
1	27,4 - 37,7	1,3641	o,652o	-	115,6	1o
2	4o,o - 59,3	1,3752	o,6558	-	1o6,o	1o
3	59,3 - 6o,5	1,373o	o,6539	-	95,3	1o
4	6o,5 - 6o,7	1,3729	o,6535	-	95,3	1o
5	6o,7 - 62,1	1,373o	o,6548	-	97,3	1o
6	62,1 - 76,7	1,3851	o,6746	55,4	1o6,9	1o
7	76,7 - 8o,2	1,3893	o,6819	61,7	1o4,6	1o
8	8o,2 - 81,2	1,3849	o,6733	72,1	96,8	1o
9	81,2 - 81,3	1,3849	o,6734	72,9	98,9	1o
1o	81,1 - 82,o	1,3859	o,6738	71,2	98,8	1o
11	82,o - 85,4	1,39oo	o,679o	64,5	1o7,2	1o
12	85,4 - 89,8	1,3962	o,6993	58,4	1o[illegible],4	1o
13	89,8 - 9o,9	1,3981	o,7119	59,o	1o1,8	2o
14	9o,9 - 91,4	1,3992	o,7161	57,9	97,6	1o
15	91,4 - 97,3	1,4o32	o,7[illegible]37	52,4	9[illegible],6	1o
16	97,3 -1o8,6	1,4o96	o,7345	52,4	98,8	1o
17	1o8,6 -1o9,8	1,4o46	o,7248	63,7	[illegible]9,5	1o
18	1o9,8 -1o9,9	1,4o4o	o,7232	65,o	99,6	1o,2
19	1o9,9 -114,6	1,4o67	o,7283	6[illegible],o	97,6	1o,5
2o	114,6 -117,7	1,4147	o,7446	53,5	99,o	1o,o
21	117,7 -12o,o	1,4182	o,753o	51,1	96,8	1o
22	12o,o -128,o	1,4216	o,7617	49,8	[illegible],6	1o
23	145,4 -154,4	1,429o	o,771o	55,2	1o2,2	5o
24	154,4 -161,9	1,432o	o,7758	52,5	1o5,7	5o
25	161,9 -191,4	1,44o3	o,79o6	51,1	1o8,9	6o
26	191,4 -225,o	1,462o	o,8269	39,6	12o,o	23
Rückst.	>225	-	-	-	-	1o

(16)

Blatt - lo -

80829

Unter den flüssigen Reaktionsprodukten des Versuches Th lol b identifizierte Kohlenwasserstoffe.

Siedebereich °C	Verbindung	Vol.% vom flüssigen Reaktionsprodukt
27,4 - 47,5	unbestimmt+)	2,8
47,5 - 73,5	3-Methylpentan	lo,9
73,5 - 85,3	2,4-Dimethylpentan	1[illegible],[illegible]
85,3 -lo2,5	2-Methylhexan 1,3-Dimethylcyclopentan	6,1 [illegible],1
lo2,5 -112	2- oder 3-fach verzweigte Octane	[illegible],1
112 -225	unbestimmt	51,3
>225	Rückstand	[illegible],4

+) Die Isopentanfraktion wurde bei dieser Destillation nicht unter den flüssigen Produkten erfasst.

Klopffestigkeit verschiedener bei der Iso-Synthese angefallenes Benzine.

Lfd. Nr.	Versuchs-Nr.	Druck at	Temp. °C	Siedebereich °C	gewaschen m. 30%iger $CaCl_2$Lsg.	Dampfdr.n. Reid	hydriert	$Pb(C_2H_5)_4$	M.-O.-Z.
1	Th 64	30	500	bis 150	+	0,79	-	-	79,5
2	Th 101 a	150	450	" 150	+	0,54	-	-	78,0
3	Th 101 a	150	450-75	30-150	+	0,45	-	-	80,0
4	Th 101 a	150	450-75	30-165 (Gesamt-Produkt)	+	0,42	-	-	79,5
5	Th 101 a	150	450-75	70-150	+	0,16	-	-	78,8
6	Th 101 b	150	375	bis 150	+	0,75	-	-	79,0
7	Th 159	150	370	bis 150	+	0,71	-	-	80,5
8	Th 64	30	500	" 150	+	0,40	+	-	84,0
9	Th 101 a	150	450	" 150	+	0,53	+	-	85,7
10	Th 159	150	370	" 150	+	0,41	+	-	83,0
11	Th 101 a	150	450	" 150	+	0,53	+	0,08 V.%	95,0
12	Th 159	150	370	" 150	+	0,41	+	0,08 V.%	89,6
13	Th 159	150	370	" 150	-	0,75	-	-	84,5

Copy No. 20.

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
OP23F2
Serial 4000P23
26 Nov. 1945

TECHNICAL REPORT No. 280-45

8C831

SYNTHETIC COATINGS FOR GASOLINE TANKS

August 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

80832

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N. Y.

File: A9-16(3)(40/mb)

Serial: 891

31 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 280-45, Synthetic Coatings for Gasoline Tanks - Forwarding of.

Enclosure: (A) (HW) Seventeen (17) complete copies of subject report as listed in distribution.

1. Enclosure (A) is forwarded herewith.

2. CNO (OP-16-PT) is requested to make complete additional copies of this report for forwarding to such other agencies as may be interested.

HARRY D. HOFFMAN,
Captain, U.S.N.
Acting.

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80833

U. S. NAVAL TECHNICAL MISSION IN EUROPE
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New York, N. Y.

File: A9-16(3)(40/mb)

Serial: 891

31 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
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Harry D Hoffman
HARRY D. HOFFMAN,
Captain, U.S.N.
Acting.

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(2)

[redacted]

80834

TECHNICAL REPORT No. 280-45

SYNTHETIC COATINGS FOR GASOLINE TANKS

SUMMARY

The application of synthetic coatings to the inside of tanks used for gasoline storage was investigated. For small tanks (up to 250 gallons) baked phenol-formaldehyde resin coatings were used. For larger tanks where baking was impractical or impossible, a plasticized, nitrocellulose, air-dried lacquer was used. This lacquer, however, was modified by the addition of a soluble urea-formaldehyde resin which was cured by the addition of phosphoric acid to effect good adhesion and to render the film insoluble in gasoline. Tanks coated with this lacquer have been satisfactorily in service for a period of at least three years.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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[redacted]

SYNTHETIC COATINGS FOR GASOLINE TANKS

1. Introduction.

Information was desired on the methods used by the Germans for the coating of steel tanks to be used for the storage of gasoline. In particular, the steel tanks used on their warships were reportedly not appreciably corroded after at least three years of service.

A visit was made to the Schwalmer Iron Works at Schwelm which made tanks and containers of all sizes. This firm had made many of the large tanks used in German warships and tankers and also claimed to be one of the larger producers of "jerry" cans, the ingenious closure of which was developed by Herr Grünvogel of this firm. Details of the application of the coatings to the insides of these tanks were obtained from this company.

The composition of the lacquers used was learned from the Wiederhold Lacquer Company at Hilden which supplied them. Information concerning the resins used in the lacquers was obtained at I. G. Farbenindustrie in Höchst. Here, also, the method of coating concrete tanks used for the storage of gasoline was obtained from Dr. Dietz who supervised the construction of such tanks in North Africa, Western France, and elsewhere.

The details of the coating of the steel tanks is the subject of this report. The information pertaining to the concrete tanks is being included in a more comprehensive report. The coatings used for the concrete tanks is reportedly a phenol-formaldehyde resin coating modified to render it resistant to alkali.

2. Discussion.

For tanks up to approximately 250 gallons capacity used for gasoline, satisfactory results have been obtained with a regular baked phenol-formaldehyde coating. This type of coating is well known in the United States and will not be discussed. The men interviewed stressed the important but often ignored fact that

80836 [redacted]

2. **Discussion (Cont'd).**

the proper application of the coating was as necessary as the choice of the material used.

For larger tanks a baked lining was impractical. The technique involving the use of infra-red lamps recently exploited in the United States has not been developed to any great extent in Germany. Consequently, an air drying nitrocellulose lacquer was used which contained a plasticizer and a small amount of a soluble urea-formaldehyde resin. The addition of phosphoric acid to the lacquer effected further condensation of the urea- formaldehyde resin to the infusible state. This type of coating was used on tanks of up to 30,000 gallons capacity.

The method of application, together with the composition of the lacquer used, is as follows: The steel used was ordinary drum steel and was prepared for coating by the usual sand blasting technique. Three coatings of the lacquer were then applied. These coatings were brushed instead of sprayed because a more impervious coating was obtained and healthier working conditions prevailed. A higher boiling thinner than normally used was employed to delay drying sufficiently to permit brushing. The seams and rivets were carefully painted first, and then the whole surface including the seams and rivets was painted.

The composition of the lacquer was:

Vehicle 20.0 percent
Pigment 20.0 percent
Thinner 59.5 percent
Phosphoric acid 0.5 percent.

The vehicle consisted of two parts nitrocellulose and one part tricresyl phosphate (a plasticizer) to which was added 10 percent by weight of "Plastopal" AT. The pigment was one part iron oxide yellow and four parts aluminum for the first and third coats and all aluminum for the second coat. The variation was for the purpose of identification only. The thinner-solvent mixture was one part turpentine (B.P., 160 to 180°C.), one part decahydronaphthalene, and two parts of either ethylene or propylene glycol.

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[redacted]

2. Discussion (Cont'd).

The "Plastopal" used was one of a series of similar formulations produced by I. G. Farbenindustrie at Ludwigshafen. They are primarily soluble urea-formaldehyde resins which are used as additives to different types of lacquers, often in conjunction with plasticizers, to improve certain properties of the coatings obtained. "Plastopal" AT specifically is a mixture of 23 percent urea-formaldehyde resin, 27 percent ester of trimethylol propane and adipic acid, and 50 percent butanol. In addition to an improvement in the resistance to corrosion, an improvement in adhesion is claimed for the acid curing of the "Plastopal" AT.

These lacquers dried in 30 minutes on the test panel, but in actual use 3 to 4 hours were allowed to elapse between coats. Air at 30°C. was blown through the tanks to expedite the drying and to remove the solvent vapors.

The test work on panels coated in such a manner was done in Berlin and was consequently not available at the time of the investigation. However, tanks so coated, had been in service for at least three years and no failures had been reported.

Although no extensive study of the coatings industry has been made, this type of lacquer seems to indicate one trend in the German industry towards a cold-cured, plasticized lacquer which can be applied to surfaces where baking of the heat-setting resins is impractical or impossible.

Prepared by:

J. W. BIDDLE,
Technician.

6

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
OP-23-F2
Serial no. 4000P23
dated 26 Nov. 1945

80838

TECHNICAL REPORT No. 281-45

THE PRODUCTION OF MONOMERIC VINYL ACETATE IN GERMANY

AUGUST 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

80839

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(10/Hn)

Serial: 876

30 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 281-45, The Production of Monomeric Vinyl Acetate in Germany - Forwarding of.

Enclosures:
(A) (HW) Complete copies Nos. 1 - 5 of subject report as listed in distribution.
(B) (HW) Fourteen (14) copies of subject report Nos. 12 - 25, without photographs, as listed in distribution.
(C) (HW) One (1) set of negatives of photographs in subject report with copy No. 26, without photographs.

1. Enclosures (A), (B) and (C) are forwarded herewith.

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80840

[redacted]

TECHNICAL REPORT NO. 281-45

THE PRODUCTION OF MONOMERIC VINYL ACETATE IN GERMANY

SUMMARY

Nomoeric vinyl acetate was produced in Germany by the vapor phase reaction of acetylene and acetic acid in the presence of zinc acetate catalyst at 170 to 200°C. The catalyst was supported on activated carbon and had a maximum life of 800 tons of vinyl acetate per 2.2 tons of catalyst, or four months at the rated capacity of 200 tons per month. The reactor was a tube and shell vessel with 50 mm tubes 3.5 meters long in which the yield per pass was 32 per cent. Development work indicated that 35 mm tubes would effect higher yields. Efficiencies were reportedly very high with only traces of acetaldehyde formed.

August 1945

U.S. NAVAL TECHNICAL MISSION IN EUROPE

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[redacted] 80841

1. Introduction.

This report describes the process used in Germany for the production of monomeric vinyl acetate. The information was obtained from Dr. Alexander Wacker & Company at Burghausen who have been making vinyl acetate by this process since 1928. More recently a plant was installed at the I. G. Farbenindustrie works at Hochst for which the Wacker process was used. The capacity at Brughausen was 200 tons per month, whereas that at Hochst was reportedly 900 to 1,000 tons per month.

The basic principles of this process are known in the United States. The details are described in this report, to supplement the existing information.

2. Description of the Process.

Vinyl acetate was produced at Burghausen by the vapor phase reaction of acetylene and acetic acetic acid in the presence of zinc acetate catalyst. Activated carbon was used as the catalyst support. The temperature of the reaction was raised from 170°C to 200°C as the catalyst became less effective.

A simplified flow sheet of the process has been drawn in Figure 1. (A copy of a more detailed flow sheet and a copy of a drawing of the reactor which could not be reproduced with the available facilities have been forwarded to the Bureau of Ships).

The acetylene was prepared from calcium carbide and cleaned with aqueous chlorine previous to delivery at the vinyl acetate unit. Here it was dried by passage through calcium carbide (I) and subsequently cleaned by a mixture of sodium dichromate, sulfuric acid and kieselghur (II). These two cleaning operations were very important, because any impurities in the acetylene caused by-product formation and efficiency losses.

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[redacted]

2. Description of the Process (Cont'd).

The clean, dry acetylene was introduced by a blower (III) to the acetic acid vaporizer. The upper portion of this vaporizer was packed with 1-in. raschig rings to prevent entrainement. A steam coil was inserted above the rings to vaporize any liquid which might still have been in the gases. The ratio of acetylene to acetic acid was regulated by standard flow meters and rotameters not shown on the flow sheet.

The mixture of acetylene and acetic acid vapors was preheated to 135° to 150°C in (V) and further heated to 160° to 170°C in the heat exchanger (VI). From here the gases flowed through electric heaters (VIII) which were necessary in the absence of high temperature steam to boost the temperature to 200°C when the catalyst was old.

The reactor (VIII) was an iron tube and shell vessel approximately 8 feet in diameter and 18 feet high and contained 789 tubes 50 mm in diameter and 3.5 meters long. Oil was circulated around the tubes to maintain a desired temperature. At Hochst the regular reactors for the Fisher-Tropsch process were used. Recent work in a pilot plant reactor showed that 35 mm tubes gave better yields per pass (80 per cent instead of 32 per cent).

The catalyst was prepared by impregnating 3 mm cubes of activated carbon (I.G.'s Akt-3) with 70 per cent by weight of zinc acetate. The longest life for any one batch of catalyst was reported to have been 800 tons of vinyl acetate for 2.2 tons of catalyst, or four months at the rated capacity of 200 tons per month. The life of the catalyst was shortened if the unit was overloaded or the temperatures were erratic.

If the raw materials were prepared properly, the temperature of the reactor controlled nicely, and the capacity of the unit not exceeded, no by products other

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FLOW SHEET

PRODUCTION OF VINYL ACETATE

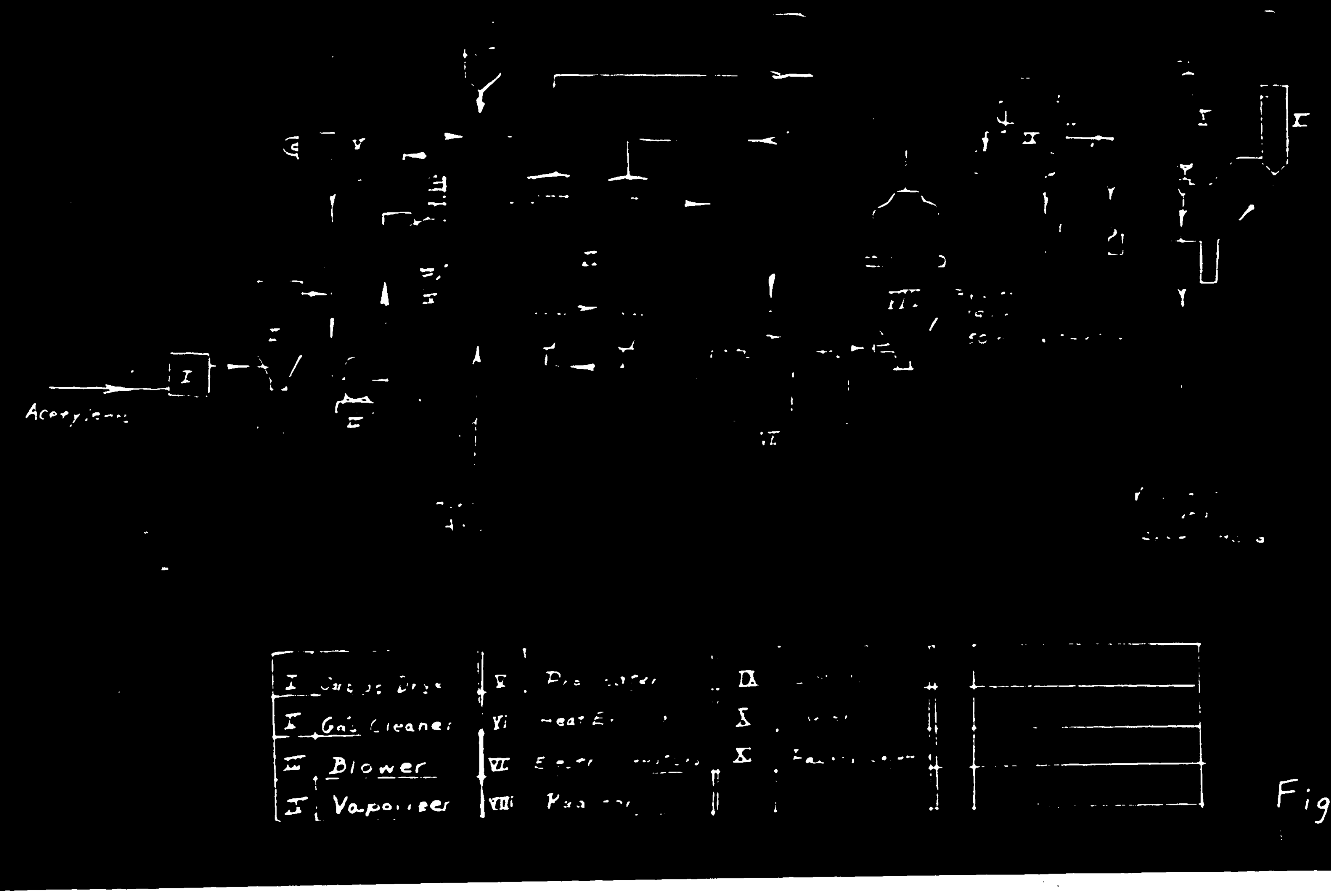

Fig. 1

2. Description of the Process (cont'd).

than a trace of acetaldehyde were formed. As could be expected, moisture in the feed caused the formation of acetaldehyde and high temperatures caused the formation of acetone.

The reaction products were cooled in a series of coolers (IX and X) were most of the vinyl acetate and acetic acid condensed, and the remaining gases were passed thru and scrubbed (XI) to remove the remaining traces of liquid from the gas before it was recycled.

The liquid from the coolers contained approximately 40 per cent vinyl acetate, dissolved acetylene, and acetic acid. Separation of this mixture was in packed distillation towers. No difficulties with polymerization in the columns was claimed, although hydroquinone was sometimes added to inhibit polymirization.

Generally speaking the materials of construction recommended were iron for the vapor phase and stainless steel for the liquid phase. Aluminum had been satisfactory for the storage of acetic acid, but stainless steel was preferred.

3. Uses.

The vinyl acetate produced at Alexander Wacker & Company was used primarily in emulsion polymerization to make hydrosols of polyvinyl acetate. Smaller amounts however, were used in suspension and solution polymerization. For the emulsion polymerization 5 per cent polyvinyl alcohol (based on monomer) was used and for the suspension polymerization 0.02 per cent was used.

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[redacted]

3. Uses (Cont'd).

Copolymers of vinyl chloride and vinyl acetate containing 40 per cent vinyl acetate were also made by a suspension polymerization in which a small amount of polyvinyl alcohol served as the suspending agent. These copolymers which are of higher vinyl acetate content than normally produced in the United States are used mainly in lacquers.

Prepared by:

J. W. BIDDLE,
Technician.

8

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
OP-23-F2
Serial no. 4000P23
dated 26 Nov 1945

80846

TECHNICAL REPORT NO. 333-45

GERMAN NAVAL FUEL OIL

SEPTEMBER 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

860

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

80847

File: A9-16(3)(10/Hn)

Serial: 1009

14 September 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 333-45, German Naval Fuel Oil - Forwarding of.

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H A Schade
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80848

TECHNICAL REPORT NO. 333-45

GERMAN NAVAL FUEL OIL

SUMMARY

This report covers the study of German Naval Fuel Oils. The data was obtained from Danisch Nienhoff, Kiel, Flensburg and Flemhude.

September 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE.

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GERMAN NAVAL FUEL OIL

1. Introduction.

In order to complete the general survey by the U. S. Naval Technical Mission in Europe of the German synthetic oil industry, a trip was made to Kiel, Hamburg and Flensburg to study German Naval fuel oils. The problem of fuel oil supply during the war was a difficult one for the Germans, due to the lack of natural petroleum and the scarcity of certain synthetic components for proper blending. The manner in which these difficulties were analyzed and overcome is of considerable interest to the U. S Navy, in view of current long range planning to develop shale oils and synthetic products.

In general, the Germans were faced with the same problems of stability and compatability, in storage and on board, as the U. S. Navy. They have also had accidents due to explosive fuels which they have overcome successfully. They have studied their problems in much the same manner as our navy but have not attempted to construct a unit such as the N.B.T.L. test heater. Furthermore, the synthetic oils used and the limitations of furnace design required an additional study of combustion characteristics within the furnace which the U.S. Navy has not, in general, had to do. It is interesting to note that every ship in the German Navy, including submarines, was equipped with a Jentsch oil testing unit which was operated by specially trained personnel. A constant check on all the important specifications was hence always available without requiring shipment of samples to land-based laboratories. The Jentsch test unit is particularly valuable for discovering explosive fuels.

2. Conclusions and Recommendations.

The information and data obtained on the manufacture, blending and use of synthetic fuels should be carefully reveiwed by U.S. experts as a guide to future long range programs.

[redacted]

Conclusions and Recommendations (Cont'd)

The use of the Jentsch Test Unit should be studied as a possible means of spotting dangerous explosive fuels, both on board ships and in bulk storage installations.

3. Demands for Fuel Oil

The German Navy required in 1942 and 1943 an average monthly supply of fuel oil of:

For the fleet and coastal defense craft	80,000 tons
For transports, cargo, and general operations	10,000 "
Total	90,000 tons

At the beginning of 1945, the demands were:

For the fleet and coastal defense craft	65,000 tons
For transports, cargo and general operations	5,000 "
Total	70,000 tons

At the beginning of the war the following quantities were on hand:

From Mexican and Roumanian crude	450,000 tons
Lignite tar oil	12,000 "
Hydrogenated pitch oil	15,000 "
Total	477,000 tons

At the end of the war, the following quantities were on hand:

Various residues	133,000 tons
Crude petroleum	53,000 "
Finished fuel oil blends	60,000 "
Total	246,000 tons

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4. Sources of Supply

The main sources of German Naval fuel oil were as follows:

(a) **Petroleum**

- (1) Roumania (Pacura and others)
- (2) Germany (Nienhagen)
- (3) Mexico (up to 1940)
- (4) Iraq (from captured French supplies)

(b) **Shale Oil**

- (1) Esthonia
- (2) Wurtemburg

(c) **Hard Coal**

- (1) High temperature distillation tar
- (2) Low temperature distillation tar
- (3) Hydrogenation of same

(d) **Lignite**

- (1) Low temperature distillation tar
- (2) Hydrogenation of same

(e) **Bitumen**

- (1) Hydrogenation of same.

In general, the German Navy's supply of fuel remained fairly constant throughout the war. Bombing caused damage to both petroleum refineries and synthetic oil plants, but the loss from the fo[illegible] was generally made up by quantities of synthetic middl[illegible]s which could not be finished to gasolines at other p[illegible] and hence were available as Naval fuels.

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Sources of Supply (Cont'd)

(a) Petroleum

The German Navy's supplies of natural petroleum fuel was very limited at the outset of the war and remained so throughout. Various residues were available from Roumania, especially Pacomra, which were of such inferior quality as to be unuseable for hydrogenation to better products. For this reason it was given to the Navy. Due to its very high pour point (+ 40°C) the Navy could only use it in coastwise vessels. At the outbreak of the war, the Roumanians supplied Germany with 30,000 tons/month. After Germany occupied that country the yield was raised to 90,000 tons/month. This increase allowed Germany to supply Italy with 50,000 tons/month for a year or so.

The oil production from the German field at Nienhagen was always reserved for lubricating oil manufacture, and only small amounts ever entered Naval fuel supplies.

Mexico supplied Germany with considerable amounts of oil before the war, but as the supply was cut off at the outbreak of hostilities, it played only a small part in the prosecution of the war.

Of greater importance to Germany were the large supplies of French Naval Oil taken after the fall of France. This oil was almost wholly reduced Iraq crude having a very high viscosity. As such it had to be blended, since its average viscosity was 35° Engler at 20°C (Max. values as high as 100° Engler at 20°C), to meet the German specifications of 12-15° Engler at 20°C.

(b) Shale Oil

All shale oil used as a fuel oil came from Esthonia. This supply was cut off when Russia took over that country in 1939 but was again available after Germany invaded Russia. It amounted to 8,000 tons per month.

At the end of the war, considerable development of the Wurtemburg shale deposit was under way. As far as

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Sources of Supply (Cont'd)

is known, only a very small amount of heavy Diesel fuel resulted from this work. The quality was poor and the oil was used only in farm tractors and not on Naval vessels.

The Esthonian shale oil is fairly heavy (API of 10°) and is very viscous at 5°C (470° Engler). It is fairly aromatic having a conradson carbon of 4.1.

(c) Hard Coal Tars

Distillation units produced hard coal tars for the Navy through out the war at Hochfeld and Duisberg-Neiderich. These were bombed out in 1945, but extra capacity was made available for the Navy at Rauxel which kept up the yields of tars.

These tars by themselves are difficult to use because the anthracine and maphthalene which they contain settles out at 8°C. To overcome this, a hydrogenated pitch oil was added to the blend, which was made at Ruhrol GmbH. This plant was bombed in 1944, so that the overall quality of Naval fuel oil was considerably lowered. The Navy partly overcame this quality change by altering their heating procedure in the ships bunkers.

(d) Lignite Tars

Considerable lignite tar was available in Germany for the Navy. This, like hard coal tar, was unuseable by itself as it contained 20% wax and had a pour point of 38°C.

A lignite tar oil was produced at Dea Rositz for the Navy at the rate of 12,000 tons/month. This plant was bombed in July 1944, greatly reducing the quality of the fuel blends.

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5. Blending Procedure

As was the case with other fuels, all heavy fuel oil blends were made at the Naval storage depots. The components were sent by their respective manufacturers to the Zentralburo who in turn diverted the stocks to the Naval Dumps, Achim, Flemhude, Blechhorde, Gydinia, and Wilhelmshaven.

Here the chemist in charge would analyze the fuels and blend them to meet pre-established specifications. In no case was a final blend made at the original source of supply, i.e. hydrogenation plant, coal distillation unit.

It is also important to note that the Germans were forced to use two quality fuel oils; one for ships entering the North sea where contact with British ships and planes was expected, and another of inferior quality for coastal and Baltic operations.

6. Quality of Components

The quality of the component used in blending up a finished oil is given in the following table.

The finished oil resulting from this blend was not unlike Navy Special Fuel Oil. The viscosity was 12-15° Engler, pour point below 0°C, sulfur content not over 0.05%. At the end of the war, due to shortages, the pour point rose to 8°C in the Baltic service. Also the large amount of pitch blends used often produced stack sparks which were most undesireable.

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PROPERTIES OF GERMAN FUEL OIL COMPONENTS

Specification	Topped Iranian Residue	Esthonian Shale Oil	Lignite Tar	Distilled Coal Tar	Hydregen-atedCoal Oil Residue
Color(Ostwald	10	10	10	10	10
Sp.Gr.@20°C	0.923	1.005	0.947	1.015	1.096
API	22	10	18	8.5	-2
Visc.Engl.					
@5°C	210	470	6.5	2.15	77.0
@20°C	58	82	2.7	1.5	17.0
@50°C	5.5	7.3	1.3	1.1	2.4
@100°C	1.7	1.3	1.05	1.0	1.3
High Heat Value KCal	10,325	9,460	9,912	9,752	9,578
Low KCal Value	9,744	8,955	9,375	9,309	9,245
Analysis* C%	85.43	87.07	85.71	89.45	91.37
" H_2	11.03	9.61	10.20	8.42	6.33
" S	1.81	0.86	0.66	0.34	0.58
" Creosote	0	26.0	16.0	4.0	0
Water Content	1.10	1.0	0.3	0.2	0.2
Ash Content	0.06	0.01	0.005	Trace	Trace
Acid Content (as SO_3)	0.04	0.1	0.28	0.024	0
Solvency-norm.Gasoline	0.65	7.8	2.8	0.02	0.23
Solvency-Alcohol Ether	3.61	0.5	0.8	0.05	0.35
Solvency-Xylol	0 .02	0.76	0.16	0.05	0.02
Con Carbon	5.9	4.1	0.7	0.25	1.4
Flash Pt Pensky Martens °C	110	94	85	95	135
Pour Pt. °C	+1	-15	-15	-20	-21
Fire Pt.°C	186	146	136	130	184

* These data do not add up to 100%. The C & H_2 were probably found by combustion. The creosote was found separately.

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RESULTS FROM JENTSCH TEST UNIT

Flash Pt.°C	112	96	89	94	132
Vaporization Time Secs.	160	90	50	30	70
Self Ignition Tem.	265	304	298	441	485
Higher Priming Value	500	550	540	600	580
Lower Priming Value	6.2	4.2	4.9		
Characteristic Priming Value	5.5	3.4	3.6		
Ignition Lag @320°C	1.5		11.3		
330°C	1.1		5.0		
340°C	0.8		2.2		
350°C	0.5		1.7		
550°C				2.5	0.9
Residue @ 500°C	5.5	3.4	Trace	Trace	2.2
350°C	61.0	3.6	7.6	0.6	22
Boiling No.	1	7	24	48	1
Comparison No.	35	21	23		
Oxidation Value	9.7	9.8	5.2	2.3	5
Oxidation Residue Height	8.5		12	20	10

The comparison numbers and ignition lag indicate that the topped Iranian crude has a much greater paraffincity than the other components. The oxidation residue heights show that the distilled tar oil is the most susceptible to chemical change while the topped Iranian crude and the hydrogenated coal oil are the least so.

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7. Scope of German Tests

A great deal of work has been done on combustion testing. Dr. Meyer wrote an extensive report covering work done by the "Chemische und Physikalische Versuchs Anstalt" of the German Navy in 1939. In this he analyzed approximately 100 oils, both natural and synthetic, individually and in blends with one another. This report is available. A subsequent report on a much larger scope, dealing mostly with synthetic oils and their blends was printed but has been lost due to bombing. An attempt is being made to obtain a copy of this report as its contents should be very valuable.

Dr. Meyer proved that very heavy synthetic asphalts could be used as fuel oil if cut back with a non-asphaltic petroleum stock and a tar oil from carbonizing coal. To prevent the heavy asphaltic material from dropping out of solution, the relative amounts of distilled tar and petroleum cutter-stocks should be about the same.

He also did considerable work on measuring surface tension, as this has a large effect on miscability. He reports the following values.

1.	Petroleum	27	dynes/sq.cm
2.	Heavy Petroleum	31	"
3.	Lignite Tar Oil	33	"
4.	Hard Coal Oil	34	"
5.	Esthonian Shale Oil	34	"
6.	Hard Coal Tar Oil	40-41	"
7.	Hydrogenated Pitch	42	"

The work on compatibility and stability of blends was done by Dr. W. Deman of the Krupp Gesellschaft at Essen. He was trying to develop means of using low temperature distillation coal tars in blends of fuel oil. Since this material contained much free asphalt and carbon,

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Scope of German Tests (Cont'd)

the problem was a difficult one. He found that in blending tars and Diesel oils, certain blends could be used while others produced considerable sludge. That he was successful is proven by the fact that the German Navy was using mostly pitch as a fuel oil at the end of the war, without encountering any noticable sludge trouble.

8. Analysis of Fuel-Oils and Blends

In general the Germans analyze their fuel oil much the same way as is done in the U. S. The standard test of specific gravity, water content, viscosity, flash and fire points, pour point, and conradson carbon are always made. In addition to these, certain solvency tests are run using "normal" gasoline, ether-alcohol, and xylol as solvents instead of benzol, cyclo-hexane, and isopentane as is done in the U. S. The "normal" gasoline is a narrow boiling range product having both iso and normal compounds.

These solvency tests are interpreted in much the same way as in the U. S. An attempt is made when making blends to get the proper distribution of solvency to keep the free carbon and heavy asphaltic compounds in solution. This is very important when mixing tars from coal distillation, hydrogenation, residues, etc. The danger of mixing a parrafinic cutter-stock with an asphaltic residue is well understood in Germany.

No attempt has been made by the Germans to develop anything like the N.B.T.L. test heater. Certain tests were run at Deschimag, Bremen on small boiler installations, but these were more of a burner development program than an oil testing procedure.

Considerable work has been done on measuring the surface tension of various oils. This was in conjunction with the Saacke burner which breaks up the oil drops to the desired size through a rotary spinning device. The optimum drop size and corresponding steam requirements of

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Analysis of Fuel Oils and Blends (Cont'd)

of the burner were thus obtained.

9. Analyses

The combustion tests are carried out to obtain the proper burning characteristics i.e. flame length, ignition lag, smoke, residue, ash, while the compatibility tests deal with the problem of sludge formation under long time storage.

The combustion characteristics are generally measured on a "Jentsch Primary Value Tester". This piece of apparatus is placed aboard every German Naval vessel including submarines. The following tests are made on the one piece of equipment.

(a) Flash point
(b) Fire point
(c) Self ignition temperatures
(d) Lower priming value
(e) Higher priming value
(f) Characteristic priming value (from (d) and (e))
(g) Residue at 350°C and 500°C
(h) Conradson carbon
(i) Vaporization time factor
(j) Boiling number
(k) Oxidation value
(l) Ignition lag

From the above data, a comparison number is obtained through nomograms by which the various fuels can be compared with one another.

The unit consists of a solid steel block having 4 round chambers, 15 mm diam, and 38 mm high. The block is surrounded by a heating unit of high resistance wire, properly insulated. The temperature is controlled by a rehostat. In the middle of the block, between the 4 chambers, is a hole leading to the bottom of each of the 4 chambers. Through this, oxygen is passed from a measuring device which controls the quantity by an orifice.

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Analyses (Cont'd)

An auxiliary stand with a mirror, electric light and air jet completes the general assembly.

One of the salient features of this unit is the small quantity of oil required. In many tests only drops are needed. The temperatures can be accurately measured, either by thermo-couples in the 4th chamber or by a thermometer.

The first figure obtained is the self ignition temperature. This is the lowest temperature at which the oil spontaneously ignites when oxygen is added. Many oils may have the same self-ignition temperature but the quantity of oxygen may vary from 1 to 10. The two variables, temperatures and oxygen content are combined in a factor, the lower priming value. It is: $\text{l.p.v.} = \frac{t}{b + 1}$, where t = the lowest self ignition temperature and b is the number of oxygen bubbles/min. 60 bubbles/min equal 5 cc of oxygen per minute.

Next the "higher priming value" is found. This is the temperature at which combustion occurs with no oxygen added, hence

$$b = o, \text{ and } \text{h.p.v.} = \frac{T}{0 + 1} = t.$$

From the above two quantities, the "characteristic priming value" is found:

$$\text{c.p.v.} = \frac{th - te}{b + 1}$$

where t_h and t_e are the temperatures of higher and lower priming values, and b = the no. of oxygen bubbles/min for the l.p.b. For low ignition delay, such as is wanted in diesel and fuel oils, the c.p.v. should be as high as possible i.e., a fuel should require small amounts of oxygen to produce its l.p.v. A gasoline to have good octane numbers should have a c.p.v. as low as possible, i.e.

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Analyses (Cont'd)

it should be able to be heated to a high temperature without igniting spontaneously, even in an oxygen rich atmosphere.

These facts are brought out in the nomograms drawn up by Dr. Jentsch for the two types of fuels. The physical characteristics are set by the boiling range and self ignition temperature. The final results, or "Comparison number" is comparable to octane and cetane ratings.

The boiling range is obtained on the test unit by an ingenious timing method in which the oil is put in a cylinder at 400°C and the volumetric amount remaining after a specified time is obtained.

The Conradson carbon value is obtained by placing 12 drops of fuel in a cup in the cylinder at 500°C for 2 minutes. The material remaining after that is placed in a colorimetric tester and a very quick value obtained.

The final test of importance is the oxidation test. This somewhat resembles the stability test used in America, but is again carried out on the Jentsch unit. One cc of oil is heated up in the unit to 250°C for 12 minutes while oxygen, at the rate of 300 bubbles/min. is passed through it. At the end of this time, the oil is mixed with 10 cc of "normal" gasoline (a mixture of iso and normal parafines) and allowed to stand for 15 minutes. At the end of this time the height of sludge is measured volumetrically.

Prepared by:

R. C. ALDRICH
Lieut. U.S.N.R.

[redacted]

10. Bibliography

(a) "Vorschriften für die Pflege der Schmierstoffe sowie Heizöle und der Flüssigen Kraftstoffe" (Instructions for Handling Lubricating Oils as well as Fuel Oils and other Liquid Fuels). Published by the German Navy-1938, M.Dv.Nr. 847

(b) "Bericht über Heizöle und Mischungsversuche mit Heizölen" von Dr. Meyer, Chemische Physikalische Versuchsanstalt (Report on Fuel Oils and Blends of the same, written for the Naval Physical and Chemical Laboratory, Dr. Meyer).

(c) "Mischbarkeit von Heizölen" von Dr. W. Demann, Essen, Sonderabdrukt aus Nr. 5 Jahrgang 1940 der Berg und Huttenmannischen Zeitschrift Gluckauf" (Miscibility of Fuel Oils by Dr. W. Demann)

(d) An article published by Dr. Demann in Forschungberichte Feb. 1943. "Viscosimetric Methods of Evaluating the Miscibility of Hydrocarbons, especially Fuel Oil".

(f) Patent of Dr. W. Demann
D.R.P. 710.665 Kl 42
Applied for 14-6-39
Awarded 18-0-41

(g) An article published by J. Pluckthun in "Forschungsberichte Jan 1942 entitled "Versuch über gegenseitige Lösungsfärhigkeit von Teerölen" (Experiments on the mutual solubilities of tar oils).

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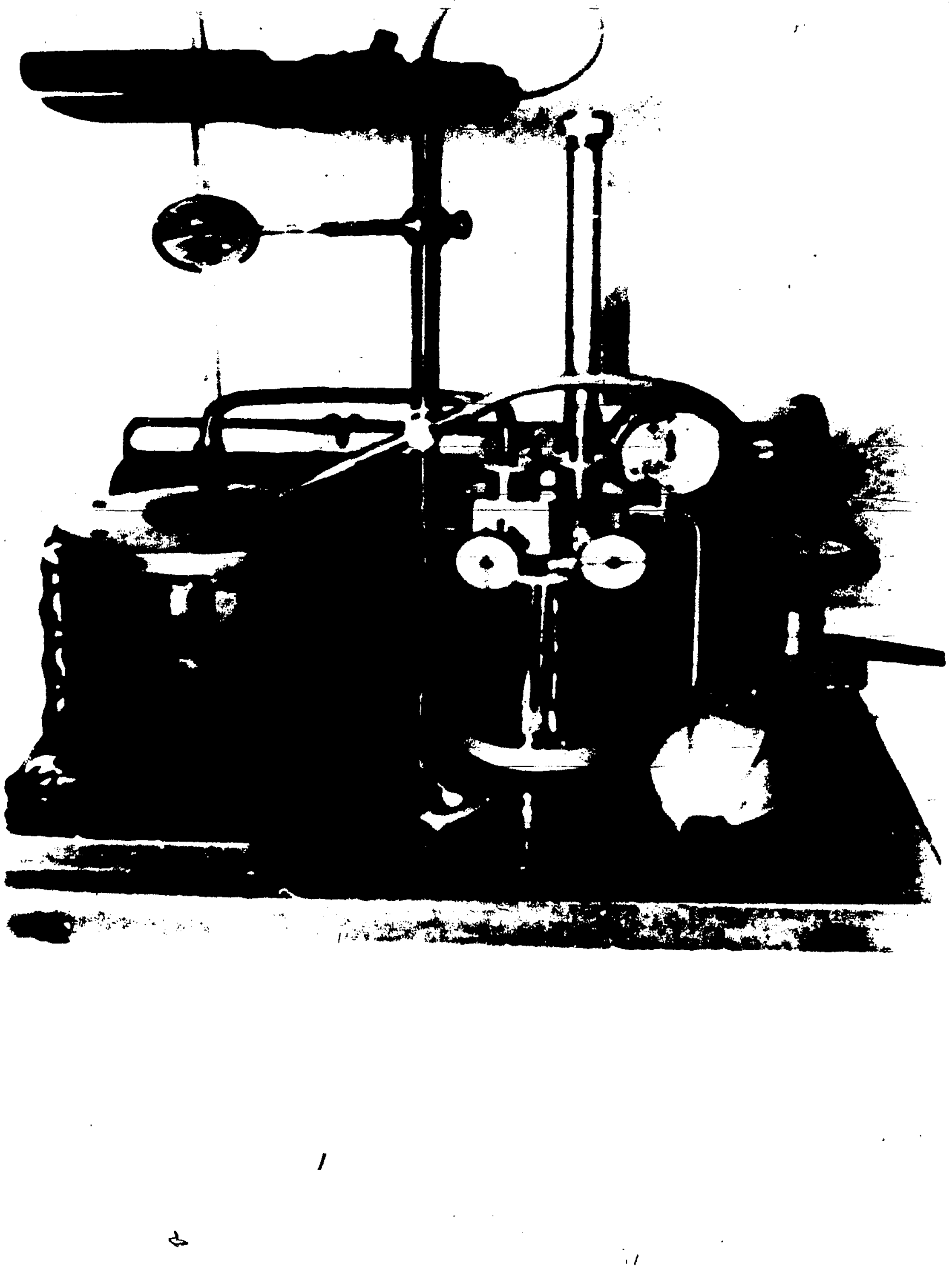

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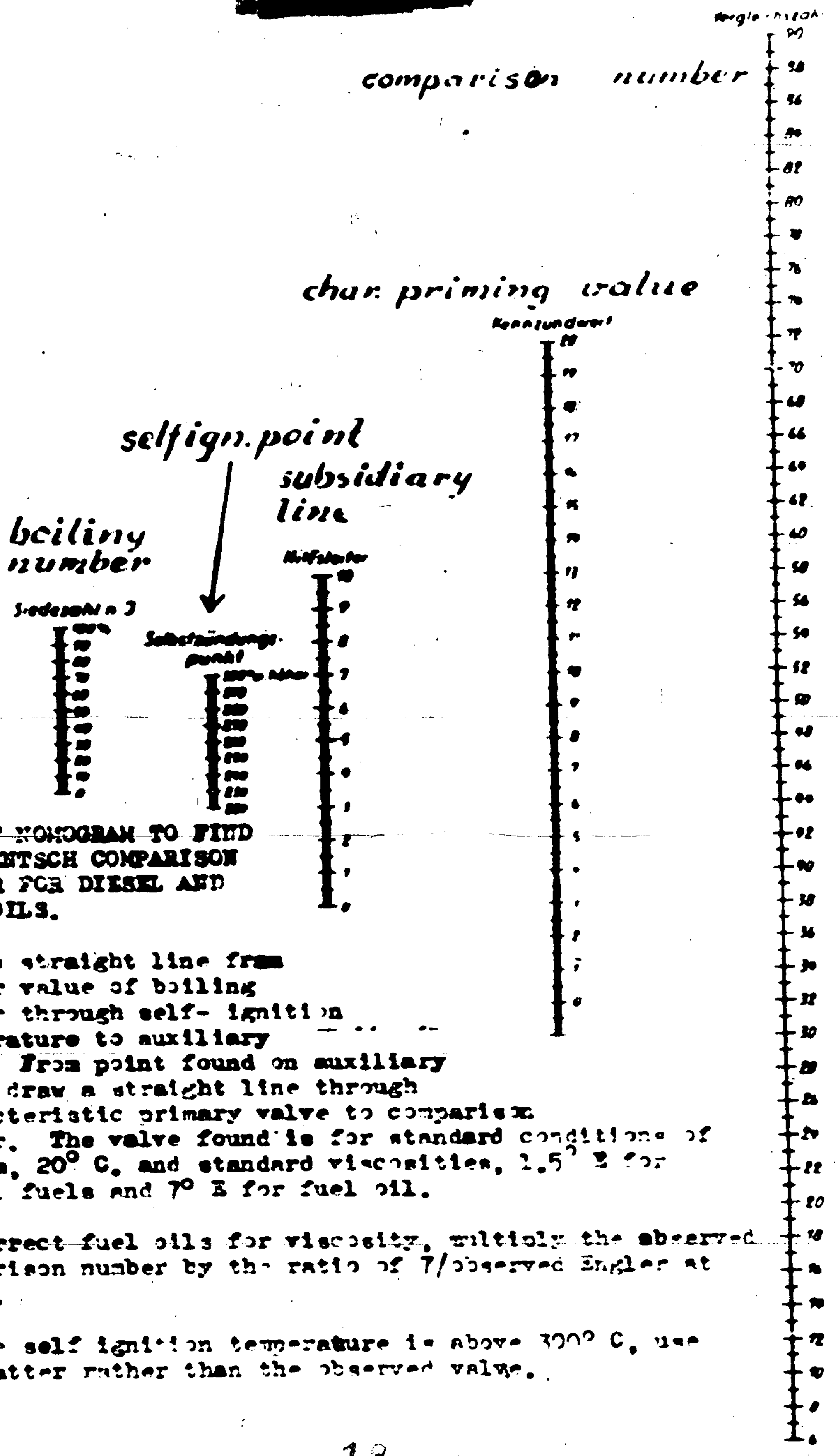


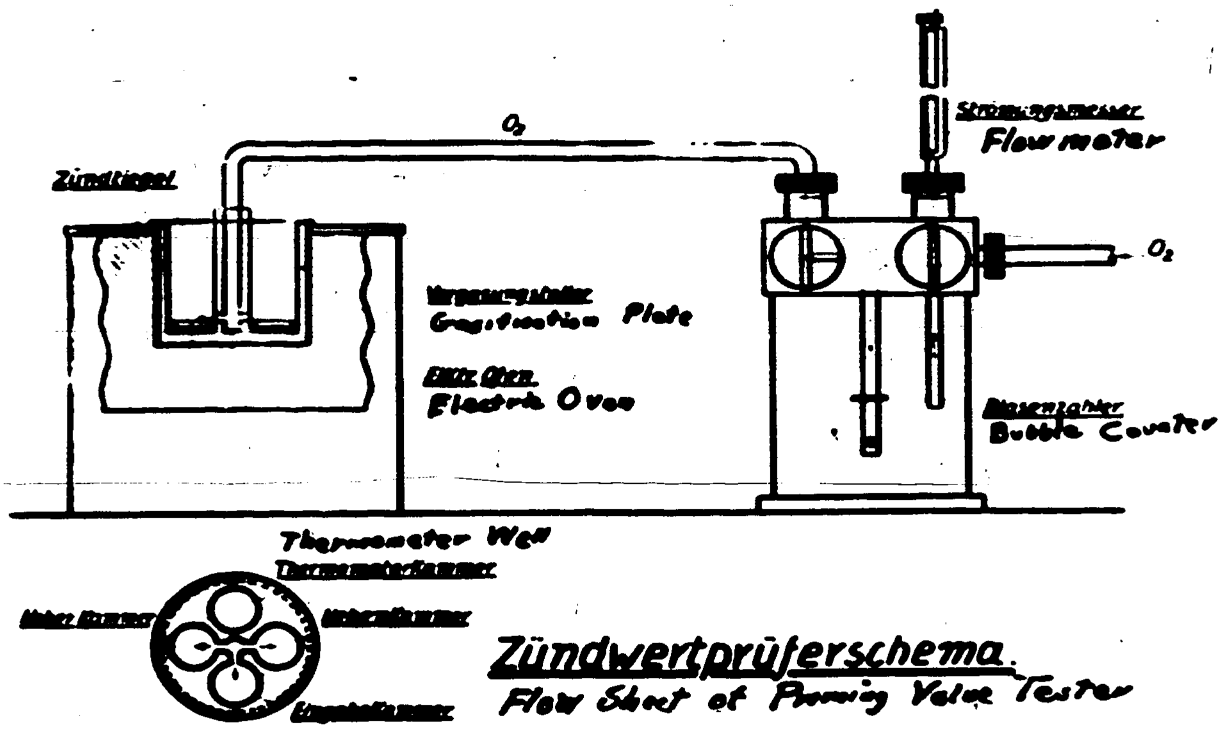
USE OF NOMOGRAM TO FIND THE JENTSCH COMPARISON NUMBER FOR DIESEL AND FUEL OILS.

Draw a straight line from proper value of boiling number through self- ignition temperature to auxiliary axis. From point found on auxiliary axis, draw a straight line through characteristic primary valve to comparison number. The valve found is for standard conditions of 760 mm, 20° C. and standard viscosities, 1.5° E for Diesel fuels and 7° E for fuel oil.

To correct fuel oils for viscosity, multiply the observed comparison number by the ratio of 7/observed Engler at 20° C.

If the self ignition temperature is above 300° C, use the latter rather than the observed valve.

[redacted]



Zündwertprüferschema.
Flow Sheet of Priming Value Tester

Schnitt durch den Zündtiegel.
Cross Section through Ignition Chamber

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
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Serial no. 4000P23
dated 26 Nov 1945

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TECHNICAL REPORT No. 388-45

ADDITIVE FOR LUBRICATING OIL

September 1945

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Serial: 1100

[redacted] 19 September 1945.

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To : Chief of Naval Operations (OP-16-PT).

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Capt. U. S.N.
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TECHNICAL REPORT No. 388-45

ADDITIVE FOR LUBRICATING OIL

SUMMARY

Description of an additive to lubricating oil developed for decreasing the break-in period of aircraft gasoline engines from 50 hours to 10 hours.

This information was previously forwarded as NavTecMisEu Letter Report No. 119-45, File No. A 9-8 (10/Ma), Serial 452, dated 12 June 1945.

September 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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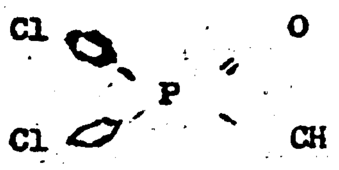
ADDITIVE FOR LUBRICATING OIL

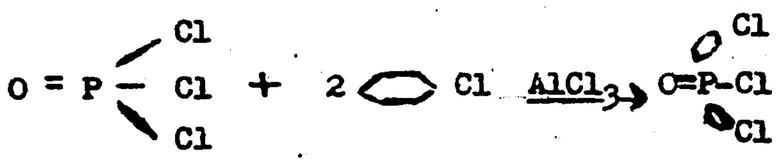
1. The information reported herein was obtained during an interrogation of Dr. Werk of the I-G Farbenindustrie at the Leverkusen Plant on 26 May 1945. To speed up delivery of aircraft engines, effort was directed toward finding an oil additive to decrease the time for the break-in period. In a long research which involved the preparation of many compounds, one successful compound was developed. This is a condensation product of phenyl chloride with phosphorous oxychloride to give:



The solubility of this compound in lubricating oil was increased by preparing its stearylamine salt. The additive is used in concentrations of 0.5 to 1.0 percent by weight based on the phosphorous and was successful in reducing the break-in period from an average of 50 hours to an average of 10 hours. A quantity of approximately 10 tons per year was manufactured by directive of the Luftfahrt Ministerium and the entire production was used by Deimler-Benz and Junkers, manufacturers of engines for aircraft.

2. This additive is somewhat corrosive, a property claimed to be desirable for the break-in period, but not desirable for general use. For this reason it is not proposed as a general use additive for oils.

3. Phenyl chloride and phosphorous oxychloride react in the normal manner of a Friedel-Crafts condensation in the presence of aluminum chloride according to the following equation:



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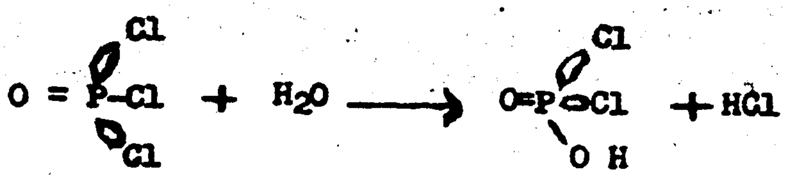
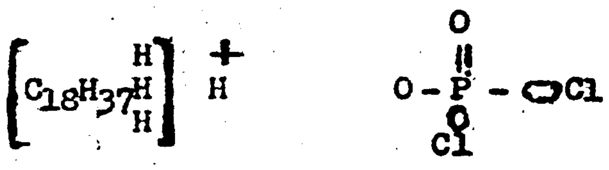
4. The apparatus used is a conventional glass-lined steel autoclave equipped with an agitator and effluent duct for the by-product hydrogen chloride. The optimum reaction temperature is given as 130° C. Aluminum chloride is not used in catalytic quantities but in amounts varying from one to three mols per mol of phosphorous compound. The crude reaction product is then hydrolyzed by treating with water:



$$\mathrm{O{=}\overset{Cl}{\underset{Cl}{P}}{-}Cl + H_2O \longrightarrow O{=}\overset{Cl}{\underset{OH}{P}}{-}Cl + HCl}$$

5. The phosphorous compound is separated from the aqueous media by extraction with benzene. The benzene is removed by distillation and the resulting acid phosphorous compound is treated with stearylamine to give the following compound:



$$\left[\mathrm{C_{18}H_{37}}\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right]^{+}\mathrm{H}\qquad \mathrm{O-\overset{\overset{O}{\|}}{\underset{\underset{Cl}{O}}{P}}-OCl}$$

6. Other amines including the ethanelamines, have been tried but were not as successful as the stearyl compound. In spite of the shortage of stearin, containing materials which are among the edible fats, it was deemed important to use the stearylamine here instead of a less desirable substitute material.

7. It is to be noted that a production of only 10 tons per year was contemplated which, in concentration of one percent means only 1000 tons of lubricating oil. No information given as to the quantity actually produced. Furthermore the fact that the product is corrosive, and that its use is advocated by only one German technician, leads to the belief that this is not a currently used additive, but one which is merely in the process of development, under the guidance of Dr. Werk.

Prepared by:

F. H. ROBERTS,
Technician.

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TECHNICAL REPORT NO. 556-45.

METHANE CRACKING BY PARTIAL COMBUSTION WITH OXYGEN OR AIR IN GERMANY

OCTOBER 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

U.S. NAVAL TECHNICAL MISSION IN EUROPE
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From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 556-45, Methane Cracking by Partial Combustion with Oxygen or Air in Germany - Forwarding of.

Enclosure: (A)(HW) Five (5) complete copy of subject report as listed in distribution.

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TECHNICAL REPORT NO. - 45

METHANE CRACKING BY PARTIAL COMBUSTION WITH OXYGEN OR AIR IN GERMANY

Summary

This report records information obtained by technical investigators on processes for the cracking of methane in coke oven gas and of pure methane by the partial combustion with oxygen or air in Germany for the production of hydrogen, hydrogen-carbon monoxide mixtures, hydrogen-nitrogen mixtures and acetylene.

The report describes several processes and the factors controlling them. The emphasis has been upon those parts of the processes which are not common in the United States, the more common elements having been omitted. The appendix contains flow diagrams and copies of selected original German documents pertinent to the subject, which serve to elaborate on the chemical engineering phases and the development of the processes.

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U.S. NAVAL TECHNICAL MISSION IN EUROPE

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INTRODUCTION

In spite of the scarcity of hydrocarbons in Germany it has been only since the beginning of the war that the Germans have developed and brought into large scale use, processes for converting the common methane or methane-containing gases into hydrocarbon products suitable for chemical purposes. Until comparatively recently coke oven gas, as well as residual hydrogenation Fischer-Tropsch residual gases were only processed in Germany to recover by absorption the propane and heavier components, the remaining methane and ethane being then used principally for fuel gas. During, or just prior to the war, experiments were carried out on the cracking of these gases to yield feed gases for other important processes. As a result of this work several processes have been developed and commercial scale plants built and put in operation in Germany. One method, the Häuber Process for ethane cracking was developed by I. G. Farbenindustrie in Leuna and is discussed in a Naval Technical Mission report on Aviation Gasoline. Another, the direct Electric Arc cracking process for producing acetylene from methane, was developed and put into operation at the Hüls plant of I. G. Farbenindustrie and is the subject of another Mission report. This report is therefore limited to a consideration of the cracking of methane by partial combustion with oxygen or air.

I. G. Farbenindustrie at Ludwigshafen, the Lurgi Company at Frankfort and H. Koppers Company at Essen have worked on this problem, and several commercial scale plants using the processes have been built and put in operation. The commercial installation at the Oppau works of I. G. using that company's process was inspected and Dr. Sachsse and Dr. Kosbahn were interrogated. Documents were also obtained from the Lurgi Company. A Koppers process installation was inspected at Rheinpreussen, Dr. Karl, Dr. Ackeren, Dr. Daniels and Dr. Koppers were interrogated at the Koppers offices, and documents were obtained.

The partial combustion of methane can be utilized for the production of useful products by two general processes designated by the type of products made as follows: (I) Either carbon monoxide-hydrogen mixtures for the Fischer-Tropsch, methanol etc syntheses or a nitrogen-hydrogen mixture for the ammonia synthesis, and (II) Acetylene plus the synthesis gases in I. This report treats these in separate sections due to the widely different combustion conditions required.

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(I) SYNTHESIS GAS PRODUCTION BY PARTIAL COMBUSTION

Methane oxidizes to produce carbon monoxide and hydrogen according to the following three equations:

(1) $CH_4 + CO_2 \longrightarrow 2\ CO + 2\ H_2$

(2) $CH_4 + H_2O \longrightarrow CO + 3H_2$

(3) $CH_4 + 1/2\ O_2 \longrightarrow CO + 2\ H_2$

To obtain a favorable equilibrium and rate in any of these three reactions a temperature of over 800°C must be used with a catalyst (or over 1000°C. if no catalyst is used). The first two reactions are endothermic and the third is exothermic. Therefore, by using a process carrying out reaction (3) simultaneously with one or both of the other reactions, the necessary endothermic heat for the first two reactions is supplied directly in the process and the problems of heat transfer equipment at high temperatures and the difficulties of pressure operation are largely avoided. In addition, by varying the relative extent of the three reactions in the combined reaction process adopted, close control can be easily maintained over both the $CO:H_2$ ratio of the product and the temperature of the reaction.

In this section two processes are described for the production of synthesis gases by partial combustion. The first one, employed by I. G. at Oppau, is a continuous process employing a nickel catalyst. The second one is an intermittent or regenerative cycle operation without a catalyst.

(A) Partial Combustion with a Nickel Catalyst

A flow sheet for the production of synthesis gases by partial combustion of methane in a gas mixture with a nickel catalyst is shown by Drawing Op 631 N-Sch 1 in the appendix to this report. This flowsheet (and the equipment shown thereon) can be employed to produce either an ammonia synthesis gas mixture or various carbon monoxide-hydrogen mixtures for such syntheses as methanol, isobutanol, Fisher Tropsch, etc. The principal difference in the process for producing these two types of gas mixtures is that when the need is for gas for the ammonia synthesis, part of the oxidation or combustion oxygen is obtained by using air instead of pure oxygen to the extent necessary to yield a ratio of $N_2:H_2$ of 1:3 in the final gas.

In the flow-sheet for synthesis gas production the coke-oven gas is first saturated with water at about 70°C. This is shown in Item 11. It is next preheated to about 500-600°C in the gas preheater Item 13, and then goes to the burner in the upper part of the combustion chamber, Item 15. The controlled amount of oxygen (or air) similarly saturated with water in Item 12, is preheated in Item 14 and is then mixed with the gas at the burner. Combustion takes place initially at about 1200°C, but the temperature becomes reduced to about 1100°C. due to the endothermic reaction with the water present. At this temperature the gas passes down through the Nickel-on-Magnesite catalyst situated immediately below the combustion chamber, leaving the bed at about 900°C. The outlet gas is first used to preheat the incoming feeds, is next cooled to 85°C. by direct contact with water in Item 17, and is passed through a coke "Schacht" filter Item 18 for removal of the carbon formed during the decomposition. The gas is next cooled in a heat exchanger Item 19 and passed through an iron oxide box Item 20 for H_2S removal. After the sulfur is removed the gas passes back through the other side of the heat exchanger. It is lastly passed through a direct contact heat recovery tower to heat the saturating water for the inlet gas saturator, Item 11, and the oxygen saturator, Item 12. The product gas is then ready for the synthesis process.

With respect to capacities, a larger unit located at Oppau operates at substantially atmospheric pressure, has a capacity of 8000m^3 of coke oven gas per hour, and produces 15000m^3 of synthesis gas per hour. For $CO + H_2$ operations about 22 volumes of O_2 per 100 volumes of coke oven gas are required. For NH_3 synthesis gas operation about 10 volumes of O_2 per 100 volumes of coke oven gas are supplied, with air used to furnish the remainder of the feed. In either operation the amount of O_2 is varied to control the temperature of the reaction.

Approximate analyses for the inlet and outlet gases are as follows:

	COKE OVEN GAS FEED	CRACKED FOR $N_2 + H_2$	CRACKED FOR $CO + H_2$
CO_2	3%	5%	5%
CO	9%	9%	10%
H_2	55%	48%	80%
N_2	7%	16%	5%
CH_4	25%	0.2%	0.2%

It will be noticed from these data that the partial combustion process is directed toward the decomposition of the CH_4 in the coke oven gas, covering it into CO and H_2. Thermodynamic equilibrium is said to be substantially obtained.

The carbon formed in the combustion to the extent of 50-200 mg/m^3 outlet gas is removed in the "Schacht" filter. The filter chambers are rectangular, about 3m x 9m in cross section with a bed of 2-8mm particle size coke 5m deep. About 2 liters of coke are removed from the bottom of the bed for each 1000 m^3 of dry gas through the filter. This coke is washed with water to free it of the collected carbon and is then replaced on top of the bed. No attempt has been made to use the carbon washed from the coke, and it is believed to be too coarse for use as carbon black. It is so fine, however, that it gives no trouble by plugging of the catalyst bed or the piping.

The catalyst used in this process is made by saturating 10-22mm particle size magnesite with a $Ni(NO_3)2$ solution to give about 3-4% Ni content by weight in the catalyst. The life of the catalyst is said to be indefinitely long, nevertheless a nickel solution is sprayed on the catalyst bed in sufficiently quantity to add about 1 mg of Ni per m^3 of outlet gas. This addition serves to replace any nickel lost by formation of carbonyl.

The combustion-catalyst chamber unit used in this process is circular in cross section, is lined with silimanite and is in addition insulated to a thickness of about 15 inches. The combustion chamber at Oppau is about 3m in diameter and 3m high, while the catalyst chamber beneath is 3m diameter and 6m high with the catalyst bed 2m deep. It was stated that in commencing operation about eight days are required to bring this unit up to its operating temperature in order to minimize the thermal strains in the masonry.

In the operation of the process the gas composition is controlled primarily with the aid of an infra-red CO recorder and a gravitometer which indicates the amount of N_2 + CO in the exit gas. The operating temperature is controlled by varying the amount of oxygen added to the burner as mentioned above.

A series of experiments carried out at the Bohlen plant by the Lurgi Company in 1941 and 1942 are reported by E. Kapp under the title "Druckspaltung methanhaltiger Gase der Druckvergasung", and a copy of this report is included in the appendix. While the purpose of the investigation was primarily to study the pressure cracking of gases obtained from the Lurgi pressure gas producer (as the name implies) a good general study was also made of the effects of varying several factors influencing the partial combustion process. Only a brief summary and a few comments on these effects are given below. Complete data from the work done are contained in the report.

The combustion chamber originally used in the work described in the above report was designed with an integral preheater, but leakage through the masonry finally forced the abandonment of this idea. Later a regenerative type preheater was designed. The inlet gas used was a mixture which varied slightly in its composition, but the approximate analysis of the gas used in most of the experiments was:

H_2	35.0%
CO_2	32.0%
CO	15.0%
CH_4	1.5%
H_2S	1.4%
C_nH_m	0.9%
N_2	1.4%
O_2	0.2%

In these tests the methane was cracked to about 0.5-4.0%, or a decomposition efficiency of 75-97%, whereas the theoretical equilibrium would be under 0.01% CH_4. The best cracking temperature was found to be 1250-1300°C. In this temperature range the theoretical and actual results were quite close together, as shown by the comparision curves. Simultaneous increase of pressure and throughput improved both the capacity and the cracking. Increase of gas inlet volume without simultaneous pressure increase decreased the available reaction time and reduced the extent of the reaction. It appears that the cracking effect is entirely dependent on this reaction time within the range of capacity of the apparatus, and that in practice, pressure alone did not appreciably alter either the equilibrium or the reaction velocity. Increase in the methane concentration made a higher reaction temperature (about 1400°C.) necessary for the same percent conversion. The quantity of carbon in the outlet gases was appreciably increased as the methane concentration increased. Presence of higher molecular weight hydrocarbons also greatly increased the amount of carbon in the outlet. Higher water content of the inlet gas reduced carbon formation and at the same time increased the usage of inlet gas and of oxygen per m^3 of ideal synthesis gas. Based on this result the water content should be kept as low as possible consistent with control of the carbon formation and of the $CO:H_2$ ratio in the reaction product.

It will be noticed that no hydrogen sulfide was removed in the cracking but some of the organic sulfur compounds were decomposed, principally to SO_2. This was dissolved and eliminated in the wash water. Incidentally, a small part of this SO_2 sometimes reacted with H_2S to form elementary sulfur which appeared as a white turbidity in the water. The SO_2 in the water has caused some corrosion difficulties with the steel in the piping and equipment.

Later, additional experiments were performed to further investigate the behavior of the sulfur compounds in the combustion and were reported March 17, 1943 in a report entitled "Spaltung von Reingas mit Schwefelbestimmungen". This report is also included in the appendix, and gives more accurate data on sulfur determinations, but the conclusions are about the same.

It was found in both series of tests at Böhlen that the resin-forming compounds that give trouble in the organic sulfur purification step, or "Feinreinigung", and in the subsequent synthesis operations were completely removed by the combustion.

The $CO + H_2$ concentration is approximately constant for any given feed gas at a constant percent conversion. Control of the cracking process to favor one or the other of the three basic reactions will also vary the $CO:H_2$ ratio. This ratio can be still further changed if desirable by inserting a shift reaction converter employing the reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The CO_2 thus produced can be scrubbed out by any suitable process, such as a water wash under pressure. When this methane cracking process is employed to produce gases for the ammonia synthesis, this shift reaction is used to convert the CO into CO_2, yielding additional hydrogen, and the resulting gas is then treated to remove undesirable constituents.

The economy of this methane cracking process depends to a great extent upon the availability of commercially pure oxygen at a low cost. The oxygen for this process is generally made in Germany by the Linde-Franckel low temperature air fractionation process. Since the several Linde-Franckel processes for gas separation are widely used throughout Germany and are covered in other Naval Technical Mission reports the details are not repeated here.

(B) Partial Combustion in a Regenerative Cycle.

In addition to the cracking of methane by partial combustion with oxygen, H. Koppers GmbH, Essen, developed a straight thermal cracking process employing steam without a catalyst. The process used the absorbed heat of a refractory packed tower maintained above 1200°C. to supply the heat for the reaction. The reaction proceeds according to the following equation: $CH_4 + H_2O \dashrightarrow CO + 3H_2$ (-50 cal.). One commercial installation consisting of 3 sets of units installed in 1938-39 was inspected at the "Steinkohlenbergwerk Rheinpreussen Treibstoffwerk" in the Fischer-Tropsch synthetic oil plant near Homberg. It was stated that this was the only installation in Germany using this process, but that others had been built for the Japanese. A simplified flow sheet for this process entitled "Umformungsanlage" showing gas composition, material balance, temperatures, general layout, power consumption, and a rough cost estimate report. In this process the cowper or cracking tower operates on a 16 minute cycle, 8 minutes cracking and 8 minutes heating. The capacity of each cowper unit is about 8,800 normal cubic meters of cracked gas per hour, or about 17,700 normal cubic meters per hour output for a continuous production unit. The temperature in the cracking tower head ranges from 1500°C. at the beginning of the cracking cycle, down to about 1300°C. at the end of the cycle. The cracking tower is completely filled with a special shaped refractory packing, each piece being shaped as follows:

The outside diameter is about 10 inches. The diameter of the center hole in the packing is 4 inches and the sides are also arcs of a 4 inch diameter circle so that the units mesh together to form a geometric pattern of tubes. Each of the pieces is 8 inches high and they are stacked so that the assembled packed tower consists of many refractory tubes of 4 inches diameter extending the full cowper tower height.

When the tower is on the cracking cycle as shown in the equipment on the upper part of the flow sheet (item 6 of the appendix), feed gas is preheated in the gas fired Rekuperator to 100°C., mixed with steam in a ratio 0.85 Kg per normal cubic meter of gas, and is passed through the cowper where it is cracked. The cracked gases then pass through the Brennschacht and the regenerator, leaving this latter unit at about 400°C. They next pass to the tar separator, thence to the precooler washer (leaving at 50°C.), thence to the Theisen water washer, and finally the after-cooler, leaving this last unit at a temperature of 25°C. When the tower is being heated as shown in the lower diagram on the flow sheet, combustion air enters through the regenerator or air preheater, is heated to 1000°C. and is combusted with heating gas in the "Brennschacht" or burning head. The hot gases then pass through the cowper or cracking tower and thence out at a temperature of two hundred fifty to three hundred fifty degrees centigrade.

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Inlet and outlet gas compositions are as follows:

Inlet Coke Oven Gas		Outlet Cracked Gas
CO_2	6.8%	5.1%
C_nH_m	2.5%	-
O_2	0.2%	-
CO	11.5%	19.7%
H_2	46.3%	69.1%
CH_4	24.0%	1.0%
N_2	8.5%	5.1%

A small quantity of carbon black (30mg/Nm^3) is also produced but it is not used.

The Koppers methane cracking process is characterized by its bulky equipment, particularly the large mass of refractory packing needed to store and supply the heat for the reaction and to maintain the high temperatures required.

Part II ACETYLENE PRODUCTION BY PARTIAL COMBUSTION

Acetylene is produced in Germany by partial combustion of methane in much the same way as that already described for synthesis gas production. The key difference in the two methods is that in the acetylene production process (a) only relatively pure methane or ethane is used, (b) the gases coming out of the combustion chamber are immediately quenched with a direct water spray, and (c) no catalyst is used.

A special burner is used in order to get the best possible mixing of the feed gas and the oxygen, and thus obtain efficient cracking in the extremely short cracking period. A drawing for such a burner and combustion chamber is shown on Drawing OP 648 - "Acetylenbrenner" in the appendix to this report. In this burner the methane and air enter at the top on opposite sides, flow through separate channels (packed with arranged raschig rings for obtaining homogeneity of the flow), and are mixed at the preheat temperature of about 400°C., at which point reaction begins. Cooling water tubes pass through this initial combustion point, apparently to control the final temperature of the reaction at the desired 1400°C. The reacting gases then pass down through a thick, perforated tile and are quenched with water immediately below.

A cost estimate entitled "Kostenschatzung für die Gewinnung von 70% igem Acetylen und Synthesegas aus Kohlenwasserstoffen" was prepared in December 1940 by the I. G. Farbenindustrie at Oppau on this process. This report pertains to a unit for the Heydebreck plant, and contains estimated operating costs, estimated construction costs, analyses, heat and material balances, and flowsheets for the process. A copy of the report is contained in the appendix as Item 5.

The two general flowsheets following page 4 of the above estimate show schemes for the process whereby the residual gas after removal of the acetylene is put through another partial combustion to make synthesis gas for ammonia and for Fischer Tropsch processes. This is a customary secondary step with this process.

The recovery of the acetylene is the matter of primary interest. In this process the cracked gas from the burner is compressed to 29 atmospheres and washed with water to remove the acetylene. The absorbed gas is recovered from the water by a three stage expansion. The gas from the first expansion stage is recycled to the compressor and the other two fractions are combined to yield a gas containing 70% acetylene. The third expansion is under vacuum. The lean gas from the absorption is put through the second partial combustion to react the remaining hydrocarbons. Then the gas, now called Cracked Gas II, is passed through a converter to carry out the shift reaction, replacing the CO and H_2O with CO_2 and H_2. When ammonis synthesis gas is produced, the quantities and analyses of the gases based on ethane feed for this process are as follows:

GAS	VOLUME m^3/hr	C_2H_2 %	CO_2 %	CO %	CH_4 %	H_2 %	N_2 %
Ethane Feed	3,070						
Oxygen Feed	3,130						
Cracked Gas I	10,000	9.3	4.0	32.3	6.0	48.4	---
Recycled Gas	446	37.5	15.9	19.5	4.6	22.4	---
C_2H_2 Rich Gas	1,294	70.6	27.7	0.8	0.2	0.7	---
Lean Gas	8,706	0.2	0.5	37.0	6.9	55.5	---
O_2+N_2 Second Combustion	3,738						
Cracked Gas II	11,250	--	3.2	31.2	0.2	42.2	23.2
After Oxidation	14,350	--	24.0	3.0	0.2	54.6	18.2

The flowsheet for the preparation of a hydrocarbon synthesis gas shows the compressor discharge and the water wash at 18 atm instead of 29 atmospheres, and the gas volumes and analyses are as follows:

GAS	VOLUME m^3/hr	C_2H_2 %	CO_2 %	CO %	CH_4 %	H_2 %
Ethane Feed	3,070					
Oxygen Feed	3,130					
Cracked Gas I	10,000	9.3	4.0	32.3	6.0	48.4
Recycled Gas	467	38.5	16.4	18.5	4.5	21.6
C_2H_2 Rich Gas	1,283	70.5	27.9	0.7	0.2	0.6
Lean Gas	8,712	0.2	0.5	37.0	6.9	55.5
O_2 Second Combustion	349					
Cracked Gas II	9,750	--	1.2	38.8	0.3	59.8

Rather than state the operating cost in Reichsmarks (which would have little meaning) figures representing the hourly usage of utilities, labor, etc., which can be used to estimate costs in the United States are given as follows:

	First Combustion	C_2H_2 Concentration	NH_3 Syn Gas Combustion
Ethane, (m^3)	3,070	----	-----
Air, (30 atm, m^3)	---	----	3,350
Oxygen, (m^3)	3,130	----	388
Fuel Gas, (KCal x 10^6)	1.67	----	-----
Elect. Power, (KWH)	120	2,250	-----
Water, (m^3)	160	300	50
Condensate, (m^3)	---	----	2
Labor, (hours)	5	3	3

Computations of operating costs based on these figures will

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include repair labor but will not include plant amortization. The major equipment, including 5 burners, was estimated in the report to cost 2,000,000 RM for the 18 atm installation, but these estimates of plant costs are not usually translatable to U. S. practices.

The highest acetylene concentration that has been commercially obtained from this process is about 10%. The usual range is 7% to 9% acetylene. During the course of the interrogation several of the I. G. Farbenindustrie men stated that their partial combustion process for the production of acetylene is definitely more economical than their arc process, unless the cost of electric power is very low.

CONCLUSIONS

Coke oven gas, hydrogenation tail gas, and Fischer Tropsch tail gas were commercially cracked by partial combustion with oxygen or air to produce raw material for several different syntheses. Feed gas consisting of N_2 and H_2 was produced for the ammonia synthesis, and various CO-H_2 mixtures were made for use in the methanol, isobutanol, and Fischer-Tropsch syntheses. The Fischer-Tropsch process produced gaseous, liquid and solid hydrocarbons from which gasoline, Diesel oil, lubricants, detergents and a wide variety of chemical products could be obtained.

A variation of the process was also commercially operated for the production of acetylene, which was used for the manufacture of acetone in the particular installation inspected.

W. H. Lyon, Lt. USNR

R. M. Crawford, Technician

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APPENDIX

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GERMAN DOCUMENTS ON METHANE CRACKING BY PARTIAL COMBUSTION

The following documents relating to this subject are transmitted to the Bureau of Ships.

1. I. G. Farbindustrie AG-Ludwigshafen Drawing Op 631 N-Sch 1 dated 17 April 1942 is a flow-sheet for production of synthesis gas by partial combustion of the methane in a coke oven gas mixture.

2. Report dated March 1942 by E. Kapp of Lurgi Gesellschaft Fur Warmetechnik entitled "Druckspaltung Methanhaltiger Gase der Druckvergasung" covers a series of experiments carried out at the Böhlen plant by the Lurgi Company in 1941 and 1942 on the cracking of coke oven gas.

3. Report of March 17, 1943 entitled "Spaltung von Reingas mit Schwefelbestimmungen", covering additional experiments performed to investigate the behavior of the sulfur compounds in the combustion.

4. Drawing number Op 648 titled "Acetylenbrenner" showing a special burner used to get the best possible mixing of the feed gas and oxygen and combust the gas rapidly with water quenching, to yield acetylene.

5. Cost Estimate by the I. G. Farbendustrie "Kostenschatzung für die Gewinnung von 70% igem Acetylen and Synthesegas aus Kohlenwasserstoffen" which contains estimated operating costs, estimated construction costs, analyses, heat and material balances, and flow sheets.

6. Simplified flow sheet "Umformungsanlage" or reforming plant covering the thermal cracking of coke oven gas by the Koppers Process for the production of synthesis gas.

7. Report dated July 13, 1942, by E. Kapp entitled "Berechnung von Regeneratoren für die Druckspaltung".

8. Report dated July 1, 1931 by Dr. Eckhard entitled "Die graphische Darstellung der aus Sauerstoff, Dampf und Kohlenstoff gewennbaren Mischgase" which presents data on equilibrium of synthesis gas production reactions, including production from methane.

9. Brief report dated January 10, 1936 from the Oppau Plant to Mitsubishi interests on "Methan-Krackanlage und Winkler Wassergas Generator" giving analyses of gase and utilities demand.

10. Drawing from Treibstoffiverk Rheinpreussen showing flowsheet and capacity of synthesis gas production by cracking coke oven gas in a generator.

11. Drawing from Treibstoffwerk Rheinpreussen showing flowsheet of gas cracking plant with analyses and capacities.

12. Report dated April 17, 1940 from Bohlen entitled "Methan-Spaltung' which contains theory and data on thermal cracking of methane.

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TECHNICAL REPORT NO. -45

SYNTHESIS GAS PURIFICATION PROCESSES IN GERMANY

Summary

This report records information obtained by technical investigators on processes for the purification of gases in Germany for their subsequent use in chemical and synthetic fuel production purposes. It covers those processes which are in commercial use for the purification of large volumes of gas such as are employed in the production of ammonia, hydrogen, methanol and synthetic oils.

The report describes the several processes studied and the factors controlling them. The emphasis has been on those parts of the processes which are not commonly known in the United States, the more common elements having been omitted for sake of brevity. The appendix contains flow diagrams, equipment drawings and copies of original German technical documents pertinent to the subject, which serve to elaborate on the chemical engineering, mechanical design, and development phases of the processes.

AUGUST 1945

U.S. NAVAL TECHNICAL MISSION IN EUROPE

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SYNTHESIS GAS PURIFICATION PROCESSES

INTRODUCTION

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Since the gases manufactured in Germany for chemical and synthetic fuel production purposes are put to use in chemical reactions that employ sensitive catalysts, it has been necessary to clean the gases of both their entrained solid and liquid materials and also to remove by physical or chemical means the deleterious components such as sulphur bearing gases and carbon dioxide.

This report covers the purification of feed gases for synthesis purposes, and describes the processing of these gases between their production and their utilization in the synthesis. It does not describe purification and separation of product gases by the Linde fractionation, adsorption of hydrocarbons on activated carbon, and absorption processes.

The many gases manufactured in Germany for hydrogen production or for production of synthesis gases for the Fischer-Tropsch, Oxo-synthesis, Synol-synthesis, Methanol-synthesis, Isobutanol-synthesis, ammonia-synthesis, Buna rubber synthesis, etc., invariably contained contaminating materials. The principal contaminants in the feed gases are usually one or more of the following: tar, aromatic compounds, dust, hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, hydrogen cyanide, and nitrogen, the type and quantity of contamination depending on the source of the gas. The degree of purification required depends of course upon the purpose for which the gas is to be used and the purification process is selected with that in mind. The object of this report is to present briefly the various processes that were used in Germany during the war to accomplish the desired purification of gas for these purposes.

For the purpose of presenting several processes in a logical manner in this report they are classified as follows:

1. Dusts and Tar Removal
2. I.G. Alkazid Process for Gas Purification
3. Claus Process for Recovery of Sulphur from H_2S
4. H_2S removal from Gas with Iron Oxide (Grobreinigung)
5. Removal of Organic Sulphur from Gases (Feinreinigung)
6. Gas Purification by Activated Carbon (Feinstreinigung)
7. Removal of CO_2 from Gases
8. Removal of CO from Gases

2. DUSTS AND TAR REMOVAL

Nearly all manufactured gas contains some dust as it leaves the production unit. In addition, gas made from coal in coke-ovens or coal gasifier units (as differentiated from that made from hard coke) also often contains small amounts of tar or resins. In most cases where the gas contains both contaminants, the tar is removed along with the dust. Some of the German installations, however, include a separate electrostatic tar precipitator installation which operates in the conventional manner well known in the United States.

Three methods of dust and tar removal are in general use in Germany as follows: mechanical separators such as cyclone separators, baffled separators, traps (both wet and dry) and filters; (2) Electrostatic precipitators; and (3) Water washing methods.

The mechanical separators used in Germany are of various designs and were made in Germany by several companies. A good description of the methods usually employed is given in a report dated December 12, 1936 by Dr. Geister of I.G. Farbenindustrie entitled "Entstaubung", or translated, "Dust Removal." A copy of this report is contained in the Appendix of this report and is not described further here.

A special filter found to be in use which is claimed to have particular advantages as a mechanical separator for gas cleaning is the "Oppauer Schachtfilter" in which the filter medium is a slowly moving bed of granulated coke installed in a vertical cylindrical chamber and resting on a movable grate. The gas enters the bottom and flows to the top. The coke is shaken from the grate into water, agitated and washed, then returned to the top of the bed by an hydraulic conveyor, which also serves to keep the filter bed wet. The process is described in a report by Dr. Sachsse entitled "Removal of Carbon Black and Dust from Gases with the Oppauer Schacht-filter" attached in the appendix.

Other filters that may be mentioned in passing are the Viscin air filter frequently used on the air inlet of the oxygen plants, the synthetic silk bag filters used in the separation of carbon black from gases cracked in the electric arc, and the many ordinary filters packed with metal turnings, wood shavings, and fibre glass either dry or saturated with an oil or adhesive material.

The principle of the electrostatic process is well known so details of construction were not obtained.

When electrostatic precipitation is not used, the last traces of dust in the gases are usually removed by a water wash. This water wash may be carried out in a spray tower, an ordinary packed column, may be combined with an absorption purification system for removal of H_2S, CO_2, NH_3 etc. or may be performed in a mechanically agitated washer-cooler such as the patented Theissen unit. Where a gas absorption-purification system such as the Alkazid unit is also used for dust removal, a filter is included in the process through which either continuously or intermittently a part of the circulating absorption solution is passed to remove the accumulated sludge.

3. I.G. ALKAZID PROCESS FOR GAS PURIFICATION

Chemical purification is employed where the contaminants are not removable by mechanical means. Gas impurities of a slightly acid nature such as hydrogen sulphide, carbon dioxide and hydrocyanic acid were sometimes removed from gases by basic substances such as alkali hydroxides and possibly sodium or potassium carbonate solutions that can be regenerated. However the process developed by the Girdler Corporation employing the alkylol amines especially the mono,-di-, and triethanolamine and later diaminopropanol to absorb hydrogen sulphide and carbon dioxide was not found in use. Amines are strong bases and water soluble substances which readily absorb H_2S and CO_2 at normal temperatures and liberate them when heated to 100°C, and absorb several times as much CO_2 and H_2S per unit of volume as do the potassium or sodium carbonate solutions.

The Alkazid process was developed by I.G. Farbenindustrie to remove H_2S or mixtures of H_2S and CO_2. Gas purification units of this type have been constructed in many countries all over the world. The process is used primarily to treat gas of high sulfur content before it goes to other steps for more complete purification. It also claimed the advantage of yielding hydrogen sulfide of quite high concentration, e.g., under favorable conditions up to about 90% H_2S. This unit is probably used more often in Germany to treat gases from hydrogenation or cracking operations than it is used to treat manufactured gas, but it is satisfactory for either service.

A description of the unit as applied to hydrogenation product gas treatment is given in U.S. Naval Technical Mission in Europe Report No. 87-45 "The Wesseling Synthetic Fuel Plant" and is not repeated here.

A simplified general flow sheet is shown on drawing M 2028 (Item 3 in the appendix of this report). In this sketch the raw gas enters the bottom of one or both absorber columns (labelled "Abstreifer") which can be operated in parallel or in series. The purified gas ("Reingas") leaves the unit from the top of the absorber or absorbers. The cold lean caustic solution passes countercurrent to the gas down the columns, out the bottom through a screen and is pumped through a heat exchanger countercurrent to the hot lean caustic from the bottom of the stripper. From the heat exchanger the rich caustic is fed to the top of the stripper column. The stripped gas (H_2S and CO_2) leaves the top of the stripper, passes through a condenser and separator to remove condensate, thence out of the system to the Claus Unit or other disposal. The steam to heat the kettle of the stripper is distributed between direct and indirect heating in order to hold the specific gravity of the caustic between 1.16 and 1.20. The stripped caustic leaves the bottom of the absorber through a screen, passes through the countercurrent heat exchange mentioned above, through a water cooler and to the top of the absorber.

There are two types of solutions used in the Alkazid process. "DIK Caustic", the solution most commonly used, is a solution of potassium dimethyl or diethyl alpha aminoacetate and is used to remove H_2S from gases containing CS_2. "M-Caustic" is a solution of potassium methyl alpha aminoproprionate. It will absorb both H_2S and CO_2 but is used only in the absence of CS_2. The normal effective gas charge of the solutions ranges from 10-15 volumes per volume of caustic for best removal of H_2S but can be increased to as much as 30-35 volumes per volume by the use of mechanical contacting devices and longer contact time, or by permitting a higher sulfur content in the outlet gas.

The process has been used to treat gas containing up to 10% H_2S, and will remove the H_2S to 0.07 to 0.10%. Absorption and stripping are at substantially atmospheric pressure. The optimum absorption temperature is about 5°C, but temperature up to 30°C can be satisfactorily used. The relative absorption of CO_2 by DIK-caustic increases with increased absorption temperature, and with increased time of contact over the normal one minute.

The stripper kettle temperature is maintained at about 105°C.

A new development of this process, which has not yet been put into commercial operation, absorbs at 8-10 atmospheres and strips at 1 atm without the addition of heat to the kettle except for the direct steam necessary to control caustic gravity. The effective loading of the caustic under these conditions is only 4-5 volumes/volume, but it is claimed that the extra pumping and compression cost is more than compensated by the economy of steam.

The process is also used for low pressure CO_2 removal where sulfur is not present or is present in small quantities.

A cost comparison made by the I.G. Farbenindustrie shows the Alkazid process to be cheaper than water wash, Girbotol, Koppers, Shell and several other processes; however, even if the figures are accepted, altered conditions in the U.S. may well change the results and no positive statement can be made of the superiority, of the process for all conditions. The main advantage of the process over the ethanolamine process is the lower volatility of the solute.

Many operating difficulties have been experienced with the unit. The principal trouble has been with corrosion of the steel and aluminum used in the equipment. The Germans combat this corrosion by close control of the caustic gravity, control of the temperature in the aluminum equipment, careful exclusion of air from the system, and by "passifying" the aluminum through circulation of dilute sodium silicate solution through the equipment before operation. No mercury or mercury salts are used where they can possibly enter the system. The direct steam to the stripper must be maintained dry and free from impurities. Attached is a report of visit made to the Alkazid Plant in Lutzkendorf in regard to the corrosion.

Foaming of the solution occasionally causes trouble, but the I.G. have developed an antidote known as Schaumbekampfungsmittel "I" (Foam-attacking agent "I") in the Leuna plant.

Any oxygen that enters the system during operation forms thiosulfates in the solution, destroying its effectiveness. Special precautions are taken to prevent air entering the system at pump packings, or in the solution storage vessels, etc. This difficulty limits the use of the process to oxygen-free gases.

If the gravity of the solution gets too high or the solution gets too cold, solids will settle out. Corrective measures are heating and/or dilution of the solution.

For more complete information on operating and supervision methods for the Alkazid process two reports are included in the appendix as follows:

1. "Betriebserfahrungen und Hinweise zum Alkazidverfahren"
2. "Richtlinien fur den Betrieb and Uberwachung von Alkazid-Waschanlagen."

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A more complete flowsheet which includes a NaOH wash following the Alkazid absorption is shown on drawing No. M3200-1, included in the appendix. A comprehensive technical article on both this process and the Claus process was published in the June 1938 issue of the Refiner and Natural Gasoline Manufacturer pages 237-244 and many of the details given there are not repeated here.

4. I.G. CLAUS PROCESS FOR RECOVERY OF SULPHUR FROM H_2S

The I.G. Claus process is a method for converting gaseous hydrogen sulfide into molten elementary sulfur. This process is often used as a supplementary process in connection with the Alkazid H_2S removal process. The reaction basis of the Claus process is shown by the following equations:

$$2H_2S + 3O_2 \qquad 2H_2O + 2SO_2$$
$$2H_2S + SO_2 \qquad 2H_2O + 3S$$

Drawing Zo 1416-2 in the appendix of this report presents a flowsheet of the process. In this flowsheet the H_2S comes from Gasometer Unit 14 through a blower to the two Claus "kessels" in parallel. Here it is partially burned with a controlled amount of air to yield a ratio of SO_2 to H_2S of 1:2.) This mixture then passes over the bauxite catalyst in the first Claus "ofen" at a temperature of about 300° to 400°C where the second reaction takes place. The gas from the first "ofen" passes through an "aufhitzer" where fuel gas is burned to heat the gases further before they pass through the second Claus "ofen" to complete the second reaction. Molten sulfur is drawn from the bottom of each "ofen". The tail gases from the second "ofen" consist principally of nitrogen, water vapor, and carbon dioxide (from hydrocarbon gases) with about $3.5\ g/m^3$ of unreacted SO_2 and H_2S. This gas passes through a cyclone or electrostatic separator to remove entrained elemental sulfur, then to the "Nachbrennungsofen" where a pilot flame burns the remaining H_2S over bauxite before passage to the atmosphere.

Drawings FZA1b and FZA4-a show the Claus ofen and Nachbvebrennungsofen respectively. A catalyst bed of 3m diameter and 7m high will produce about 6 tons of sulfur per day at 80% recovery. The inlet H_2S content can vary from 40% to 100%. Drawing 4A34210 shows the arrangement of equipment and piping.

The catalyst life is indefinite unless overheating causes sintering in which case only the upper layer is ordinarily affected. When this happens, the upper layer of catalyst is replaced.

The equilibria, experimental and calculated, are presented in an "Aktennotiz" dated July 11, 1941 by Dr. Orlicek under the title "Untersuchen uber die Lage des chemischen Gleichgewichtes beim Clausprozess."

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Complete operating data for the Leuna Plant are presented in a translation "Claus Ofen Operation" in the appendix.

5. H_2S REMOVAL FROM GAS WITH IRON OXIDE (GROBREINIGUNG)

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The removal of H_2S from gases by iron oxide mixtures is well known in the United States in the manufactured gas industry and no new information was obtained on this process. Briefly, the process is to pass the raw gas at low pressure and at atmospheric temperature through a vessel containing beds of wood shavings covered with crude iron oxide, beds of pelleted crude iron oxide or iron oxide mixtures. The H_2S reacts with the iron oxide to form iron sulfide and water. The Germans ordinarily add air to the inlet gas in an amount sufficient to supply about half of the theoretical oxygen to convert the iron sulfide back to the oxide and to precipitate the elemental sulfur in the bed. When the H_2S has been previously reduced by Alkzid or other process to 0.1% or less in the gas entering the oxide box, this air usually amounts to 4-6 m^3/per 1000 m^3 of gas. The hydrogen sulfide in the outlet gas is nil, the organic sulfur is not diminished. When a gas with a high sulfur content is sent to the oxide boxes, the removal may be less complete and the life of the mass is naturally proportionately shorter. The outlet sulfur is, however, rarely over 1 gram per 1000m^3, because three to four boxes are usually operated in series, with the freshest mass in the last box.

Under proper operating conditions the mass will hold 40-55% of its dry weight in sulfur before excessive H_2S break through or excessive pressure drop occur. Most plants use a continuous addition of 0.1% to 0.2% oxygen to the inlet gas to react and precipitate the sulfur, but batch regeneration by circulating inert gas with 1% to 4% O_2 has been carried out by some concerns. When the maximum sulfur loading is attained the catalyst is removed, the sulfur burned for recovery of SO_2 and the residue is discarded.

The purifying agent is usually bought under the trade name Luxmasse which is the iron oxide residue from the refining of aluminum ore, or a mixture of Luxmasse and bog iron ore. A newer agent is called Lauta-masse, which is the same general type of material containing 3-4% alkali as NaOH, Na_2CO_3 and/or $NaHCO_3$. A typical analysis of Lauta-masse is as follows:

Apparent density	0.657 Kg/L.
Water	54.00%
Fe_2O_3	22.88%
Al_2O_3	16.45%
Ca O	1.03%
Mg O	Trace

Na_2CO_3	3.15%
Na OH	0.49%
Si O_2	1.92%

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To conserve iron oxide, used Feinreinigung mass containing about 5-10% sulfur and 30% Na_2CO_3 is sometimes mixed with the fresh charge. It was stated that if too much of this material is mixed in, trouble is experienced with fusing of the carbonate due to the wet operating condition.

6. REMOVAL OF ORGANIC SULFUR FROM GASES (FEINREINIGUNG)

The previously discussed iron oxide purification process removes only the inorganic or H_2S sulfur from the gas. The organic sulphur compounds are untouched. If they are present, and must be removed, it is necessary to subject the gases to further purification.

In Germany organic sulfur in synthesis gas is ordinarily removed by a process called "Feinreinigung". After the gas has passed through the final H_2S removal it goes to this "Feinreinigung" process at approximately atmospheric temperature and pressure. Here it passes through the tubes of a heat exchanger and of a direct fired preheater to raise the temperature to 150-300°C, this temperature increasing with the age of the catalyst. The gas then goes to the catalyst chamber where it passes from the center of the chamber to the outside through an annular bed of catalyst at a velocity of about 0.25 meters per second, from the chamber through the shell side of the heat exchanger mentioned above, then through one or two more catalyst chambers similar to the first.

The catalyst is composed of 60-70% crude iron oxide and 30-40% sodium carbonate. The organic sulfur in the gas is cracked to H_2S and reacts with the oxygen present in the inlet gas, (or oxygen added before the catalyst chambers) to form Na_2SO_4, $FeSO_4$, and some elementary sulfur.

A new method of catalyst manufacture produces a much lighter, more porous mass. The method of preparation for a small batch based on 100kg of Lautamasse is as follows:

100 Kg of Lautamasse with 2% alkali content and 50% water is divided into two parts. One portion is dried, mixed with 5 Kg of Na_2CO_3, and then added to the remainder of the charge. This mixture containing 25% water is then wetted with a fine spray to proper consistency, is pressed to the desired grain size and dried. The drying is carried out first at 60-80°C until the mass is hard and then is completed at a temperature over 100°C. The resulting product is compared to the older catalyst in the table below:

	OLD	NEW
Apparent Specific Gravity, Kg/ liter	0.7	0.5
Grain strength, Kg/ cm^2	6-7	3-4
Na_2CO_3 content %	30	15

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	OLD	NEW
Fe_2O_3, %	36	44
Porosity, %	50	70
To fill chambers, tons	100.8	76
Alkali in chambers, tons	29.5	12.5
Iron in chambers, tons	36.7	33.8
Organic Sulfur Loss, g/100 m^3	1.0	0.1
Organic sulfur conversion, %	70	96.8

The catalyst grains should be coarse (8-10mm) and all dust should be removed. The catalyst dust cannot be reworked as it reduces the porosity of the finished catalyst.

A gas volume of 100,000 Nm^3/ hr with 12-15 mg total sulfur in the gas entering the unit will use an average of about 4.8 tons per day of catalyst. Each unit will process 10,000 to 22,000 cbm/hr of gas depending on the age of the catalyst, and contains about 65 tons of catalyst in two chambers. Typical operating conditions for this process are as follows:

Inlet Gas	20,000 m^3/hr
H_2S in Inlet Gas	0.3g/100Nm^3
H_2S in Outlet Gas	nil
Organic S in inlet	15.0 g/100 Nm^3
Organic S in outlet	0.20 g/100 Nm^3
Temp in 1st chamber	230°C
" out 1st "	220°C
" in 2nd "	190°C
" out 2nd "	180°C

Several operating difficulties are encountered in this process. The worst difficulty is the formation of resinous coatings on the catalyst. This is prevented by the installation of an activated carbon absorption process before the unit to remove the resin-forming materials. Excessive H_2S in the inlet gas overloads the unit and permits sulfur to break through. This is usually traced to poor operation of the previous H_2S removal unit. Excessive temperature sinters the catalyst. Poor catalyst sizing or charging causes unequal distribution of the gas or excessive pressure drop, and also causes sulfur to break through and appear in the outlet gas.

In spite of these difficulties the "Feinreiningung" process is almost without competition in Germany for general use in the removal of organic sulfur from gas.

7. GAS PURIFICATION BY ACTIVATED CARBON (FEINSTREINIGUNG)

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There are two activated carbon processes used in Germany for the purification of synthesis gas. One is the so called "Feinstreinigung" of the Lurgi Company, which consists of the absorption of hydrocarbons on activated carbon. This process is used to remove the aromatics and resin forming hydrocarbons whenever gas is obtained from coal instead of from coke, not only to purify the gas but also to protect the catalyst used in the organic sulfur removal process (Feinreinigung). The other activated carbon purification process is that of the I.G. Farbenindustrie and is used to remove hydrogen sulfide. When this process is used it replaces both Alkazid and Grobreinigung wherever the inlet H_2S concentration is less than 7 grams/m^3. These processes are described below.

In the "Feinstreinigung process of Lurgi the raw gas from the Alkazid purification unit or other source enters the Lurgi carbon chambers saturated with water at about 30°C. The water inhibits adsorption so that instead of a possible 80 hours on-stream absorption cycle time, a period of 20 hours is used. After the adsorption period the chamber is steamed for two hours, dried with heated gas for one hour, cooled for one hour and then put back into the adsorption cycle. An understanding of the process can be better obtained from the following concrete example of a Lurgi installation.

90,000 m^3/hr of gas generated from coal is passed over 75,000 Kg of activated carbon located in five parallel chambers of 5m. diameter. A sixth chamber is in the regeneration cycle. After a chamber has been in service 20 hours, it is put into the regeneration cycle and the freshly regenerated chamber put back into adsorption. The regeneration requires a total of 4-1/2 tons of dry steam at 2-1/2 atm. pressure per chamber. The recovery of hydrocarbons amounts to about 0.4g/m^3 of inlet gas and this material is added to the coke-oven gasoline. The drying cycle removes about 1500 kg of water.

One kilogram of carbon will process about 10,000 m^3 of gas before reactivation is necessary. The reactivation is carried out in a rotary kiln at 800°C with steam.

The I.G. Farbinindustrie process for hydrogen sulfide removal over activated carbon is an old process that dates from 1928, but it is still considered very satisfactory for gases containing a relatively small amount of sulfur. Drawing S92 in the appendix shows a schematic diagram of this process. The drawing shows that the raw gas goes through a blower then to a water separator, next a water cooler, and then more separators. Next a small amount of ammonia air mixture is added to it. The mixed gases then pass over an activated carbon bed at 800mm water pressure and 20-40°C temperature where the reaction:

$$2H_2S + O_2 \qquad S + 2H_2O$$

takes place with the ammonia acting as an intermediate or catalyst. The H_2S removal is substantially complete. The ammonia leaves the absorber along with the gas and is subsequently washed out in the water absorption process for removal of the CO_2 in the gas.

The sulfur found in the reaction is precipitated in the carbon bed, and when the bed is loaded the sulphur is washed out with a 20% ammonium sulfide solution in the form of ammonium polysulfide. Ammonium carbonate is also formed in the carbon and it is washed out at the same time. The ammonium carbonate must be removed from the wash solution and this is done by adding $Ca\ Cl_2$ solution to give the reaction:

$$Ca\ Cl_2 + (NH_4)_2\ CO_3 \qquad Ca\ CO_3 + 2NH_4Cl.$$

The $Ca\ CO_3$ sludge is removed from the wash solution in a Dow type thickener. Sodium sulfide is added and the following reaction takes place in the solution:

$$Na_2S + 2NH_4Cl \qquad (NH_4)_2S + NaCl$$

The solution goes to a column operating at 2 atm. and 130° kettle temperature where it is distilled. The ammonium sulfide and part of the water go overhead; the sulfur in molten form and the sodium chloride solution are withdrawn from the two liquid phases of the kettle.

A concrete example of the use of this process is the treatment of 6000 m^3/hr of gas containing 3.5g/m^3 of H_2S and 0.2g/m^2 of organic sulphur. In this case about 12-13 liters of air plus 0.2g NH_3 are added per cubic meter of gas and the mixture is passed over a 20m bed (7 tons) of activated carbon. This bed will take a "loading" of 6 tons of sulfur before sulfur removal becomes necessary. The regeneration is accomplished by filling the bed 3 times with a total of 200m^3 of ammonium sulfide solution and allowing each of the washes to stand for 1 to 2 hrs. The solution remaining after the third draining is steamed out, the bed is then dried and cooled and put back into service.

8. REMOVAL OF CO_2 FROM GASES

The removal of carbon dioxide from the gas is usually performed, if not a part of the alkazid process, in the final step of the synthesis gas preparation, after it is under pressure. Carbon dioxide is readily soluble in water at elevated pressure and the gas is absorbed by passing the CO_2 containing gas in direct countercurrent contact with water in absorption columns. The absorbed CO_2 is released in a discharge system by passing the outlet water at about 200 to 300 lbs. per square inch (the usual absorption pressure) into a Pelton water turbine whose outlet is at atmospheric temperature and pressure. The jet action of the water impinging on the pelton wheel breaks the stream into a fine spray for quick release of the absorbed CO_2 and at the same time produces power to assist in driving a centrifugal pump which recycles the cold water back into the spray tower. About half of the power required to drive the centrifugal pump can be obtained from the pelton water turbine. This water absorption system also removes the last traces of any ammonia that may be present. However, the CO_2 thus produced is usually substantially pure and in Germany is recovered, compressed and sold as commercially pure CO_2.

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9. REMOVAL OF CO FROM GASES

In the preparation of synthesis gas for the ammonia process the hydrogen is obtained from CO-H mixtures by the shift reaction changing the $CO + H_2O$ into $CO_2 + H_2$ and then removing the CO_2 by water absorption as previously described. However some unreacted CO is carried through and remains in the gas. In the ammonia synthesis carbon monoxide is a catalyst poison and it is therefore necessary to purify the gas to remove the last traces of CO.

This is done by subjecting the gas to direct contact in a counter current absorption tower with a refrigerated copper ammonia carbonate or carbonate solution at 1800 to 3500 pounds per square inch, it having been found that in that pressure range carbon monoxide is readily soluble in a cold ammonia copper salt solution.

A second method of eliminating carbon monoxide by converting it to a hydrocarbon in the Fischer-Tropsch process as a detoxification process is covered in another technical report and is not repeated here.

10. CONCLUSIONS

Gases produced in Germany for subsequent utilization in synthesis processes invariably required purification for the removal of impurities and deleterious components.

Dust and tar were removed by (1) mechanical processes, usually cyclones, (2) electrostatic methods, and (3) water washing.

Hydrogen sulfide was removed by (1) Alkazid process, (2) Carbon adsorption with subsequent $(NH_4)_2S$ wash and (3) Iron oxide process. Organic sulfur was generally removed by the "Feinreinigung" which consisted of cracking and removal of the sulfur as H_2S over iron oxide-alkali catalyst at temperatures from 150 to 300°C.

Aromatic and resin-forming compounds were removed by activated carbon.

Carbon dioxide was removed by (1) Alkazid process at low pressure (2) Water washing at high pressure and (3) Caustic solution for removal of final traces for special purposes.

Carbon monoxide was removed from hydrogen for high pressure hydrogenation by high pressure absorption with copper ammonium carbonate or formate solution.

Various other gas purification processes had been developed but were not in large scale use. Some of these processes are described in documents included in the appendix to the report.

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LIST OF GERMAN DOCUMENTS ON
SYNTHESIS GAS PURIFICATION PROCESSES

1. Report dated Dec. 12, 1936 by Dr. Geister of I. G. Farbenindustrie entitled "Entstaubung" (Dust Removal)

2. Report by Dr. Sachsse entitled "Removal of Carbon Black and Dust from Gases with the Oppauer Schachtfilter."

3. M 202-8 - a simplified general flow-sheet showing the operation of the Alkazid Process.

4. Report by Drs. Jeltsch, Sommer and Bunger of visit made to the Alkazid Plant in Lutzkendorf, in regard to corrosion.

5. Confidential Reports (2) on the operating and supervision methods for the Alkazid process, entitled:
   (a) "Betriebserfahrungen und Hinweise zum Alkazidverfahren"
   (b) "Richtlinien für den Betrieb und die Überwachung von Alkazid-Waschanlagen".

6. M3200-I - Flowsheet - showing an NaOH wash following the Alkazid absorption.

7. Zo 1416-2 - Flowsheet showing Claus process of converting hydrogen sulfide to molten elementary sulfur.

8. F.Z.A.1 b - Flowsheet showing the Claus Ofen.

9. F.Z.A.4 a - Flowsheet showing the Nachverbrennungsofen.

10. "Clausofen Operation", translated data covering complete operation of the Leuna Plant.

11. S-92 - A drawing which shows a schematic diagram of the I. G. process of hydrogen sulfide removal over carbon.

12. Drawing No. 711496 - A flow sheet of a "Grob-and Feinreinigung" sulfur removal unit.

13. Drawing No. 4A34210 - Piping and Equipment arrangement of Claus plant.

14. Several short reports from Sept. 30, 1942 to May 25, 1943 on the subject of dust removal in multi-cyclone units.

15. Reports by Herr Keinke dated Dec. 29, 1931 on "Verbrennen von H_2S zu Schwefel im Claus-Ofen" and by Dr. Hanisch dated Jan. 11, 1933 "Notiz über Versuche zur Gewinnung von elementarem Schwefel aus Gasen mitniedrigem Schwefelwasserstoffgehalt." Early data on the Claus process.

16. A report by Dr. Braus dated Jan. 21, 1935 on "Berechnung der Verbrennungstemperaturen von Schwefelwasserstoff - Kohlensäuregemischen", giving theoretical data on combustion temperature of H_2S mixtures.

17. Tables of data dated Nov. 11, 1933 on requirements of Alkazid process for utilities, equipment, solutions, operating personnel, etc.

18. Analysis results and methods for gas purification catalysts.

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19. Report by Dr. Bähr dated Oct. 2, 1936 on "Weiterentwicklung des Alkazid - und Claus Ofen - Verfahrens," reporting late developments in the Alkazid and Claus processes.

20. Report by Dr. Orlicek, dated July 11, 1941 on "Untersuchungen uber die Lage des chemischen Gleichgewichtes beim Clausprozess", on the calculated and experimental chemical equilibrium in the Claus process.

21. Drawings A-1030-4 and U 1878-1, flowsheets on carbon monoxide removal.

22. Folder containing numerous short reports and drawings on the Alkazid process.

23. Four curves on CO - CO_2 wash costs.

24. Drawing S IV 3, Flowsheet of a pressure water wash process.

25. Folder containing report and several drawings concerning the removal of carbon oxy sulfide (COS) from gases.

26. Report by Dr. Bartholomé dated Nov. 26, 1941 on "Über die Umsetzungsgeschwindigkeit des CO an Braunoxyd-Kontakt bei hoheren Drucken" giving data on reaction velocity over "Brown oxide" catalyst for the shift reaction.

27. Patent announcement dated June 27, 1939 on a process for catalytic recovery of S from gases containing H_2S.

28. Report by Dr. Kuhbier dated April 24, 1939 on "Entschwefelungs-Verfahren der Sachtleben A.G." covering data on a process reacting H_2S and SO_2 in thiosulfate solution to produce sulfur.

29. Report on a meeting to exchange information on gas purification processes, dated Nov. 17, 1939.

30. Drawing 240-8 on layout plan for a Claus unit.

31. Report by Dr. Mengdehl dated August 22, 1938 "Ein neues Verfahren zur Trennung von Ammoniak und Kohlensäure bezw. Schwefelwasserstoff" describing a new process for separation of NH_3 - CO_2 - H_2S mixtures.

32. Patentschrift No. 388857 dated 21 January 1924 to Firma Eduard Theisen in München entitled "Stufen - Gas - O. dgl. Wascher", german patent on the Theisen washer for the purification of gases.

33. Patentschrift No. 513288 dated 25 November 1930 to Firma Eduard Theisen in München entitled "Verfahren zum Reinigen Von Gasen, Luft, Dämpfen u. dgl., german improvement patent on the design of the blades of the Theisen washer presented in the above patent No. 388857.

Naval Technical Mission in Europe

Letter Reports
on
Fuels and Lubricants

Letter Report Number	Title
4-45	German Fuels, Lubricants, and Related Synthetics.
119-45	Lubricant Additive for Decreasing the Time for Gasoline Engine Break-in Periods.
123-45	The Preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals.
131-45	Tables on Special Diesel Fuel Cuts.
137-45	Lurgi Mahltrocknung Process (Pulvo-Drying).
150-45	Graphite Oxyde as a Fuel or Fuel Additive.

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Naval Technical Mission in Europe

Technical Reports
on
Fuels and Lubricants

Technical Report Number	Title
87-45	The Wessling Synthetic Fuel Plant
105-45	The Production of Tetrahydrofuran Intermediates.
106-45	The Preparation of Formamide as an Intermediate for Acrylonitril Production and Acrylonitril from Acetylene.
107-45	Synthetic Lubricating Oils.
108-45	Synthesis of Acetone.
110-45	Wartime Research on Synthetic Fuels by the Kaiser Wilhelm Institut fur Kohlenforschung.
111-45	Preparation of "Alkazid" M and DIK
115-45	The Arc Process for Acetylene Production.
145-45	The Manufacture of Aviation Gasoline in Germany.
146-45	The Manufacture and Application of Lubricants in Germany.
147-45	Internal Combustion Engines (Use of a chemical as ignition agent)
187-45	German Diesel Fuels
217-45	The Production of Synthetic Fuels by the Hydrogenation of Solid and Liquid Carbonaceous Materials.
234-45	Use of Graphite Oxide as a Fuel or Fuel Additive.

Technical Report Number	Title
235-45	The Preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals.
248-45	The Synthesis of Hydrocarbons and Chemicals from CO and H_2
280-45	Synthetic Coatings for Gasoline Tanks
281-45	The Production of Monomeric Vinyl Acetate in Germany.
333-45	German Naval Fuel Oil.
388-45	Additive for Lubricating Oil.
556-45	Methane Cracking By Partial Combustion with Oxygen or Air in Germany.
----45	Synthesis Gas Purification Processes in Germany

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NAVY DEPARTMENT
BUREAU OF SHIPS
WASHINGTON 25, D. C.

Subj: Microfilm of U.S. Naval Technical Mission In Europe Reports

1. During the course of its field trips to examine German synthetic oil plants and to interrogate German technical personnel, the members of the Oil Team of the U.S. Naval Technical Mission in Europe prepared a number of "Letter Reports" and "Technical Reports". There is presented in the following film a complete set of the reports dealing with fuels and lubricants.

2. These reports have been arranged in numerical sequence, all the Letter Reports appearing as the first group and the Technical Reports as the second. A complete index to the film appears following this page. The numbers appearing before the report numbers as the left hand column will also be found in large letters below the pages of the appropriate reports.

3. It will be noted that certain of the reports refer to an appendix. When such additional material does not appear following the pages of the report, it will be found in a separate reel which bears the same title as does the report to which it pertains.

4. In addition to the reports and the documents which appear in the appendices, other miscellaneous documents, possibly of equal technical value, were obtained and saved for more detailed examination and study. These documents have also been microfilmed and appear titled "Miscellaneous German Technical Documents".

5. The Bureau of Ships, Research and Standards Branch, would appreciate receiving, for its technical files, a copy of any translations made of the German originals incorporated in these films, or of any evaluations which are made of the data here presented. This latter information, if desired, will be maintained in a confidential status.

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