methyl adipic acid. Methyladipic acid is drawn from Leuna as a complete acid. Esterfying is done as with Ester 426.

D) **Authorisation**

The plans and drawings were gone through with Inspectorate 13 of the German Air Ministry on 5.6.42. No objections were raised in principle to the proposed undertaking. The application will be made to Inspectorate 13 in writing.

E) **Facts about buildings**

a) Main plant

The esterfying plant is in a building of area 35 x 18 m. and 26m. high. The building is constructed on a steel framework.

In the esterfying building are:

14 stirrers
16 separators
1 distillation plant
2 filter presses

The carbonoxylic acid plant consists of the stirring plant, 12 x 20 x 6m. with 4 stirrers and accessories, and of the apparatus for acidifying and distilling, with 3 stirrers and 3 distillation plants with accessories.

The tankage, including those for carbonoxylic acid and estering, are 40m. in number, each being 30 m^3 in volume. They are intended for storage of high-boiling alcohols and esters, of the danger class A III. The containers are covered with 1 metre of earth, and are protected by safety under slight pressure, safety valves, and level indicators.

b) Auxiliary plant

The water preparation plant in which the water is purified before entering the drainage canal, consists of two walled settling containers, each with a capacity of $100m^3$, and 3 static tanks of 4m diameter.

c) Extensions to existing plant

In the distillation of isobutylene an additional distillation plant of two towers, each of 1200 mm. diameter, is required for separating the higher alcohols.

Building time

Special arrangements must be made, in collaboration with the Inspector General for motor transport, to advance the commencing dates so that the low temperature motor oil is ready for operations in the winter of 1943/4.

Provisional date for beginning work on the building site:-	1st March 1943
" " " " assembly	1st Aug. 1943
" " " completing "	1st Apr. 1944
" " " starting production	1st Feb. 1944
" " " commencement of full production	1st May 1944
" " " completion of all work on the site	1st May 1944

Building and Assembly workers

	Own	Outside
Building workers	20	150
Assembly workers	50	170

Man-days for building workers 35,000 from 1st March 1943 to 1st May 1944

Man-days for Assembly workers 45,000 from 1st August 1943 to 1st April 1944.

Costs

Total Investment RM 4,300,000

Estimated building costs 1,100,000

Estimated costs of apparatus 3,200,000

I.G. Farbenindustrie is responsible for finance.

Expended on buildings up to December 31, 1942 ....nil

Material required

a) **Iron**

Total	4,800 tons
Iron for machinery	3,000 tons
Iron for building	1,200 tons

The iron requirements are made up as follows :-

	Total	IV/42	I/43	II/43	III/43	IV/43
Iron for machinery	3600	1000	1000	500	-	-
Iron for building	1200	400	400	200	100	100

b) **Non-ferrous metals in Kg.**

Copper	1900	500	700	400	300
Lead	1600	400	700	400	100
Zinc	700	100	300	200	100
Aluminium	28000	8000	15000	4000	1000
Tin	120	-	100	20	-
Chromium	11500	7000	3000	1500	-
Quick-silver	200	50	50	50	50

c) **Building materials**

Cement	1400 tons
Gravel	8000 tons

d) Bricks 620,000

e) **Wood**

Planks	500 m^3
Poles	240 sq.m.

f) Rubber 4 tons

F) Operational data

1) Raw materials and feed stock

7300 tons per annum of alcohols (160 to 250°C)
440 " " " " trimethylol ethane (P_3)
1200 " " " " methyladipic acid
120 " " " " fatty acid soap
20 " " " " middle oil fraction
120 " " " " fuller's earth

The feed stock is drawn from :-

5500 tons per annum, own production at Auschwitz, higher alcohols 1800 tons from I.G. Heydebreck.

Methyladipic acid	I.G. Leuna
Trimethylolethane	" "
Fatty Acid soap	" Oppau
Fuller's earth	" Moosbierbaum
Soda Lye	" Bitterfeld
Sulphuric acid	" Leuna

2) Catalysts: 2 tons per annum of Zinc oxide

3) Products

Ester 426 low temperature lubricant for aero-engines 1600 tons per annum
Ester 504 low temperature axle lubricant for the Reichsbahn 2400 t.p.a.

G) Labour:

1) Office staff

Commercial staff	4
Technicians	9

2) Works Staff

Technical	55
Unskilled	65

H) Energy required:

1) Current, generated by own plant	450 KW.
2) Water,	400 m^3/h.
of which re-cooling water	300 m^3/h.
3) Steam requirements	7 tons per hour 18 atm.
4) Fuel gas	350 m^3/h.
5) Coal	10,000 tons

Supplied by own pit (Fürstengrube)

J) Transport

Reichsbahn connection is available; probable maximum number of trucks arriving and leaving daily for finished products = 2 trucks.

Arriving:

a) Building materials: 3 trucks per day from 1st March 1943 to 1st January 1944.

b) Iron and steel structure) 2 wagons per day from 1st July 1943
)   to
c) Machinery   )   1st May 1944

d) For the transport of finished products :-

Arriving: 320 tank trucks per year
Departing: 350 tank trucks per year

K) <u>Summary</u>

The building project is important to the war effort in that it is to supply the Air Force and the Reichsbahn with low temperature lubricating oils, and is therefore urgent.

Memorandum Leuna, 5.2.1942

On the conference in the Ministry of Economic Development
Berlin, 3.2.42

Present: Dr. Kranepuhl, D.I. Hübner
Dr. Zorn, Dr. Wittwer, Dr. Wissel

Re: Planning a 10,000 t/year SS 900 plant

1. **Auschwitz:** the locality proposed by Dr. Zorn is Auschwitz. Three carbide furnaces for Buna are being built there. 2½ of these are required for the 30,000 t/year Buna and the other ½ is in reserve. Should part of the butadiene be made after the Reppe method, a whole carbide furnace would be available for lubricating oils. The formaldehyde required for the Reppe method would be available in Auschwitz, because 70,000 t/year methanol must be produced there. The building cost for the 10,000 t/year SS 900 oils is

Acetylene hydrogenation	4.5 million marks
Accessories	1 " "
SS Oils	3.5 " "
Accessories	1 " "
	10 " "

Electric power is laid out in Auschwitz, with 150,000 KW installed. Of these 100,000 KW are used for the following production:

30,000 t/year	Buna	11,000 t/year	A-gasoline
25,000	D:1000	5,000	Propanol
70,000	Methanol	4,000	higher alcohols
17,000	Phenols		

A power extension to 150,000 KW is required for a proposed 30,000 t/year chlorination plant for Monten. Moreover the following outside power is available:

30,000 KW from Oberlosswitz works, as from 1.7.43
50,000 1.1.44

Both Auschwitz and Oberlosswitz depend on coal from the Fürsten mines.

Buna production was originally scheduled to start on 1.6.43. 4,000 workers must now be removed, causing a postponement to 1.1.44. Dr. Eckell has so far not agreed to this. As moreover the Air Ministry desires a peace-time economy plant, it was decided to drop this Auschwitz plan.

2. **Pölitz:** Dr. Wissell states that two sources of ethylene are available in Pölitz:

1) Cracked ethylene from Dr. Hortmann
2) Ethane ethylene from Hy gases

At full production the ethylene cracked from wax would amount to 3,000 t/year C_2H_4, i.e. 2,400 t/year SS Oil. This would necessitate a 1 million mark Linde plant and a 2 million mark SS oil plant, total 3 million marks. Building time about 1½ years, starting date early 1944. The Hy gas ethane ethylene would require:

1 Linde plant to extract ethane from Hy gas.
2 generators for H_2 production
1 Häuber cracking plant
1 Linde plant to separate ethylene from Häuber cracked gas
1 steam boiler for power

Cost about 18-20 million marks, building time 2 years: starting date early 1944. The SS oil plant must be built on one of the sites belonging to the hydrogenation plant, though separate from it for A.R.P. reasons. The workers are available in Pölitz.

According to Häuber propane would give 52% yield if completely cracked into ethylene, i.e 24,000 t/year propane are required for 10,000 t/year SS Oil.

3. <u>Heydebreck</u>: According to a written communication from Dr. Miller Cunrad, 650 cu.m. coke oven gas must be delivered to Heydebreck to produce H_2. From this 15,000 t/year equalling 2.3% pure ethylene = 12,000 t/year SS oil can be obtained.

Origin of the coke oven gas:

From Fordbahn	260	million cu.m.
Karvin	120	
Gleiwitz	125	
	505	

The balance from the planned extension of Gleiwitz.

The whole plan requires:

Linde decomposition plants	8.5 million marks	7,200 t. steel
Accessories	2	400 t n.f.
12,000 t/year SS oil	4.7	4,600 t. steel
	15.2	

Starting date 3 months after the ethene lubricatingoil.

4. <u>Gendorf</u>: Dr. Wittwer informs us that Gendorf is fed with carbide from Hardt-Trostber The production for 1942 amounts to 230-250,000 t/year. It is planned to erect another carbide furnace in Hardt, whereby the capacity will rise to 280,000 t/year. The capacit of Gendorf varies as follows (in 1000 t/year):

Target	1942	Carbide	1943	Carbide
Acetaldehyde	12	23	12	23
Glycol	7.7	30	7.7	30
D.L.	15	23	-	-
SS Oil	-	-	10	50
Calcium nitrate	50	165	38	127
		241		230

The 1942 D.L. production is stored in reserve. Should D.L. be produced in 1943, which at present seems improbable, it would be done at the expense of the calcium nitrate, if SS oil must also be produced. D.L. and glycol are interconnected by the capacity of the chlorination plant. The full capacity of the D.L. plant is 48,000 tons/year, which cannot be used up at present owing to the shortage of filling and transport equipment.

Dr. Zorn made the following suggestion: considering that only the Schkopau plant can start production for the Luftwaffe in 1943, no other plant before 1944 at the earliest the Gendorf plant should now be built as a reserve and emergency plant. It can be ready by early 1943. All the equipment can be delivered before the end of 1942. In 1944-45 the Gendorf plant will be replaced by the coking-ethylene plant at Heydebreck. This emergency will cost the Air Ministry 4 million marks, 1.6 of which will be paid off by 1945: the actual cost of this emergency plan will thus be 2.4 million marks. It will afford to the whole lubricating oil scheme the security of reserve, so far still lacking.

After a telephone communication from Dr. Hübner on 4.2.42, Prof. Franck accepted this suggestion and arranged for the immediate start of building at Gendorf.

On 4.2.42 Dr. Laugheinrich informed me that in two years time another 275 million cu.m. coking gas will be available in Auschwitz. These will yield 6,000 t/year ethylene equalling 5,000 t/year SS Oil. Dr. Zorn forwards this information by telephone to Dr. Hübner in Dr. Kranepuhl's absence, and suggests utilising this ethylene in Auschwitz also for the lubricating oil and reduce in proportion the Heydebreck production.

FD 4976/45
Folder XII

Department of
Economic Research

Demand and supply of Isobutyl oil products in tons/month, end of 1944

Leuna works, 3.1.1944

Uses	Factory	Finished products tons/year	Boiling interval, % raw isobutyl oil									
			50-175° first run olefin 1.0	95-100° Propanol (pure) 1.8	105-108° Isobutyl alcohol (pure) 11.5	120-132° Iso-amyl alcohol (crude) 1.0	134-144° Dioprol 0.3	113-137° Solvent K 0.8	140-160° Intrasolvan HS (crude) 2.4	160-180° (crude) 0.7	180-200° (crude) 0.3	200-270° (crude) 1.0
Solvent;												
Polysolvan AH	Hö	-	-	-	-	60	-	-	-	-	-	-
Propylacetate	Hö	-	-	(75) 75	-	-	-	-	-	-	-	-
Propylglycol	Hö	-	-	45	-	-	-	-	-	-	-	-
Polysolvan HS	Hö	-	-	-	-	-	-	-	80	20	10	-
Solvent manufacture at Kunden	Kunden	-	-	-	-	-	-	-	-	14	6	-
Polysolvan EH	Hö	-	-	-	60	60	-	-	-	-	-	-
Sale Intrasolvan E	Ffm	-	-	-	25	15	-	-	-	-	-	-
" Solvent K	Ffm	-	-	-	-	-	-	120	-	-	-	-
" Dioprol	Ffm	-	-	-	-	-	30	-	-	-	-	-
" Propanol	Ffm	-	-	(350) 55	-	-	-	-	-	-	-	-
Softeners:												
Palatinol A (Diamylphtalate)	Off.	-	-	-	-	45	-	-	-	-	-	-
Palatinol HS	Off.	-	-	-	-	-	-	-	(350) 215	-	-	-
Tri-isohexylphosphate	Bitt.	-	-	-	-	-	-	-	10	-	-	-
Kundon	Kund.	-	-	-	-	-	-	-	5	-	-	-
Tri-isobutylphosphate	Bitt.	-	-	-	20	-	-	-	-	-	-	-
Mollitt	Mo.	-	-	-	-	-	-	-	-	60	-	-
Lacquer aid												
Acids for Soligene	Griesh.	720	-	-	-	-	-	-	-	-	-	120
Detergent												
Olefine f. Igopals		-	-	-	-	-	-	-	(150) 30	-	-	-
Lubricant:												
Inlet oil	Mo	12,000	-	-	-	-	-	-	-	-	238	850
Axle oil	Mo	960	-	-	-	-	-	-	-	20	85	-
Aviation pressure oil	Mo	660	-	-	-	-	-	-	-	-	-	-
Torpedo oil	Mo	600	-	-	-	-	-	-	-	-	12	43
Weapon oil	Mo	300	-	-	-	-	-	-	15	55	-	-
Synthetic resin												
Oppanol	Opp.	-	-	-	250	-	-	-	-	-	-	-
"	Frose	-	-	-	300	-	-	-	-	-	-	-
Ilgevine (Vinylisobutylether)	Lu	-	-	-	200	-	-	-	-	-	-	-
Harze	Maink.	-	-	-	20	-	-	-	-	-	-	-
XF-Harz	Lev.	-	-	-	-	-	-	-	-	20	10	-
Fuel												
ET 110	Mo	-	-	-	800	-	-	-	-	-	-	-
Flotation substance												
Amylxanthate	Griesh.	-	-	-	-	30	-	-	-	-	-	-
Miscellaneous												
Foam extinguisher	Hö	-	-	15	-	-	-	-	-	-	-	-
Trimethylolethane	Mo	90	-	(150) 80	2	-	-	5	-	-	-	-
Various products	Lu	-	-	-	-	-	-	-	-	-	-	-
Phenosolvan	Hö	-	-	-	100	-	-	-	-	-	-	-
Oxation	Mo	-	50	-	-	-	-	-	-	-	-	-
Total demand in tons per month			50	270 (665)	1777	240	30	125	370 (625)	189	558	1013
Total demand in tons per year			600	3240 (7980)	21324	2809	360	1500	4440 (7500)	2268	4296	12156
Production in:		tons per year raw Isobutyl oil										
Leuna		180,000	1800	3240	20,700	1800	540	1440	4320	1260	540	1800
Auschwitz		265,000	2650	4770	30,475	2650	795	2120	6360	1855	795	2650
Oppau		120,000	1200	2160	13,800	1200	360	960	2880	840	360	1200
Heydebreck		650,000	6500	11700	74,750	6500	1950	5200	15600	4550	1950	6500
Total production		1,215,000	12150	21870	139725	12150	3645	9720	29160	8505	3645	12150

Figures underlined - demand already assessable, in so far as produce may be supplied

Ref. FD 4975/45, Folder XIII

To:
The Government department for economic expansion
Mineral Oil P
attention: Dr. Kronepuhl
Berlin W.9.
Saarlandstrasse 128

Building certificates for the expansion of the ester oil plants

The present state of production planning of isobutyl oil is this:

Leuna	180,000 tons/year
Oppau	120,000
Heydebreck	800,000
Auschwitz	260,000
	1,360,000

This gives the following production figures for the manufacture of lubricating oils:

	Leuna	Schkopau	Auschwitz	Total
1) Ester 426 for aero-engine oils	1000	-	1600	2600
2) Ester 515 " " "	1500	2500	-	4000
3) Ester 504 for axle oils	1000	-	3400	4400
4) Cutting oil ester mixture	500	-	-	500
	4000	2500	5000	11,500

In the lubricant plan there had so far been suggested one ester plant at Leuna and one at Schkopau of 2200 tons/year each. Ester 515 was to be produced in these plants; it was to be used as an addition of SS oil for the production of a low-freeze aviation oil. Owing to developments in this field it has become necessary to add not only one bu a mixture of two esters, viz. 515 and 426 in order to obtain improved lubrication of the SS oil.

Furthermore the production of ester 504 had to be included in the ester production programme. This ester improves the quality and the absorption capacity of the low-freez axle oils. The latter consist of mixtures of ester 504 with the SS 900 oil, one to one, and SS 903 oil and also the residual oils remaining after the decomposition of the $AlCl_3$ residues (R-oils). These have to receive an after-treatment with aluminium chloride in order to be usable as described above. This after-treatment may be carried out in the separate SS oil plants. After the treatment with $AlCl_3$ one has to distil and refine with Fuller's earth. This treatment is to be carried out at Leuna for the aggregate R-oil of Leuna, Schkopau, Moosbierbaum and Oppau: at Heydebreck the treatment is to be carried out for the R-oil accrueing there.

The esters mentioned are produced from the following starting materials:

1) Ester 426 from trimethylolethane and the Leuna carboxylic acid derived from the alcohols of the isobutyl fraction 200-250° with the addition of 7.5% soap fatty acid.
2) Ester 515 from methyladipic acid and the alcohols of the isobutylfraction 180-260°.
3) Ester 504 from methyladipic acid and the alcohols of the isobutyl fraction 165-200.
4) Cutting oil ester is a mixture of two esters which accrue in one working process
   a) Methyladipic acid and the alcohols of the isobutyl fraction 180-250°, and
   b) the semi-esters produced in the reaction esterified with dimethylolpropan- which is made from isobutylaldehyde + formaldehyde.

For the production programme set up at the beginning of this memorandum :

2600 tons/year ester 426
4000 " " 515
4400 " " 504
500 " " Cutting oil ester

the following starting materials are necessary:

	426	515	504	Cutting oil ester	Total t/year
Isobutylalcohols					
Fraction 200-250°	5200	-	-	-	5200
" carboxylic acid "	2600	-	-	-	2600
Fraction 180-250	-	7200	-	670	7870
Fraction 160-200	-	-	7900	-	7900
Methyladipic acid	-	2000	2200	250	4450
Soap fatty acid	200	-	-	-	200
Dimethylol propane	-	-	-	45	45
Trimethylol ethene	700	-	-	-	700

In order to obtain these starting substances and in order to manufacture the end products the following plants have to be erected in addition to the present ester oil plan:

1) One distillation plant each in Heydebrock and in Auschwitz for the cutting out of the alcohol fractions of the isobutyl oils necessary for esters mentioned: 160-180, 180-200, 200-250, also small alterations at Leuna.

2) One carboxylic acid plant each at Leuna (1000 t/y) and at Auschwitz (1600 t/y) for making the acids from the alcohols of the isobutyl fraction 200-250.

3) Increase of the available productive capacity for methyladipic acids: by altering and expansion to 200 tons/month of the plant already in existence at Leuna.

4) Erection of a unit at Leuna manufacturing 45 tons/year..

5) Expansion of the Leuna ester plant WROX 5661 from 2200 to 4000 tons/year.

6) Erection of an ester plant for 5000 tons/year at Auschwitz.

7) Erection of distillation and refining plant for 3000 tons/year R-oil at Leuna.-

8) Erection of a plant for the working up of 3000 tons/year of R-oil at Heydebreck $AlCl_3$ treatment, distillation and refining.

The trimethylol ethene required (700 tons/year) can be supplied by the Leuna process after some expansion has been carried out on it. The soap fatty acid required (200 tons/y) is supplied by the Paraffin-oxidation plant at Oppau or Heydebreck.

We have informed the works at Auschwitz and Heydebreck about the measures necessary within the present ester oil programme. They in turn will apply for building certificates from the RWA.

The demand for axle oil is very likely to increase. The alcohol for this purpose is being prepared by dehydrating the secondary alcohol left in the isobutyl oil residues and consequent oxation of the olefines obtained in the dehydration. The material necessary for the building certificates has not yet been furnished. This will be sent on whenever an increased production of axle oil becomes necessary.

Department of
Economic Research

Leuna Works 31.7.42
Memorandum No. 2175

Memorandum

Ester plan as on the 30th July, 1942

(basis for building certificates)
(all data in tons per year)

The following production figures are required:

18,500 tons/year	Low cold test aviation oil
6,600	Y axle oil
25,000	Low cold test motor oil
500	Cutting oil
580	m.g. oil

Assuming the composition 1 t. A.N. of 19.6.42 (maximum), the total demand for oil production is about 21,000 tons/year ester.

This quantity is to be distributed among the localities in this way :-

	up to now	new	total capacity
Merseburg	4000	3000	7000
Schkopau	2400	-	2400
Auschwitz	4000	8000	12000
	10,400	11,000	21,400

For this ester capacity divided among the various localities the following division is proposed among the various esters:

Ester	Merseburg	Schkopau	Auschwitz	Total
515	3360 for L.c.t. motor oil and L.c.t. aviation oil	2400 for L.c.t. aviation oil and L.c.t. motor oil	7000 for L.c.t. aviation oil and L.c.t. motor oil	12,760 (2760 L.c.t. aviation oil, 10,000 L.c. motor oil
504	up to 1310 3100 for Y axle oil	-	-	up to 1310 3100 Y ax oi
426	1840 for L.c.t. aviation oil	-	2500 for L.c.t. motor oil	4540
	6510 up to 8300	2400	9500	18,410 up to 20,2

From this distribution we see that Merseburg produced:

100% Y axle oil = 6600 tons
100% L.c.t. aviation oil = 18,500 tons

and Auschwitz produces 100% L.c.t. motor oil = 25,000 tons

For 21,000 tons/year of ester the following raw materials are required:

Trimethylolethane	450 tons/year	for L.c.t. aviation oil
	610	L.c.t. motor oil
	1060 tons/year	

New installation to be erected at Merseburg:

Carbonic acid 1665 tons/year for L.c.t. aviation oil
2260 L.c.t. motor oil
3925 tons/year

The I.G. has an additional demand for ca 3000 tons/year so that the capacity available at Leuna has to be expanded by 1200 tons/year. Auschwitz also has to erect a capacity of 3500 tons/year. If necessary the apparatus may be temporarily installed and operated at Leuna.

Ester 515:
Methyladipic acid 1380 tons/year for L.c.t. aviation oil
5000 L.c.t. motor oil
6380 tons/year
Ester 504 875 tons/year for Y axle oil
up to1530

7055 "
up to 7910
Cutting oil 285
up to 8195 " total methyladipic acid

	available tons/year	to be erected tons/year	total tons/year
Merseburg	1200	1200	2400
Schkopau	2400	-	2400
Auschwitz	-	3600	3600
			8400

The Cresol demand for the methyladipic acid is met thus:

Brix with 1500 tons/year in p cresol
Blechhammer 3500 tons/year in p cresol
5000 tons/year

There is still a shortage of 3500 tons/year of cresol which must be made available from other uses.

"Oxo" plants

The Oxo-plants required to meet the alcohol demand for the ester oils shall be erected at Auschwitz and Leuna, using the "yellow oils" each plant having a capacity of 10,000 tons. This arrangement is proposed on the basis of the accumulation of neutral oils and on the assumption that the latter is insufficient.

Corresponding to the localities of production proposed one also has to erect a mixing plant for Y axle oil at Merseburg, further also a mixing plant for L.c.t. aviation oil. Auschwitz has to erect a mixing plant for L.c.t. motor oil.

This plan therefore requires building certificates for:

Merseburg for 3000 tons/year ester up to a 7000 total
1100 " P_3
1800 " Propbonic aldehyde
2300 " carboxylic acid making a total of 3500 tons/year
1200 " methyladipic acid making a total of 2400 tons/year. Installation of the plant from the hydrogenation

			stage, without taking into account the Schkopau demand. In this respect negotiation with Dr. Wulff may have to take place.
	660.	tons/year	mixing plant for Y axle oil
	18,500	"	mixing plant for L.c.t. aviation oil
Schkopau for	-		
Auschwitz for	8000	tons/year	esters making a total 12,000 tons
	3500	"	carboxylic acid making total 3500 t.
	3600	"	methyladipic acid making total of 3600 tons from Phenol decomposition.
	2500	"	mixing plant for L.c.t. motor oil.

Department for
Economic Research

Leuna Works

Memorandum

Discussion in the Reichsamt on 17.6.42

Present:
Dr. Kranepuhl R.W.A.
Dr. Giessen Leuna
Dr. Zorn Leuna
Dr. Küding Leuna

Re: Lubricants and Ester plans

I. At the beginning Dr. Kranepuhl intimated that on 15.6 of this year, he had a conference with Mr. Müchlich (R.L.M.). During this conference it was definitely ascertained that the Air Force would have to consider a lubricant consumption amounting to 5% of the maximum production of aviation spirit.

The production of aviation spirit amounts to

283,000 tons per month

corresponding to 170,000 tons/year aviation lube oil

In the quoted figure for the aviation lube oil oil there are

18,500 tons/year L.e.t. aviation oil

The demand is met thus:

Rhenania	6000	tons/year
Oslebelhausen	12,000	"
Kolin	10,000	"
Nerag	20,000	"
Pressburg	14,000	"
Lutzkendorf	5,000	"
Ruhrchemie	10,000	"
	77,000	"

Highly viscous components

Leuna I	10,000	tons/year	
II	7,000	"	Building certificate is applied for. 3000 tons on the basis of the ethane available at present, 4000 tons on the basis of DHD-ethane
Schkopau	10,000	"	
Moosbierbaum	3,500	"	60% yield
Oppau	2,000	"	
Heydebreck I	22,000	"	from 37,000 tons of ethane Blechhammer 60% yield
II	10,000	"	from coking ethylene
Pölitz (paraffin)	20,000	"	
Rhenania	6,000	"	
	90,500	"	
To this one has to add from the I.G. plant	14,500	"	from 20,000 tons/year ethane from Pölitz hydrogenation + 3000 t/yr ethylene from cracked gases from Pölitz paraffin

Total weight of highly viscous components 105,000 tons/year.

Furthere there are available an additional 25,000 tons/year of a total of 41,500 tons of ethane from Blechhammer are available as lubricants. These 2500 tons/year should best be taken into accountin the summation since it is not certain if their amount is really available for SS oil.

Apart from the Air Force demand there is an SS oil demand

25,000 tons L.c.t. motor oil with 50% of
highly viscous components
12,000 tons SS oils

The Air Force require 177,000 tons of lubricants per year; 77,000 tons of low viscosity oil are available per year; the difference, 93,000 tons/year, must be provided from synthesis. Another 12,000 tons are thus available to meet the demands of the Army. This more or less suffices, especially if one assumes that Blechhammer actually supplies 41,500 tons/year of ethane.

II According to the present progress of the ester plan the following amounts of ester should be available. Details see table

for L.c.t. aviation oil	4,600	tons/year
Y axle oil	3,100	"
L.c.t. motor oil	12,000	"
Cutting oil	500	"
M.g. oil	235	"
	21,000	" ester

corresponding to 42,000 tons/year alcohol (crude fraction). To this amount of ether, including the assumed needs of the I.G. for solvents and softeners there correspond

a requirement of carboxylic acid	ca	2000 tons/year
" " " methyladipic acid	ca	8500 tons/year
" " " P_3	ca	2500 tons/year

Meeting the demand of esters

On the basis of the actual production figures of isobutyl oils at Leuna we obtain the amounts of crude alcohol fraction of the four localities at which they are produced. The values are entered into the table. The data given by "Leuna" differ from those given by Dr. Zorn in a memorandum based on a conference with the gentlemen from Oppau. Only 23,000 tons are indicated for the plant at Heydebreck whereas, according to our experience one should be able to obtain 39,200 tons/year. The latter figure is used in the calculations below.

From the table one sees that there is a small deficit in the 180-200° fraction and a considerable deficit in the 200-250° fraction. On the whole there is an unmet demand of 12,000 tons/year of the alcohol crude fraction: this shall be met by the oxation of the neutral oils occureing during esterification. The plan of supply for the amounts of esters in question is the following:

Output scheduled for Leuna		4000	tons	ester
Schkopau is erecting plant for	ca	3000	"	"
Auschwitz has sent in a building certificate for		4000	"	"
Leuna should also produce (on basis of isobutyl oil Leuna and Oppau)		2000	"	"
The plant at Auschwitz shall be enlarged by		8000	"	"
On basis of isobutyl oil Auschwitz & Heydebreck		21,000	"	"

Meeting the demand of methyladipic acid

Available at Schkopau	3,000 tons
" " Leuna	2,400 tons
	5,400 tons

During the conference at the Reichsamt it was proposed to branch off the deficit of
1,600 tons from the normal manufacture of adipic acid. This amount will thus be lost to
the synthesis section. A percent has already been granted for the quantity of iron
required.

At the present we still require the corresponding priority. The plant has already
been ordered so that they can be erected in a very short time, i.e. after building workers
have been placed at our disposal.

Meeting the demand of carboxylic acid

In Leuna we have at present a production of carboxylic acid amounting to

ca 1,200 tons/year

which is being expanded to

ca 3,600 tons/year

on the basis of the ester plan as it exists today. The remaining 4000 tons/year may be
produced at Auschwitz on the basis of the alcohols available there.

Meeting the demand of P_3

Demand met.

Meeting the demand of oxo-plant

The oxo plant necessary to meet the requirement of 12,000 tons/year may either be
erected in one unit at Leuna or be divided up into one bigger plant at Auschwitz and a smaller
one at Leuna. The details and the question of location will still have to be discussed.

The above information was given to Dr. Kranepuhl quite informally. We have
promised to check the details on the basis of the available data till Friday 26.6. A
rough plan is to be drawn up which is to show the amount of iron required for the new
ester plan, when and at what rate the iron has to be supplied, when and how many building
workers and artisans have to be reserved in order to have the plants in readiness by the
winter of 1943, what energy is required, how many tank trucks, i.e. how much iron is neede

Ester Plan (quantities in tons per year)

Finished product	Demand tons/yr.	Composition	SS oil	V oil	R oil	Ester	Mesulfol	Crude alcohol fraction ~60% alco. Alcohol total	140/ 160	160/ 180	180/ 200	200/ 250	Carboxylic acid	P_3	Methyl adipic acid	Pentaglycol
Anti-freeze	18,500	75% SS	13,900													
aviation oil		15% 515				2,750		4,550			975	3,575			1320	
		10% 426				1,850		3,700				3,700	1850	450?		
Y axle oil	6,600	47% R oil			3100											
		47% 504				3,100		5,450		3,800	1650				1530	
		6% V 120		400												
Anti-freeze	25,000	30% SS	12,500													
car oil		30% 515				7,500		11,000			2350	8,650			3600	
		20% 426				5,000		10,000				10,000	5000	640?		
Cutting oil	800	66% 515				500		700			150	550			250	45
		33% 623														
Weapon oil	500	47% 455				235		380	290	90					120	
		48% V 120		225												
		6% Mes.					30									
		2% SS	10													
Pressure oil	400	95% V 120		380												
		5% SS	20													
Air Force, Railways etc.			26,430	1005	3100	20,935	30	35,780	290	3890	5125	26,475	6850	1090?	6820	45
I.G. demand								17,400	12,200	4000		1,200	3000	800?		
Total Demand			26,430	1005	3100	20,935	30	53,180	12,490	7890	5125	27,675	9850	1890?	6820	45
Leuna 180,000 tons per annum									4,140	1260	540	1,980				
Oppau 165,000 " " "									3,800	1150	495	1,810				
Ausch 265,000 " " "									6,095	1855	795	2,915				
Heyd. 890,000 " " "									20,500	6230	2670	9,800				
1,500,000 " " "									34,535	10,495	4500	16,505				
Excess or deficit									+ 22,045	+ 2605	-625	-11,170				

Organic Dept.

Leuna works, 24th June, 1942.

Requirement of raw material per 100 tons ester

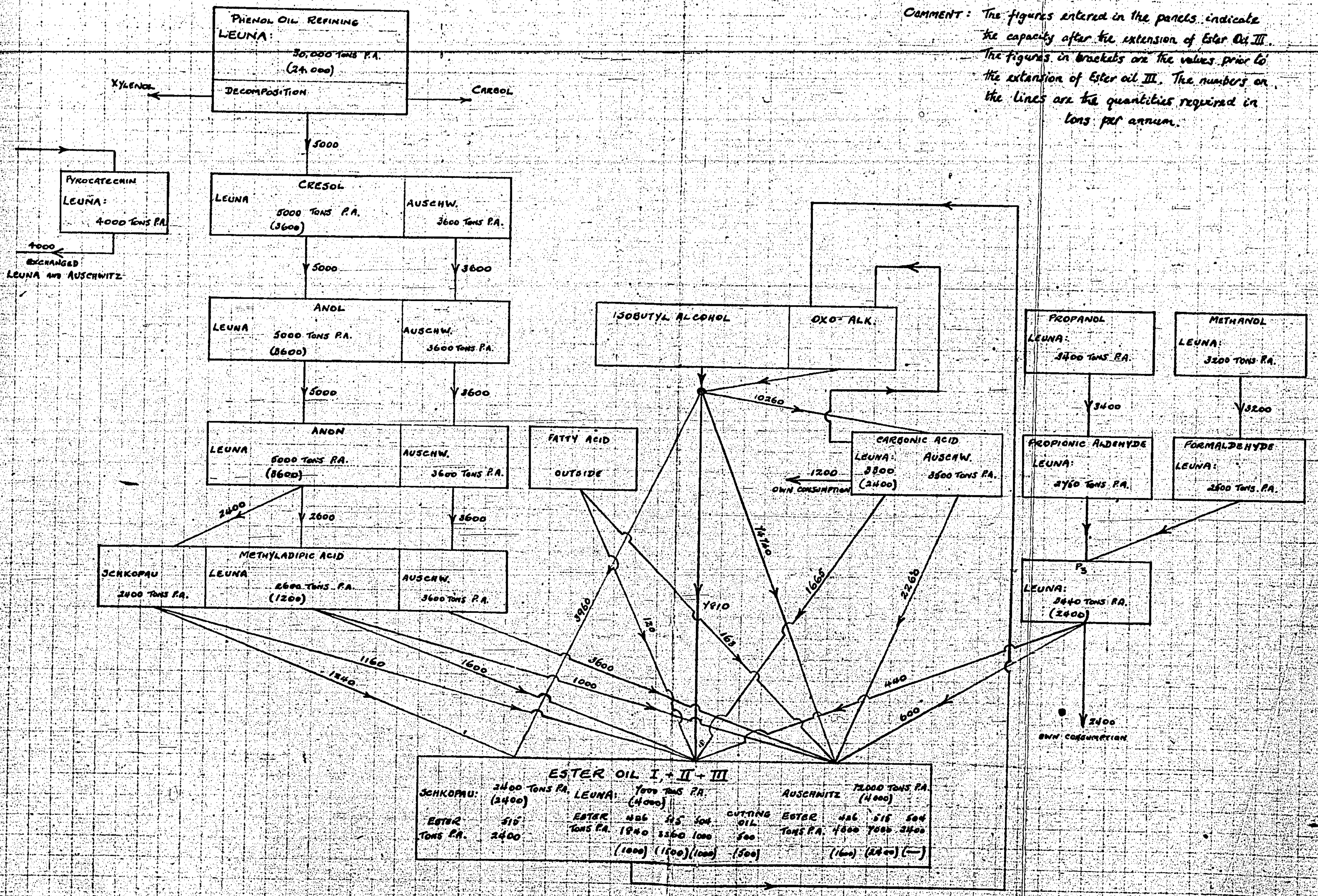
	Alcohols		Acids	
	Designation	Quantity	Designation	Quantity
Cold oil - Ester a) Ester 815	Isobutyl fraction 180-200° Isobutyl fraction 200-250	35.0 t. 123.5 t.	Methyl adipic acid	50.0 t.
b) Ester 426	Trimethylol ethane	24.5 t.	Leuna carboxylic acid 200-250° Soap fatty acid	~~122.5 t.~~* 6.5 t.
Railway axle oil - Ester Ester 504	Isobutyl fraction 160-180° Isobutyl fraction 180-200	112.0 t. 38.0 t.	Methyl adipic acid	56.0 t.
Cutting oil - Ester Ester 523	Isobutyl fraction 180-200° Isobutyl fraction 200-250° Pentaglycol	28.5 t. 109.5 t. 9.0 t.	Methyl adipic acid	57.0 t.
Weapon oil - Ester Ester 455	Isobutyl fraction 140-160° Isobutyl fraction 160-180	121.0 t. 37.0 t.	Adipic acid	48.0 t.
Mollitt Ester	Trimethylol ethane	29.7 t.	Leuna carboxylic acid	114.2 t.

* (pencil note on original document - 90,00 t. with Butyl 21.7.42)

FD 4775/45
Folder XIV

EXTENSION OF ESTER OIL III TO 21,400 TONS PER ANNUM
RAW MATERIAL PLAN AS PER TABLES OF 11·8·42

COMMENT: The figures entered in the panels indicate the capacity after the extension of Ester Oil III. The figures in brackets are the values prior to the extension of Ester oil III. The numbers on the lines are the quantities required in tons per annum.



Ref. FD 4975/45 - Folder XXII

Letter for attention of Dr. Eckell   11th August 1942.

The plenipotentiary for special problems of chemical production

Leuna Alcohols

In reply to your letter of 6th inst., we pass to you the following information, which please treat as confirmation of our discussion of the same date.

Under the Ester plan, it is proposed to use the alcohol fractions of the manufacture of isobutyl oil which have not so far been considered and are not at present under consideration. You will be aware that for the production of palatinol HS products the fractions 140-160° are used. Hardly any of these are used for the production of esters, and you will have observed from the plan that it is just those oils of which a surplus is expected. Nor does the soap section require any of the higher fractions, since here also it is the fractions 140-160 which are required.

As regards the Oxo plants, we confirm that the products which will come from the plant set up by Ruhrchemie cannot be used for Ester oils, and that we therefore propose to establish too new Oxo plants, to be supplied with raw materials which will contribute to the production of Ester.

As regards the quantity of methyladipic acid which is available, according to the latest estimates 8560 tons will be required, of which 3600 tons are covered by the plants to be set, leaving about 5000 tons still to be accounted for. We request you to note the figures in the accompanying table which concern you.

We trust that this is the information which you require.

Leuna Works, 11th August 1942

Raw material requirements for the Ester plan

Esters required in tons per annum

Product	Vol. tpa.	Ester 426					Ester 504					Ester 515					Other Esters					Total				
		Vol. tpa.	A	C	P	M	Vol. tpa.	A	C	P	M	Vol. tpa.	A	C	P	M	Vol. tpa.	A	C	P	M	Ester	A	C	P	M
L. temp aero engine oil	18500	1850	3700	1670	450	-						2750	4550	-	-	1450						4600	8250	1670	450	1450
Weapon oil	500																235	375	-	-	115	235	375	-	-	115
Axle oil	6600						3100	5450	-	-	1600											3100	5450	-	-	1600
Cutting oil	500																500	700	-	-	250	500	700	-	-	250
L. temp motor oil	25000	2500	5000	2260	600	-						10000	16500	-	-	5160						12500	21500	2260	600	5160
Total	51100	4350	8700	3930	1050	-	3100	5450	-	-	1600	12750	21050	-	-	6590	735	1075	-	-	365	20935	36275	3930	1050	8555

A = Alcohol fraction; C = Carboxylic acid: P = P_3 M = Methyl adipic acid

Department for
Economic Research

Leuna, 29.4.1943

Capacity of the Ester plants :-

Leuna Me 981	1800 tons p.a.
Schkopau	2400 " "
Leuna Ester plant I and II	4000 " "
	8200 " "

Requirements

Weapon oil ester Me 985	25 tons p/mth.	= 300 tons p.a. = 50 weapon oil
Mollit	10 "	120 " "
Methyladipat	5-10 "	80 " "
Cyclohexanolester (3022)	5 "	60 " "
Vanhatin	10 "	120 " "
Smaller esters	5 "	60 " "
Mesulfol	5 "	60 " "
		800 " "

Ester for Y axle oil (40% ester content) Ester 504

December 1943. 220 tons per month of Y axle oil = 88 tons per month of Ester = 1056 tons p.a.
July 1944 280 tons per month of Y axle oil = 112 tons per month = 1344 tpa
December 1944 500 tons per month of Y axle oil = 200 tons per month = 2400 tpa

Ester first light oil: 10,000 tons with 5000 tons of Ester 515 = 5000 tpa
8200 tpa

Alcohol requirements (figures in tons per annum)

	140/ 160	160/ 180	180/ 200	200/ 270	Carboxylic acid
For 300 tons p.a. E. 455	573	162	-	-	-
120 " " Mollit	-	375	-	-	188
120 " " Vanhatin	-	375			188
2400 " " 504	-	2240	1960		-
5000 " " 515	-	-		8660	
	573	3152	1960	8660	376
Carboxylic acid					
for I.G. alcohol				1200	600
for sale					

Department for
Economic Research

Leuna 29.4.1943

Position on 5th April 1943

Composition of crude isobutyl oil

above 140°	in all	5.01%
HS - first runnings		0.35%
HS, crude	145-160°	2.40%
Fraction	160-180°	0.66%
	180-200°	0.59%
	200-270°	0.85%
Losses & Deposits		0.09%
Olefines		1.02%

Amount available after completion of development (percentages on the basis of the product when deprived of other) in tons per annum :-

	Raw Isobutyl-oil tons per ann.	Isobutanol	Raw propanol	Propanol 1st runs for re-hydrog.	Fraction 95-110°	Isobutyl 2nd runs	K frac.	Raw Amyl	HS Prog. for A-Benzin	HS Frac.	Isobutyron Deposit	Fraction 160/180	180/200	200/270
		12.35%	1.47%	0.33%	0.43%	0.71%	0.88%	0.96%	0.31%	2.40%	0.30%	.66%	.59%	.85%
Merseburg	180,000													
de-etherised	175,500	21,674	2580	580	755	1246	1544	1685	544	4212	526	1160	1035	1490
Oppau	160,000													
"	156,000	19,266	2290	515	670	1108	1370	1500	484	3745	469	1030	920	1326
Auschwitz	260,000													
"	253,500	31,300	3730	840	1090	1800	2231	2434	786	6090	760	1670	1500	2165
Heydebreck	890,000													
"	868,000	107,200	12,760	2860	3730	6160	7640	8330	2690	20,830	2605	5730	5120	7380
etherised	1,490,000	179,440	21,360	4975	6805	10,314	12,785	13,949	4504	34,877	4360	9590	8575	12,361
de-etherised	1,453,000													
Raw methanol total	560,000	0.5-0.8%												
		0.65%												
distilled ~90%	~500,000	3250												
		182,690												

Manuscript Note with
letter to Dr. Eckell

Telephone communication to Dr. Kranepuhl on 8.1.43

Auschwitz: 2400 tons per annum of 504 -
1200 tons methyladipic acid, October '44

Leuna: 1000 tons per annum of 504 -
500 tons methyladipic acid, October '43
1500 tons per annum of 516 -
750 tons methyladipic acid, January '44
500 tons of cutting oil -
250 tons methyladipic acid October '43

Schkopau: 3000 tons of 615 -
1550 tons of methyladipic acid Aug '43

4250 tons methyladipic acid

Leuna 180 tons per annum of 455 90 tons per annum adipic acid

Ref. FD 4975/45 - Folder XIII

Department of
Economic Research

Leuna works 31.7.42
Memorandum No. 2175

Memorandum

Ester plan as on the 30th July, 1942

(basis for building certificates)
(all data in tons per year)

The following production figures are required:

18,500 tons/year	Low cold test aviation oil
6,600	Y axle oil
25,000	Low cold test motor oil
500	Cutting oil
500	M.g. oil

Assuming the composition L.c.t. A.N. of 19.6.42 (maximum), the total demand for oil production is about 21,000 tons/year ester.

This quantity is to be distributed among the localities in this way :

	up to now	new	total capacity
Merseburg	4000	3000	7000
Schkopau	2400	-	2400
Auschwitz	4000	8000	12000
	10,400	11,000	21,400

For this ester capacity divided among the various localities the following division is proposed among the various esters:

Ester	Merseburg	Schkopau	Auschwitz	Total
515	3360 for L.c.t. motor oil and L.C.t. aviation oil	2400 for Lct aviation oil and Lct motor oil	7000 for L.c.t. aviation oil and L.C.t. motor oil	12,760 (2760 L.c.t. aviation oil, 10,000 Lct motor oil
504	up to $\genfrac{}{}{0pt}{}{1310}{3100}$ for Y axle oil	-	-	up to $\genfrac{}{}{0pt}{}{1310}{3100}$ Y axle oi
426	1840 for L.c.t aviation oil	-	2500 for L.c.t. motor oil	4340
	6510 up to 8300	2400	9500	18,410 up to 20,200

From this distribution we see that Merseburg produces:

100% Y axle oil = 6600 tons
100% L.c.t. aviation oil = 18,500 tons

and Auschwitz produces 100% L.c.t. motor oil = 25,000 tons

For 21,000 tons/year of ester the following raw materials are required :

Trimethylolethane	450	tons/year for L.c.t. aviation oil
	610	L.c.t. motor oil
	1060	"

New installation to be erected at Merseburg :

Carbonic acid	1665	tons/year	for L.c.t. aviation oil
	2260		L.c.t. motor oil
	3925	"	

The I.G. has an additional demand for ca 3000 tons/year so that the capacity available at Leuna has to be expanded by 1200 tons/year. Auschwitz also has to erect a capacity of 3600 tons/year. If necessary the apparatus may be temporarily installed and operated at Leuna.

Ester 515:

Methyladipic acid	1380	tons/year	for L.c.t. aviation oil
	5000		L.c.t. motor oil
	6380	"	
Ester 504	675	"	for Y axle oil
	up to 1530		
	7055		
	up to 7910	"	
Cutting oil	285		
	up to 8195	"	total methyladipic acid

	available tons/year	to be erected tons/year	total tons/year
Merseburg	1200	1200	2400
Schkopau	2400	-	2400
Auschwitz	-	3600	3600
			8400

The Cresol demand for the methyladipic acid is met thus:

Brix	with	1500 tons/year	in p cresol
Blechhammer	with	3500 tons/year	in p cresol
		5000 tons/year	

There is still a shortage of 3500 tons/year of cresol which must be made available from other uses.

"Oxo" plants

The oxo-plants required to meet the alcohol demand for the ester oils shall be erected at Auschwitz and Leuna, using the "yellow oils" each plant having a capacity of 10,000 tons. This arrangement is proposed on the basis of the accumulation of neutral oils and on the assumption that the latter is insufficient.

Corresponding to the localities of production proposed one also has to erect a mixing plant for Y axle oil at Merseburg, further also a mixing plant for L.c.t. aviation oil. Auschwitz has to erect a mixing plant for L.c.t. motor oil.

This plan therefore requires building certificates for:

Merseburg for	3000	tons/year	ester up to a 7000 total
	1100	"	P_3
	1800	"	Propionic aldehyde
	2300	"	carboxylic acid making a total of 3600 tons/year
	1200	"	methyladipic acid making a total of 2400 tons/year.
			Installation of the plant from the hydrogenation

			stage, without taking into account the Schkopau demand. In this respect negotiation with Dr. Wulff may have to take place.
	6000	tons/year	mixing plant for Y axle oil
	18,600	"	mixing plant for L.c.t. aviation oil
Schkopau for	-		
Auschwitz for	8000	tons/year	esters making a total 12,000 tons
	3500	"	carboxylic acid making total of 3500 t.
	3600	"	methyladipic acid making total of 3600 t. from Phenol decomposition
	2500	"	mixing plant for L.c.t. motor oil

The Commissioner for the
Four years plan

8th July 1942.

The plenipotentiary for special problems of chemical production

Department for Mineral Oil
For the attention of Dr. Kranepuhl
Berlin W.9.
Saarlandstr. 128

Subject: Low temperature motor oil

Ref. your communication of 30.6.1942. We should like to lay before you the following proposals for the location of plants for low temperature motor oils, which we consider the most suitable :-

Ester plants Leuna 2000 tons per year extension
Auschwitz 10760 " " " in all

Carboxylic acid: Leuna 3300 tons per year extension
Auschwitz 3300 tons total (if necessary, the plant could be set up and put into operation temporarily at Leuna).

Trimethyl-ethane: Leuna 1200 tons per annum extension

Propionaldehyde: Leuna 1800 tons per annum extension

Methyladipic acid: Leuna 2400 tons per annum in all
Auschwitz 2000 tons per annum in all
(covered for the present by the development of the n-adipic acid plant at Leuna, which is given priority).

Cyclohexanol: Leuna 3700 tons per annum extension
(if possible that a plant will be built at Auschwitz for 2000 tons)

Oxo-plant: Leuna 10,000 tons per annum
Auschwitz 10,000 tons per annum.

The date fixed by you for commencing the above at your plant can in our opinion only be adhered to if the necessary allocations of building materials and iron are delivered punctually. This requires that the constructional workers and fitters arrive punctually, and that their numbers are increased. Otherwise the date will have to be postponed to February 1944.

As regards the extension programme for the Oxo plants, we should like to add that on going over the figures for alcohol it appeard that it is necessary for the Ester programme that in addition to the neutral oil obtained from ester production and from carbonoxylic acid production the first run oil from the isobutyl oil plants should also be utilised. Since, according to the above plant these products are drawn about half from Central Germany and half from Upper Silesia, it is thought that unnecessary transport costs can be saved by erecting an Oxo plant in both places. This dispersal is to be recommended in the case of carboxylic acid and methyladipic acid for reasons of air defence.

It will only be possible to check the provisional estimates of iron requirements and capital expenditure when the details of construction have been thoroughly revised. It is not expected that the figures will differ greatly from those which you gave.

Heil Hitler!
Ammonia Works
Merseburg, G.m.b.H.

Proposed production for the Ester plan - posn. at 21.7.42

Table I

A. Location		Leuna	Schkopau	Auschwitz
1) Ester No.	515	2000 tons p.a.	2400 tons p.a.	8360 tons p.a.
2)	426	2340 " "	----	2000 " "
3)	623	600 " "	----	----
4)	Mollitt	1200 " "	----	----
5)	455 Weapon oil	235 " " (500 t. weapon oil)	----	----
6) Carboxylic acid		(600) " "	----	----
7) Ester	504	3100 " "	----	----
Total Ester in tons p.a.		9375 " "	2400 " "	10360 " "
B. 1 to 6 as A		A (6275 tons p.a. Ester)	2400 tons p.a.	10360 tons p.a.
7) Ester 504		2640 " "	----	-----
Total Ester in t.p.a.		8915 " "	2400 " "	10360 " "
C. 1 to 6 as A		A (6275 tons p.a. Ester)	2400 tons p.a.	10360 tons.pa.
7) Ester 504		1320 " "	----	-----
		7595 " "	2400 " "	10360 " "

Case A of Table I

Consumption of raw materials under the Ester plan - posn. at 21.7.43

Table II

Location Leuna	Alcohol fraction 140/160	Alcohol fraction 160/180	Alcohol fraction 180/200	Alcohol fraction 200/250	Carboxylic acid 140/180	Carboxylic acid 200/250	Total requ'mts of Fraction 200/250	Tri-methyl ether	Methyl adipic acid	Tons p.e.
1) Ester No. 515			700	2570			2570			
2) 425									1000	
3) 623						2107	4215			
4) Ester for Mollit	1900	700	145	520			520	573		
5) Ester for weapon oil	280	90			1372			360	885	
6) Carbonoxylic acid							1200		115	
7) Ester 504		3470	1177			600				
Total	2180	4260	2022	3090	1372	2707	8505	933	1735	
									3135	
Location Schkopau										
Ester No. 515			840	3085						
Total			840	3085			3085		1200	
							3085		1200	
Location Auschwitz										
Ester No. 515			2925	10730			10,730			
426						1800	3,600	490	4180	
			2925	10,730		1800	14,330	490	4180	
Sum Total	2180	4260	5787	16,905	1372	4507	25,920	1040+	8515	also I.G. requirement 440
								1823		explosive 680
								2463		

Total of carboxylic acid 5879

Continuation of Table II

		Alcohol fraction				Carboxylic acid		Total requ'mts of	Tri-methyl ether	Methyl adipic acid	
		140/ 160	160/ 180	180/ 200	200/ 250	140/ 180	200/ 250	Fraction 200/ 250			in tons per annum
Case B of Table I	Location Leuna										
	1 to 6 as above 7)	2180	790 2960	845 1003	3090	1372	2707	8505	933	1400 1478	
	Total	2180	3750	1845	3090	1372	2707	8505	933	2878	
	Schkopau & Auschwitz										
	as above			3865	13815		1800	17415	490	5380	
	Sum Total	2180	3750	5713	16905	1372	4507	25920	1423 1040+ 2463	8258	+ required for I.G. explosives
Case C of Table I	Location Leuna										
	1 to 6 as above 7)	2180	790 1480	845 502	3090	1372	2707	8505	933	1400 739	
	Total	2180	2270	1347	3090	1372	2707	8505	933	2139	
	Schkopau & Auschwitz										
	as above			3865	13815		1800	17415	490	5380	
	Sum Total	2180	2270	5212	16905	1372	4507	25920	1423 1040+ 2463	7519	+ required for I.G. explosives

Provisional estimate of tank trucks required for the despatch of alcohol for the Ester plan

Given: production distributed according to Table I
Raw material requirement " Table II Case A
Raw isobutyl oil production:

Leuna	180,000 tons p.a.
Oppau	165,000
Heydebreck	890,000
Auschwitz	265,000
	1, 500,000 tons p.a.

Carboxylic acid plant in:
Leuna: about 6000 tons p.a.
possible addition
later of 3000 tons.p.a. Auschwitz

Oxo plant for about 11,000 tons p.a. in Auschwitz
This plant is to be operated on: 1) The fraction 75-200^0 of the first-run oil of the manufacture of raw isobutyl oil, which is transported to Auschwitz for this purpose, and is there distilled with a yield of 60%, 2) Deposits from Ester manufacture at Auschwitz.

Ester deposits available at Auschwitz: $\frac{2915 + 795}{2}$ = 1865 tons

Required for Oxo plant	10707
Covered by deposits from Ester production	1865
To be covered by first run oil	8842 = 15,700 crude 1st run oil
Available at Auschwitz	2,900
To be transporte to Ausch.	12,800 tons

Turn-round of the tank trucks: from Oppau or Oberschlesien to Central Germany 14 days
from Heydebreck to Auschwitz 4 days

Add 15% to the calculated number of tank trucks as a safety margin and for repairs.
Load per tank truck reckoned as 15 mm^3.

Number of tank trucks required without provision for repairs, etc. 70.27
with provision for repairs, etc. 82 trucks

Also required: 6 aluminium trucks (content 20 m^3) for transporting carboxylic acid to or from Auschwitz.

Table IV

Alcohol fraction 140-160 no transport

	Reqd. in tons p.a.	available in works	Transport to middle Germany m³	 tons p.a.	 from middle Germany m³	 tons p.a.	 from Heydebreck to Auschwitz tons p.a.	 m³	Req. for loading at Auschwitz long turn round	 Auschwitz short turn round	Req. tank-wagon loads long turn round	 short turn round	Remarks
Alcohol fraction 160-180													
Oppau				1155									
Schkopau													
Merseburg	4260	1260											
Heydebreck													
Auschwitz				1855									
			3600	3010					240		9.2		
Alcohol fraction 180-200													
Oppau			590	495					39				
Schkopau	840												
Merseburg	2022	540											
Heydebreck			2210	1837			833	99	147	66		0.73	
Auschwitz	2923	795*											* with 1287 tons from Oxo plant
		1335	2332	2800			833	99	185	66	9.2	0.73	
Alcohol fraction 200-250													
Oppau			2180	1816					146		5.6		
Schkopau	3085												
Merseburg	8505	1980											
Heydebreck			9280	7795			1995	2370	617	168	23.7	1.74	
Auschwitz	14,330	2915*											* with 9420 from Oxo plant
	25,920	4895	11,460	9610			1995	2370	763		29.3	1.74	10,707 used in Oxo plant
First run oil for Oxo plant							from Auschwitz						
Oppau							1000	1420		25	3.7		* Raw first run oil from which
Merseburg							2000	2880		192	7.4		
Heydebreck							9800	14,200		945		10.4	8842 t of firstrun oil fractions to be
Auschwitz	15,700	2900									11.1		
							Total of tank-wagon load				11.1	10.4	produced by distillation at Auschwitz
							12,800	18,800		1232	57.8	12.47	= 70.27 t-wagon

Organic Division

Leuna Works, 29th June, 1942.

Raw materials reqd. for Ester plan in tons per annum

	Annual reqmts	Composition	Required for SS Oil	Required for V Oil	Required for R Oil	Required for Mesulfol	Ester	Required for Isobutyl oil fraction: Total Alcohol	140/160	160/180	180/200	200/250	Required for: higher acid	lower acid	Methyl adipic acid or kresol	Ps	Pentaglycol
Cold temp. aero engine oil	13,500	75% SS oil	13,900														
		15% Ester 515					2750	4550			970	3,550			1430		
		10% 426					1850	4510				4,510	1670			450	
Cold temp. motor oil	25,000	50% SS oil	12,500														
		40% Ester 515					10,000	16,500			3500	12,850			5160		
		10% 426					2,500	5,000				6,520	2260			610	
Y axle oil	6,600	60% R oil			3960												
		20% V oil		1320			(3100)*	(5450)*							(1600)*		
		20% Ester 504					1320	2110		1480	630				740		
Cutting oil	500+	100% Ester 623					500	665			145	520			235		45
Weapon oil	500	47% Ester 658					235	375	280	90					115		
		45% V oil		225													
		2% SS oil	10														
		6% Mesulfol				30											
Aero engine pressure oil	400	95% V oil		380													
		5% SS oil	20														
Mollitt L 85	1200+	Ester 910						2600	1900	700				1392		360	
Reqd. for Ester plan			26,430	1925	3960	30	19,155	37,250	2180	2270	5245	27,550	5315	1372	7880	1420	45
Reqd. by Army															(8560)*	600	
Reqd. by I.G.							1,200	3,600		2400		1,200	600			440	
			26,430	1925	3960	30	20,355	40,850	2180	4670	5245	28,750	5915	1372	7520	2460	45

° Estimated

* pencil alteration on original document.

			Isobutyl oil fractions 140/160	160/180	180/200	200/250
Leuna	180,000	tons p.a. raw isobutyl oil	4,140	1,260	540	1,980
Oppau	165,000	" " " " "	3,800	1,150	495	1,810
Auschwitz	265,000	" " " " "	6,095	1,855	795	2,915
Heydebreck	890,000	" " " " "	20,500	6,230	2,670	9,800
	1.500,000	" " " " "				
		reqd.	34,535	10,495	4,500	16,505
		balance	+32,355	+5,825	-945	-12,255

	1942	1943	1944	1945	1946	
Production of SS oil (without Politz & Rhenania)	93.0	15.500	45,575	63,500	64,500	t
" " " " with new SSoil plant in [illegible]	–		–	76,000	77,000	t.

Organic Department

Leuna Werke 25th June 1942
Dr.Ha./Me.

Comparison between the raw materials required and available for the Ester plan, in tons per annum

	Required					Available				
	Isobutyl oil fractions					Isobutyl oil fractions				
	140-160°	160-180°	180-200°	200° End	R oil	140-160°	160-180°	180-200°	200°End	R Oil
Oppau	-	-	-	-	-	3,790	1,155	495	1,815	120
Schkopau	-	-	1,400	5,140	-	-	-	-	-	600
Merseburg	284	3,966	775	12,160	3,960	4,140	1,260	540	1,980	1,050
Auschwitz	-	-	3,600	11,220	-	6,100	1,855	795	2,915	-
Oxo plan									ca. 11,500	
Heydebreck	-	-	-	-	-	20,570	6,230	2,670	9,790	1,920
Moosbierbaum	-	-	-	-	-	-	-	-	-	180
	284	3,966	5,775	28,560	3,960	34,600	10,500	4,500	16,500 (with Oxo ca 28,000)	3,870

	Annual Requirements	Composition	SS Oil	V Oil	R Oil	Mesulfol	Ester	Total Alcohol	140/ 160	160/ 180	180/ 200	200/ 250	L-Acid	P_3	Methyladipin-acid	Pentaglycol
Low temp. aero-engine oils	18500	75% SS-Oil	13900													
		15% 515					2760	4620			970	3550			1380	
		10% 426					1840	4510				4510	2855	450		
Y axle oil	6600	60% R-oil			3960											
		20% V-oil		1320												
		20% 504					1320	2110		1480	630				740	
Low temp. motor oil	25000	50% SS oil	12500													
		40% 515					10000	16350			3500	12850			5000	
		10% 426					2500	6120				6120	3060	610		
Cutting oil	500	100% 623					500	665				145	520		235	45
Weapon oil	500	47% 465					235	375	280	90					115	
		45% V oil		225												
		2% SS oil	10													
		6% Mesulfol				30										
Aero engine pressure oil	400	95% V oil		380												
		5% SS oil	20													
Required by Army			26430	1925	3960	30	19155	34655	280	1570	5245	27550	6315	1060	7520	45
by I.G.							1200	3600	-	2400	-	1200	600	600 800	-	-
			26430	1925	3960	30	20355	38255	280	3970	5245	28750	5915	2460	7520	45
		Leuna	180,000 tons per annum						4140	1260	540	1980				
		Oppau	165,000 " " "						3800	1150	495	1810				
		Auschwitz	265,000 " " "						6095	1855	795	2915				
		Heydebreck	890,000 " " "						20500	6230	2670	9800				
			1,500,000 " " "						34535	10495	4500	16505				
									+34255	+6525	-745	-12255				

	Annual Requirements	Composition	SS-Oil	V-Oil	R-Oil	Mesulfol	Ester	Totel Alcohol	140/160	160/180	180/200	200/250	Propylene	L Acid	Methyladipinacid	Pentaglycol	P3
Low temp. aero engine oils	18500	75% SS oil	13900														
		15% 515					2760	4520			970	3550			1380		
		10% 1153					1850	1120				1120	925	560		835	
Y axle oil		60% R oil			3960												
		20% V oil		1320													
		20% 504					1320	2110		1450	630				740		
Low temp. motor oils	25000	50% SS oil	12500														
		40% 515					10090	16350			3600	12850			5000		
		10% 1153					2500	1520				1520	1250	760		380	
Cutting oil	500	100% 623					500	668			145	520			285	45	
Weapon oil	500	47% 465					235	375	280	90					115		
		47% V oil		225													
		2% SS oil	10														
		6% Mesulfol				30											
Aero engine pressure oil	400	95% V oil		380													
		5% SS oil	20														
Required by I.G.			26430	1925	3960	30	19165	25560	280	1570	5345	19550	2175	1320	7520	600	-
							1200	3600	-	2400	-	1200	-	600	-	-	1400
			26430	1925	3960	30	20365	29250	280	3970	5245	20760	2175	1920 x)	7520	600	1400
Available Alcohols 1.5 mill. t									34535	10495	4500	16505					
									+ 34255	+ 6525	-745	-4255					

x) Total chlorine required, tons p.a.

	Annual Requirements	Composition	SS-oil	V Oil	R Oil	Mesulfol	Ester	Total Alcohol	140/160	160/180	180/200	200/250	Ethene or Propyl	L acid	P_S	Methyl adipic acid	Penta-glycol
Low temp. aero engine oils	18500	75% 1155					13800	9820				9820	7450	4910			2030
		25% 515					4700	7700			1650	6050				2350	
Y axle oil	6600	60% R oil			3960												
		20% V oil		1320													
		20% 504					1320	2110		1480	630					740	
Low temp. motor oils	26000	50% SS oil	12500														
		40% 515					10000	16350			3500	12850				5000	
		10% 1153					25000	1520				1520	1250	760			320
Cutting oil	500	100% 623					500	665			145	520				285	45
Weapon oil	500	47% 455					235	375	280	90						115	
		47% V oil		225													
		2% SS oil	10														
		6% Mesulfol				30											
Aero engine pressure oils	400	95% V oil		380													
		5% SS oil	20														
Requirements by I.G.			12530	1925	3960	30	33055	39640	280	1870	5925	29760	8700	5670	-	8490	2395
							1200	3600		2400	-	1200		600	1400		
			12530	1925	3960	30	34255	42140	280	3970	5925	30960	8700 x)	6270	1400	8490	2395
Available alcohols 1.5 mill. t								34536		10495	4500	16505					
								+34255		+6525	-1425	-14455					

x) Total chlorine requirement 17420 tons p.a.

	Production tons p.a.	Ethane requirements	Ethylene requirements	Estimated date for commencing production
Leuna I	10,000	20,000	-	-
Leuna II	7,000	14,000	-	1.4.1944
Schkopau	10,000	-	12,500 from C_2H_2	1.4.1943
Heydebreck I	22,000	37,000	-	1.1.1944
Heydebreck II	10,000	-	12,500 from coking gas	1.10.1944
Moosbierbaum	3,500	6,000	-	1.3.1944
Oppau	2,000	-	2,500 from coking gas	1.4.1944
Pölitz	12,500	17,000	2,500 from coking gas	1.10.1944
	77,000	148,000	30,000	
for the Army	12,500	17,000	2,500	
for the Air Force	64,500	131,000	27,500	

Of the 64,500 tons of SS oil, 13,900 tons are required for the manufacture of 18,500 t of low temperature aero engine oil, so that only 50,600 tons are available for mixing with mineral oils. If the 18,500 tons of low temperature aero engine oils were produced as ethylene-oxide ester oils, this would require 7,500 tons of ethane (= 4,500 tons of SS oil). In this case the volumes of lubricating oil at the disposal of the Air Force would be as follows :-

64,500 - 4,500 = 60,000 tons p.a. SS 906
+18,500 " " Ethylene-oxide - Ester oils
78,500 " "
+26,000 " " paraffin
+77,000 " " mineral oil
181,500 " "

Department for
Economic Research

Leuna Works
18th June, 1942

Notice

Discussion in the Reichsamt on 17.6.1942

Those present were: Dr. Kronopuhl (Reichsamt)

Dir.Dr. Giesen }
Dr. Zorn } Leuna
Dr. Käding }

Subject: Development of Ester oil (figures in tons per annum)

For the following products:

18,500	low temperature aero-engine oil
6,600	Y oil, red
25,000	low temperature motor oil
500	cutting oil
500	weapon oil
400	pressure oil

the following quantities of ester or alcohol are required:

low temperature aero-engine oil	4,600
Y oil	3,100
low temperature motor oil	12,500
cutting oil	500
weapon oil	235
pressure oil	-

≙ about 21,000 of ester or about 42,000 of alcohol (crude fractions)

Between 160 and 250°, about 32,500 tons per annum of crude fractions become available, which means that there is a demand for more alcohol, which can be met by Oxo-treatment of the neutral oils produced by esterifying.

There are also required :

about 7000 methyladipic acid
about 8000 Leuna - carboxylic acid

Oxo plant for about 10,000 tons

In the course of the discussion, the following proposals were made to Dr. Kranepuhl without any commitment being entered into. They will be investigated more closely at Leuna.

How the demand for esters can be met :-

Leuna hopes to produce	4000 esters
Schkopau has a plant for	3000 esters
Auschwitz report that they are all ready to produce	4000 esters

New proposal

At Leuna (based on isobutyl oil Leuna + Oppau) an additional	2000 esters
At Auschwitz (based on isobutyl oil Auschwitz + Heydebreck)	8000 esters
	21,000 esters

Methyladipic acid

Available at Schkopau	3000
" " Leuna	2400
	5400

There is thus a deficiency of about 1600, to be met out of phenol production at Auschwitz.

We suggested that these 1600 tons should be met from normal adipic acid at Leuna, so that for a time this amount would be lost to the synthetic section. The necessary iron has been released by the Government Department. Only the necessary priority is lacking at the moment. As the orders for the plant have already been placed, it could be erected in a very short time, once the building workers had been made available.

Carboxylic acid

At Leuna there is at present a carboxylic acid plant for about	1200,
which is to be extended within the framework of the ester plan to produce	4200
The missing	3800
can be produced in Auschwitz from an alcohol base.	

Oxo-plant

There is a plant at Leuna for about	3000
The remaining 7000 odd are to be produced at Auschwitz using the neutral oil of the ester plant for a base.	

We have promised to lay before Dr. Kranepuhl a rough draft, based on the above figures, by 26.6.42. This will need to be checked in detail. From it, it will be possible to deduce the quantity of iron required for the new Ester plan, when and at what rate the iron will be allocated, how many building workers are required - and when - if the plants are to be ready to start production by winter 1943, the amount of energy required, and how many tank trucks or how much iron will be required for this.

(signed) Räding.

Diag. as in Folder XIV

Ref. FD 4975/45 - Folder XXVIII

From the Commissioner for the 4-year plan
The Superintendent for special problems of the
Chemical Production,
to the C. in C. Armed Forces, Defence Economy and
Armament Division.
Attention: Col. Pecht

29.8.1941

Synthetic Plant Auschwitz

With the building declaration of 2.5.41 a plan was submitted for a synthetic plant at Auschwitz, providing for the production of :

23,000 tons p.a. gasoline
22,000 tons p.a. middle oils (diesel)
30,000 tons p.a. paraffin

When the new Goering plan was prepared, the Air Ministry requested that if possible 100% of the total aviation fuel production should be high duty gasoline. From the raw materials contained in the waste gases of hydrogenation plants etc., a proportion of only 75% can be achieved by means of alkylate plants. The minimum iso-octane content demanded by the Luftwaffe is not attained, and additional iso-octane must be produced to reach the standard for high duty fuel. This is possible if the processing of synthetic gases at Auschwitz is not carried out according to the declaration of 2.5.41; this project should be replaced by one for the production of 25,000 t/year of iso-octane, which would also give 11,000 t/year motor gasoline, 4,000 t/year of higher alcohols and 5,000 t/year propanol. This switch-over of the plan would involve no change in the gas production. The small loss of motor gasoline (12,000 t/year) is definitely admissible in view of the production of a much larger quantity of iso-octane. Moreover it will be possible to import motor gasoline until the new plant will start operations in July, 1943. The loss of 30,000 t/year of paraffin is not so great for the future synthetic grease production; it has indeed been proved that only about one-third of the paraffins obtained by this method are suited to fatty acid oxidation. Moreover, as cobalt supplies appear to be improving it may be possible to produce paraffins best suitable for the preparation of fatty acids by the conversion of existing Fischer plants. The loss of 22,000 t/year of diesel oil should likewise be covered by imports from July, 1943. Should the diesel oil shortage still exist, there is the possibility to convert one of the hydrogenation plants, e.g. Leuna, and produce a quanity of diesel fuel corresponding to the additional aviation fuel production, instead of the aviation fuel prepared there.

The orders for the materials required at Auschwitz have been placed to cover all parts not affected by the alteration of the plan. As , however, also the orders for the Equipment likely to be altered must soon be dispatched, a prompt elucidation is required I should also point out that this conversion offers at the same time the possibility to carry out the augmented methanol programme.

(Signed) ------

AUSCHWITZ GASOLINE

QUANTITY DIAGRAM AS AT 6.6.41.

75000 t.p.a. Gasoline = 8.57 t.p.h.

7500 " Gasoil = 0.857 "

365 days @ 24 h/d = 8760 h/yr

Yield per Nm³ CO+H₂ = 140g Gasoline + 14g Gasoil of Gasoil 00% in residual gas + 60% in product

Supplementary Diagram
- a) Synthesis plant
- b) Treatment of gasoline with fuller's earth
- c) Treatment of residual gas with A-carbon

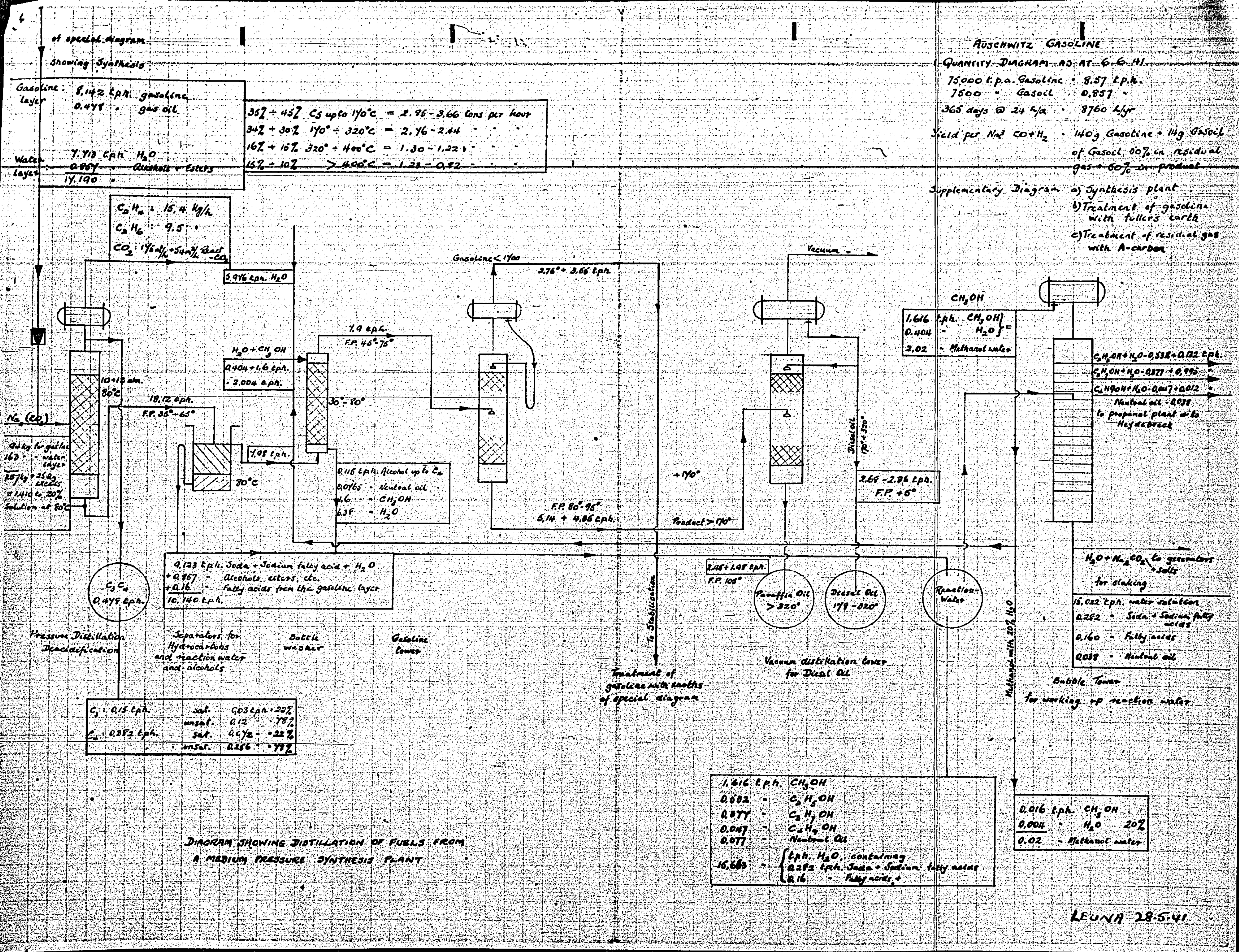
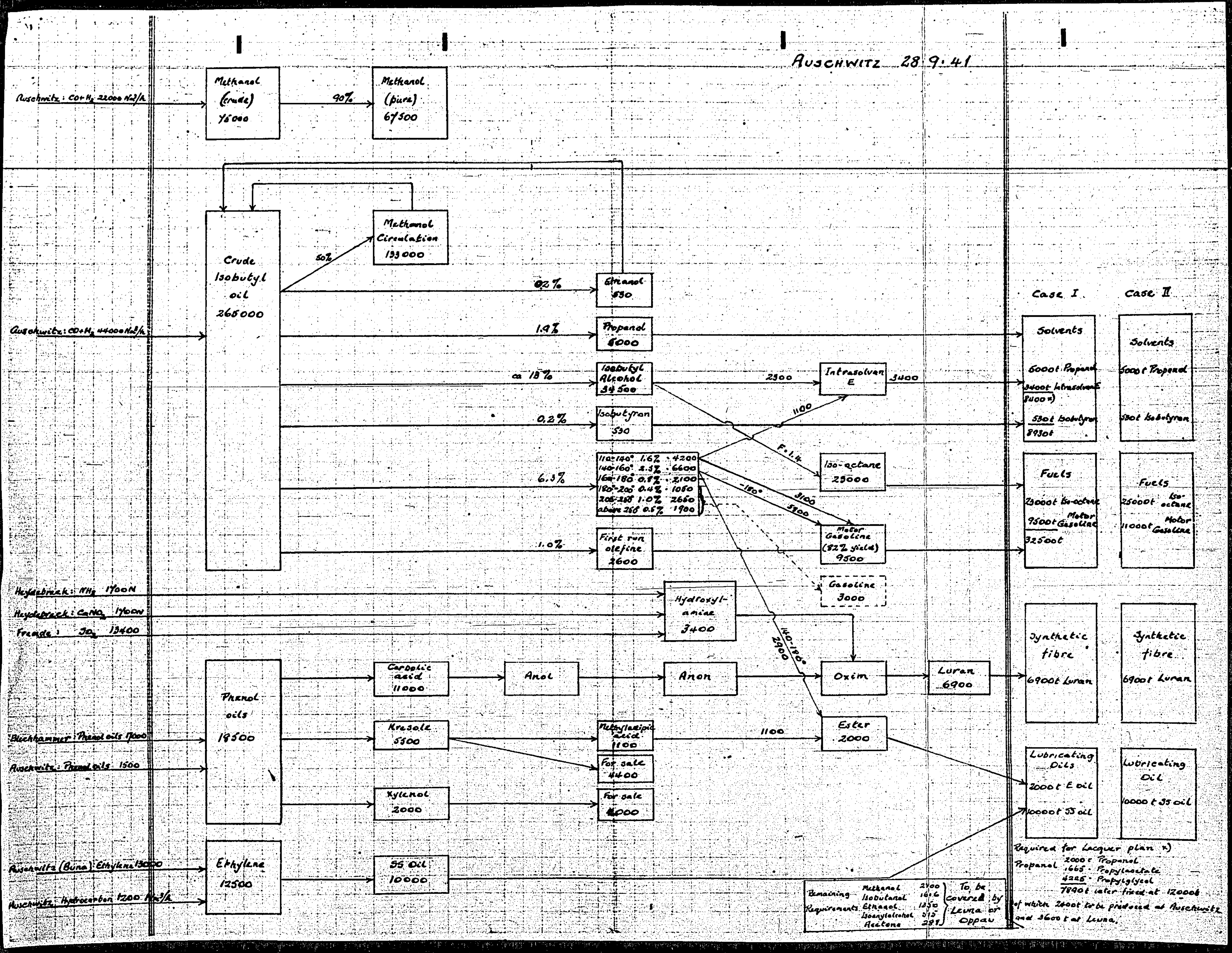


DIAGRAM SHOWING DISTILLATION OF FUELS FROM A MEDIUM PRESSURE SYNTHESIS PLANT

LEUNA 28.5.41

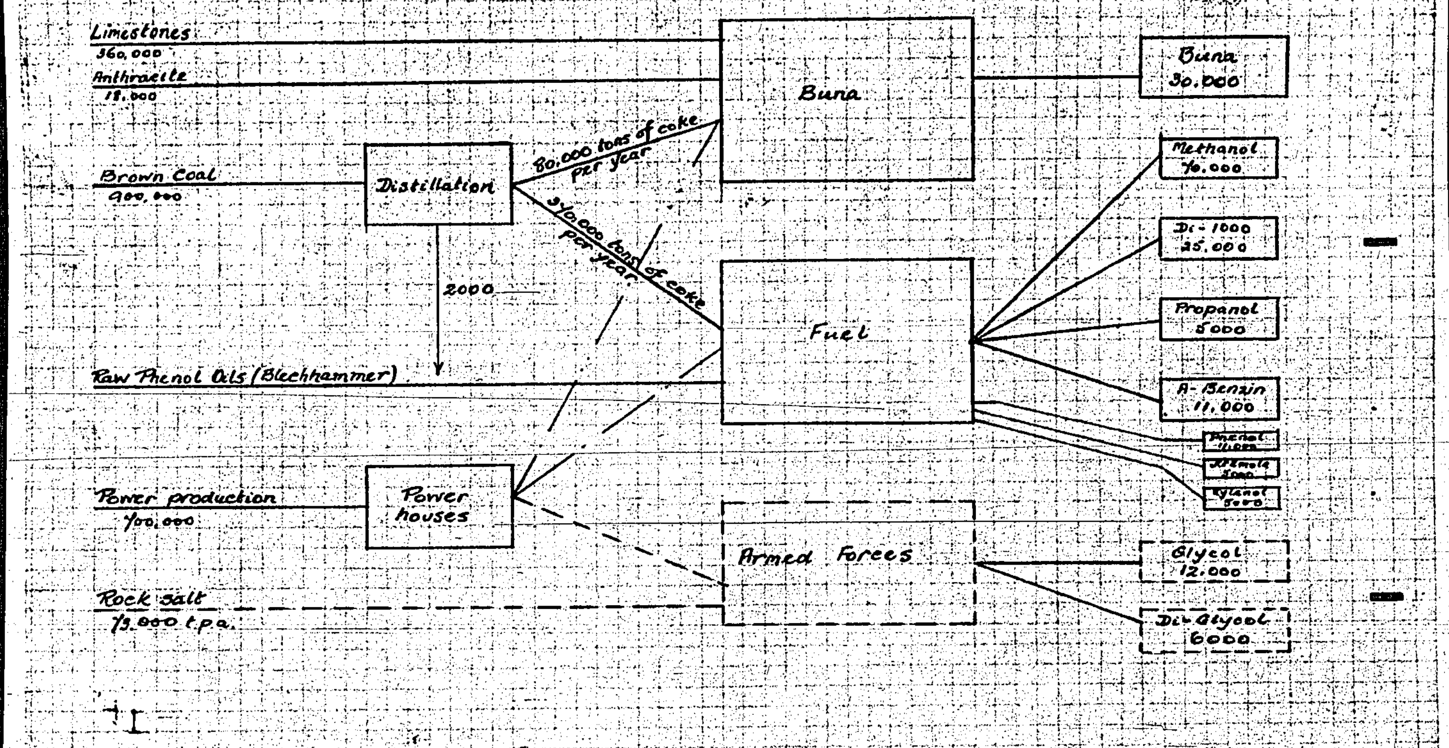


Remaining Requirements	Methanol	2700	To be covered by Leuna or Oppau
	Isobutanol	1616	
	Ethanol	1350	
	Isoamylalcohol	515	
	Acetone	289	

Required for Lacquer plan x)
Propanol 2000t Propanol
1665 · Propylacetate
4225 · Propylglycol
7890t later fixed at 12000t
of which 2400t to be produced at Auschwitz and 3600t at Leuna.

PRODUCTION AUSCHWITZ

in tons per year



Ref. FD 4075/45 - Folder XXX.

Organic Division II

Research and Development problems under investigation

Process	
Mepasin manufacture Mesapon production Operators: 1 lab. technician 1 junior chemist.	Preparation of block-like detergents on a pure Mersolat basis by working out suitable solidifying agents. The block soaps of today are still prepared from fatty soaps. The fats used here are lost for nutritional and other important purposes
Process. Mesamoll manufacture Operators: 3 assistants 1/1 1 junior chemist	Experiments to find new corrosion-protectors and bore-oils on basis of amino-carboxylic acids were carried out in order to remedy the great want of suitable materials in this field
Process: Phenol operation Operators: 1 lab assistant 1 assistant	In the crude pyrocatechin fractions of the Brüxer Phenosolvan-Extr., besides the pyro catechins considerably quantities of resorcinol were present. A method was sought for the technical preparation of the resorcinol which serves as the starting material for important resins
Process: Anol manufactures Operatores: 1 lab assistant 3 assistants 1/1	Owing to the shortage of phenol the conversion of pyrocatechin into cyclohexanol is of interest. The tests serve to investigate the most favourable reaction conditions and conversion for the technical scale.
Process: Anon- and methyl-adipic acid manufacture Operators: 1 lab. assistant 1 process worker 1 assistant 1/2	Determination of the physical data and chemical properties of the methylcyclohexanones and of their anoles in so far as these are useful for separating the products and for preparing methyl adipic acid. Elucidating the oxidation of the o, m, and p. methylcyclohexanones with air and investigating the oxidation products which arise in the process with the the aim of directing the course of the oxidation, oxidising mixtures of m, p-methyl cyclohexanones and m, p-methyl cyclo hexanols with the aim of saving the methyl cyclohexanone oxidation.
Process: Luran manufacture and K.V.P. laboratory process Operatores: 1 chemist 1 chemical assistant 1 chem. assistant (F.) 1 lab. asst (F) 1/1 3 assts (F) 1/1 2 assts (m) (1 French P.O.W., 1 Czech person)	Polyamides at low temperature can be used only to a limited extent owing to their brittleness. It is important to find new compounds which have good properties (stability, resistance to low temperatures, low volatility) Elucidating the chemical reaction by rearranging the cyclohexanonoxium to give caprolactam. Physical and chemical properties of caprolactam, of their derivatives and of the substances which give the former. Experiments are carried out to replace the discontinuance process for the preparation of caprolactam by means of a continuous process.

The staff used in the research and development experiments consisted of:

1 chemist
4 laboratory assistants
1 lab. ass. (F)

2 technicians
1 assistant
2 assts (1 F. Pow, 1 Czech)

2 junior chemists
1 process worker (F) 1/1
9 assistants (F) 1/1
1 assistant (F) 1/2

Total : 24 members of the staff

Problems which cannot be carried out owing to shortage of manpower

Caprolactam which serves ad the starting material for the manufacture of igamides is obtained by rearranging cyclohexanon oxim. The rearrangement process has to be improved upon: similarly experiments have to be carried out in order to investigate how by using the same test-plant the purity of the oxim and the lactam can be improved upon.

Required for this purpose: 1 chemist
1 laboratory assistant

Address of the laboratory assistant to whom reference has to be made:

Wilhelm Volk born 17.4.1910
resident of Darmstadt.
Feldpost no. 42527

Ref. FD 4975/45 - Folder XXXII

Memo dated 19.4.44

The replacement of "Kogasin" by other basic materials for Sulfo-chlorination - report for the "Waro" experts' conference 28.3.1944.

Generally speaking Kogasin has proved to be a very good initial substance for Sulfo-chlorination. Its cost-price, however, is relatively high, for it is chemically a very homogeneous, pure, synthetic paraffin oil. Its production depends also upon the number of existing "Fischer" plants, thus limiting the quantity at our disposal. Finally one must not forget the Government's control of raw materials which enable the authorities to direct the distribution of Kogasin according to the actual situation of these raw materia Therefore an attempt was very soon made to substitute other cheap and easily available commercial oils for the Kogasin. A mineral oil product was obviously indicated for this purpose. If the production of capillary active substances is also aimed at, one should first of all turn to the mineral-oil distillates used for Diesel oils. Director Dr. HEROLD spoke already briefly in the "Waro" session of February 2nd, 1943 about the possibilities of substituting mineral oil products for Kogasin II in order to produce "Mersolate". Therefore a short summary is here repeated of the results before dealing with the more recent experiments.

It is not possible to sulfo-chlorinate mineral oils if they are not treated beforehand, but Kogasin II can in principle be sulfo-chlorinated without any preliminary treatment though, because of the chlorine addition to the olefinic bonds, the final product contains more chain chlorine compounds than the sulfo-chlorinated "Mepasin". In the case of paraffinic mineral oil distillates it is sufficient to use the conventional mild hydrogenation as a preliminary treatment for the sulfo-chlorination which is carried out at a temperature of approximately 380°, a temperature which is higher by about 50° compared with the Kogasin. Nickel tungsten sulfide is present as a catalyst. The oils which are then obtained can be sulfo-chlorinated, though a higher content of chain chlorine compounds can always be noticed in the final product when compared with the Mersols obtained from Kogasin. When high density mineral oils are used, a large proportion of which will be readily absorbed in sulfuric acid, we recommend strongly treating these oils before the hydrogenation with liquid SO_2 or with another solvent of greater catalytic efficiency. This will diminish the content of cyclic compounds in the oil which facilitate the formation of chain chlorine compounds. Such oil can in principle be sulfo-chlorinated after hydrogenation, though the reaction is somewhat slower in comparison to Mepasin and though the content of chain chlorine compounds is a little higher. The following table shows the difference when the various basic oils are transformed to Mersol:

Table I

Product	Duration of sulfo-chlorination	Hydrolysable chlorine	Chain chlorine compounds	Density
Rumanian paraffinic oil pre-extracted and hydrogenated. 240-320°	11 hours	5.2	1.3	0.801
Mepasin	8 hours	5.3	0.8	0.776

There was no difficulty in saponifying the Mersols obtained from the middle oils to Mersolates. The colour of the Mersolates, however, is often unsatisfactory. Whilst Mersolates on a basis of Kogasin are colourless or slightly yellow, those on a mineral oil basis show colours varying from yellow to chocolate-brown. The colour is more intensive in those cases where more cyclic compounds are found in the basic oil, particularly such with condensed ring-systems, e.g. of the Decalin type. Therefore colourless or only faintly coloured mineral oil Mersolates are only obtained from mineral oils which either originally contain only a low proportion of cyclic hydrocarbons or from which a large proportion of these undesirable cyclic constituents have been extracted by means of a pre-treatment with solvents. Great progress was made in the production of light mineral oil sulphonates by adding a little sodium hydrosulphide to the saponifying solu- tion before vaporizing. But the greatest problem in the production of mineral oil Mersolates consists in restoring the recycle oils which are given off during the saponifi cation of Mersol H. They can again be sulfo-chlorinated without further preliminary treatment in the case of Mepasin, but mineral oil products must at first be hydrogenated in order to eliminate the substances which would inhibit the sulfo-chlorination. This hydrogenation itself runs smoothly, but it involves problems of corrosion because the recycle oils contain chlorine. These corrosion problems appear to have been solved in laboratory tests, but need confirmation by tests on a large scale.

An extensive use has recently been made of Mersol H in which the hydrocarbons accom- panying the sulfo-chloride do not appear as a recycle oil after the conversion but remain in the final product. These are the Höchst drilling oils which are produced by convert ing the Mersol H into the corresponding sulfamide - the Mesulfan H - and by the further action of chloroacetic acid on the sodium compound of the Meulsfam H. The effective sub stance of the drilling oils is the sodium salt of the sulfo-amido-acetic acid of Mepasin. But the presence of hydrocarbon oils is also necessary. This is in fact the case, since Mersol H carries approximately 50 to 55% hydrocarbons. The whole process necessary with recycle oils is thus eliminated when producing drilling oils, and therefore the use of other oils instead of Kogasin commends itself very strongly for the production of Mersol which we used for making drilling oils.

The drilling oils hitherto usually manufactured for the metal engineering industry were on the basis of spindle oil. Since the new Höchst drilling oils should be substitutes for these products, it was obvious that the Government placed spindle oils at our dispose But some difficulties were met when using these oils. The hydrogenation had to be carried out first of all by means of the spray process. The yields, however, were quite small considering the time and space needed. Secondly it was not possible to sulfo- chlorinate the oils smoothly. This was particularly true for oils obtained by means of relatively mild hydrogenation at 330° preserving as much as possible the molecular size o the hydrocarbons. These oils proved to be very unsatisfactory for sulfo-chlorination. Firstly it was found that the sulfo-chlorination was very slow, and secondly, it was foun that considerable quantities of chain chlorine compounds were formed. This was very undesirable. These products can therefore not be used for the manufacture of drilling oil because of the danger of corrosion caused by the liberation of halogen. We even observed the formation of notable quantities of sulfuryl chloride during the sulfo-chlori ation of the spindle oils which were treated preliminarily in this way. Thus such products should not be used for sulfo-chlorination. The results were better when hydrog enation of the spindle oils was carried out at higher temperatures. But then it was fou that the hydrocarbon molecules cracked in part and that these products had boiling points upto the range of the boiling point of gasoline. Generally hydrogenation was carried ou in such a way as to obtain products containing not more than 20% constituents boiling below 200°. After distilling the constituents which boiled below 200° and perhaps bleaching the residue; this residue could be sulfo-chlorinated with greater speed, but i was even more important that the quantity of chain chlorine compounds was considerably less. By the intensive treatment with hydrogen the original oil has obviously been freed from the substances inhibiting the sulfo-chlorination (chain inhibitors). But the values for chain chlorine compounds are still far above those which were found for Mepasi

Table 2

Product	Hydrolysable chlorine	chain chlorine compounds
Mepasin	5.3	0.8
Spindle oil hydrogenated at 340°	6.0	3.2
Spindle oil hydrogenated at 380°	5.6	2.0
Paraffin, Rumanian Mineral oil	5.2	1.3

In spite of these facts Mersol H products were obtained in many cases, particularly from spindle oils from Dollbergen, and the Höchst works considered these Mersol H products suitable for the manufacture of drilling oil. Unfortunately the Government permit for this kind of spindle oil was unobtainable. All types of spindle oil released by the Government were subject to a preliminary treatment involving hydrogenatio and cracking. The products of this preliminary treatment were ill-suited for the manufacture of Mersol H used in drilling oil factories. This means that spindle oil cannot be considered at present as a substitute for Kogasin for the purpose of drilling oil production on a Mepasin sulfonate basis. The end of the tests showed that a cracking hydrogenated spindle oil of low viscosity of Messrs. Brabag Zeitz was nearly as good as the oils from Dollbergen. Some of the Diesel fuels of Austrian and Polish origin were released by the Government but proved also to be unsuitable for the manufacture of Mersol H, since they formed too many chain chlorine compounds after hydrogenation. Oils of this type can probably only be used for the production of Mersol H if they are pre-treated with liquid sulphur dioxide before subjecting them to hydrogenation. Thus a Hungarian gas-oil was treated by extraction with liquid SO_2, and after hydrogenation a saturated oil was obtained with a density of 0.807. When sulfo-chlorinated a Mersol H with 5.3 hydrolysable chlorine and with 1.3% chain chlorine compounds was obtained, which means that this product was similar to the product which was obtained already from a highly paraffinic hydrogenated Rumanian gas-oil well suited for the manufacture of drilling oils. The Government, however, refused to release highly paraffinic.Rumanian gas-oils for the manufacture of drilling-oils. Other gas oils with a larger quantity of cyclic compounds could not be used, because no suitable "Edeleanu" plants were available and these plants are needed for the SO_2 extraction.

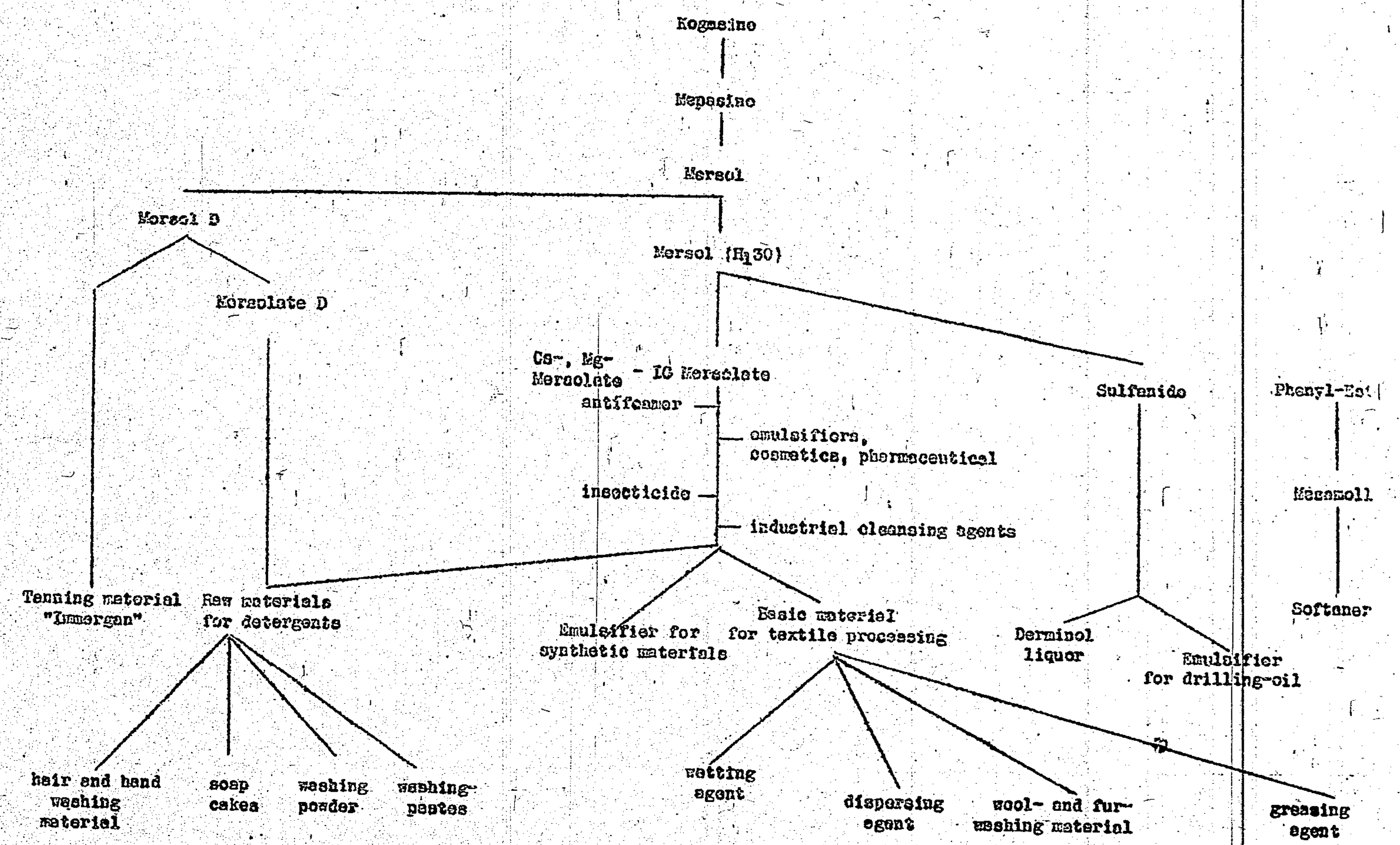
Some time ago two other industrial special products were tested as to their suitability for sulfo-chlorination. These are the first runnings of crude paraffin by Zeitz and the first runnings of lubricating oil by Pölitz.

The first product is formed when hydrogenating the Zeitz crude paraffin, because it has to be pre-treated by hydrogenation for the purpose of oxidation of the paraffin. This leads necessarily to a cracking, forming products of a lower molecular weight. When the fraction 230-320° is distilled off from the first running constituting approximately half of this first running, and when it is then carefully hydrogenated again at 320°, a saturated oil is obtained with the density 0.802 which is suitable for Mersol H production. The result is a Mersol H with 5.5% hydrolysable chlorine and 1.4% chain chlorine compounds. The product is in Höchst to be tested. The data show that is is probably suitable for the manufacture of drilling oils.

The other oil is formed by the cracking of hard paraffin, and the resulting olefins were then polymerised with $AlCl_3$. Thus a first running of lubricating oils is obtained. Its boiling point is within the range of 230-360° at a density of 0.792. It is easily hydrogenated. The density drops to 0.785 during this process without altering the boiling curve very much. This shows that it is a highly paraffinic product. The sulfo-chlorination gives in fact a Mersol H with 5.0% hydrolysable chlorine and 0.9% chain chlorine compounds, i.e. a product with approximately the same qualities as those which were obtained on a Kogasin basis. This Mersol H also is in Höchst for testing. The analytic data of this Mersol indicate that it will also be suitable for the drilling oil production. 100 tons per month would be available if the Government were to release these two oils which were just described, so that a planned development of the drilling oil production to a total of 700 tons per month would relieve to a certain extent the demands on Kogasin.

(signed) Smeykal

Mersol and its derivatives



Possibilities for the uses of Mersol or Mersolate as washing materials

A) Toilet

	Tons per year, Mersolat 100%	
Standard Fancy Toilet Soap	12,000	
Shaving Soap	4,160	
Shampoos	490	
Toothpastes	160	16,810

B) Washing Material

Washing powder	30,000	
Washing soap (curd soap)	4,400	
MS soap	5,800	
Fine washigg material	2,900	
Cleansing material of all kinds	4,800	47,900
	Total Mersolat	64,710

Required quantity of Kogasin	45,000 tons
"Rif" quantities for 1944	38,000 tons
Kogasin for non-soap Mersol (and other purposes)	14,000 tons

Uses of Mersol
apart from washing materials
1943

	Tons per year	
	Mersol or Mersolat of 100%	Manufactured products
Mesanoll	2358	3818
Drilling oils (Höchst)	1000	2300
Emulsifier for synthetic materials	630	900
Liquor oils (Licker-öl)	450	1640
Processing materials for textiles	250	291
Industrial cleansing materials	300	9000
Anti-foamer	173	484
Tanning material Immergen	90	110
Insecticide	75	1750

Memo dated 3.4.44

Present state, uses and prospective development of the Mersol D and Mersolate production

The Mersol plants at Leuna and Wolfen were recently enlarged in a relatively short time, and so the most urgent requirements of the washing material industry could be satisfied. The two Mersol plants had reached their expected output already in the beginning of 1942, and up to the beginning of 1944 a total quantity of approximately 187,000 tons Mersol D had been supplied. Leuna supplied 123,740 tons; Wolfen 63,254 tons. Table 1 shows the development of the Mersol D production during the last four years. At the same time the table shows the total supplies up to date of Mersol (calculated as Mersol D) and the present total capacity of the two Mersol plants.

The production reserves - shown in table 1 - could not be utilised because of the shortage in raw materials. It was not so much the small quantity of Kogasin, then available, but the insufficient supplies of sulphur dioxide and particularly chlorine. Thus the Mersol production had temporarily to be curtailed considerably in 1943 because of the shortage of chlorine. See table 2 (shortage of chlorine from August onwards).

In spite of the compulsory reduction of the Mersol production the cost price droppe again, so that the selling price for Mersol D could again be reduced to 67 Reichsmarks per 100 kg. from January 1st 1944. Table 3 shows the price development during the last four years.

The drop of the cost price is due to improvements in method and equipment (larger reaction vessels, corrosion resistant piping, lower costs for repairs, saving of raw material).

The production of washing materials with the help of Mersol D has now more and more increased, also in those industrial regions which are under Germany's supervision. This freed also natural fats for food or urgent technical requirements.

Table 4 shows the uses of Mersol D in the various border regions of Germany. The quantities are given in tons per year as released for these countries by the "Rif". The actual Mersol quantities used in these countries were smaller than planned which was due to traffic and transport difficulties and a shortage in other raw materials (lye, soda, etc.).

Mersol D has in any case been able to fulfil its war task in spite of certain deficiencies, when used for the production of washing materials.

It should, however, be noted that the disadvantage of Mersol D is its relatively high content of unsaponifiable constituents and of disulfonic chlorides. The disulfonates which are produced during the saponification have hardly any detergent properties.

These deficiencies of course very soon caused the development of improved products with increased efficiency. The decisive factor for this development was the fact that when the sulfo-chlorination was only partly carried out and was prematurely interrupted much less disulfo-chloride was formed. Now the Mersolates are produced from the compounds which had only been partly sulfo-chlorinated, i.e. from Mersol H, only half sulfo-chlorinated, or from the Mersol 30, only one-third sulfo-chlorinated. These Mersolates are mostly superior to the Mersolate D, produced from the Mersol D of the cleansing material industry, as regards their detergent properties, and it was found that it could be used in many more ways in other spheres.

We endeavour of course to substitute the Mersol D or the Mersolate D in the washing materials for Mersolates which were produced by us, since this would increase the "cleansing power" obtained from the basic raw material, i.e. the Kogasin. There was a conflict of opinions with a tendency against the processing of I.G. Mersolate - Mersolate H or 30 - with the slogan: "Fight for the soap kettle". The soap industry continues to quarrel, at times in an unfair and biased way. The noticeable pressure exerted by the various groups in the soap industry on the responsible authorities has to say the least greatly delayed the development of Mersolate plants which we wanted. But the I.G. Mersolate proved to be so clearly superior to the Mersolate D that it gained access to the soap factories even under these difficult circumstances.

Both Wolfen and Leuna have now developed smooth and simple methods for the production of improved Mersolates and the two works have already applied these methods in practical manufacture. The two methods differ a little. The essential principle, however, is the partial sulfp-chlorination. It should be mentioned here that also the problem of continuous partial sulfo-chlorination as a working process has already been solved, and it is probable that Wolfen and Leuna will shortly use it in their works.

Wolfen bases the production of Mersolate on Mersolate H or Mersolate 30, not quite half of which is sulfo-chlorinated, viz. 45%. Table 5 shows diagrammatically the Mersolate H production at Wolfen.

Continuous saponification of Mersol H with 50% lye in a given saponification mixture; thus the lye concentration is approximately 17% and the main quantity is separated hot, lower layer after cooling. Repeat oil separation by adding Methanol, then boil down to Mersolate of 70%. The Mersolate H is given off and obtained as a paste which can be easily pumped and stored. During this year it is expected to develop the Wolfen plant in such a way as to have a yield of 10,000 tons per year.

Leuna starts its Mersolate production by sulfo-chlorinating Mersol 30 only by a third. Table 6 shows the Leuna process as it was worked out in our experimental laboratory:-

Saponification with a caustic soda solution of 10%. Hot separation of the oil, cooling, separation of lower layer. Dilution of upper layer with approximately the same quantity of water, so that the oil can be removed practically without leaving a residue when boiled down in coil boilers. The Mersolate 30 is obtained on cooling drums in the form of scale, in pouring machines it is obtained in the form of tablets.

At present Leuna's Mersolate production is about 150 tons per month, but it will probably be increased to 300-400 tons per month during the next few weeks. Further developments are still under discussion. They are made difficult by the already mentioned resistance put up by the soap industry which is afraid of interference with their sanctum, viz. the kettle house.

Mersolate H and Mersolate 30 have already proved that they are superior to Mersol D or Mersolate D respectively as cleansing materials, but they can also be used for produc for which Mersolate D is only little or not at all suitable.

Here are the amounts of the Mersol products used as cleansing materials :-

Uses for cleansing materials in 1943

Mersol D	58,584 tons
Mersolate H paste	2,717 tons
Mersolte-scales	185 tons

The relatively small quantity of solid (scale) Mersolate was due to the present sma scale of manufacture. The solid Mersolate was furthermore mainly used for other purpos (emulsifier, textile processing materials, industrial cleansing materials).

The main quantity of Mersol D or Mersolate respectively was used in the rough washing powder for household use whilst approximately 7000 tons Mersol D and Mersolate H paste were used for the making of MS-soap for large laundries.

Mersol D is not so suitable for soap cakes (washing or curd soap, toilet soap, shaving soap). The small content of disulfonate in Mersolate 30 or Mersolate H, furthe the small amount of unsaponifiable chloride and sodium chloride facilitates considerably the working up with fats and fatty acids, so that many parts in the fatty ingredients of soap cakes can be replaced by Mersolate.

Even today fatty ingredients are still used for the production of the present day standard soaps with their high kaolin content, but they could now be exclusively made on the basis of Mersolate only with the aid of inorganic solidifiers.

According to a plan which was made some time ago further additional considerable quantities of Mersol in the form of the I.G. Mersolate can still be used. Table 7 show these possibilities for consumption in Greater Germany including Bohemia and Moravia. The quantities are referring to Mersolate of 100%.

45,000 tons of Kogasin would be required for about 65,000 tons Mersolate, whilst the "Rif" will probably only release 38,000 tons for cleansing materials for the year 1944. It should be noted here that Kogasin in the form of Mersol D does not give by far so much "washing power" as in the form of the I.G. Mersolate.

The numbers show in any case that even in the lean cleansing materials of today there are still considerable quantities of fat which can be replaced by Mersolate. The quantity for the raw materials necessary as a basis for Mersol, however, is limited as regards the Kogasin supply, for there are only about 52,000 tons of Kogasin available including the unsaponifiable proportion which is again obtained in the soap factories when using Mersol D. But Mersol and Mersolate are more and more used in other fields too and not only for the manufacture of cleansing materials. That means that for a number of important purposes another 12-16,000 tons of Kogasin will be required per year.

Thus the available quantity of 52,000 tons of Kogasin will be completely used up in the following way :-

38,000 tons for cleansing materials
14,000 tons for other purposes

We deal in another report with the possibility of using other hydrocarbons for the production of Mersol apart from the synthetic product Kogasin.

A "Mersol Family Tree" shows those Mersol products which have already gained some importance. Table 8 shows that Mersol and Mersolate are important in other fields too apart from their use as cleansing materials. The uses which were made of the Mersol and Mersolate quantities for purposes other than for cleansing materials in 1943 are shown by Table 9. The quantities are given in terms of Mersol or Mersolate of 100%, for the two match one another completely. The table also shows the quantities of the individual products which were made from them.

It can be seen that Mersol can now be used in many important fields, a development which is caused by the War in the first place. It can, however, be expected that these possibilities will continue to be further developed later in the open market, particularly at a time when these developments can be really freely exploited.

TABLES

Table 1 Development of the Mersol D production

Year	Leuna (tons)	Wolfen (tons)
1940	7145	–
1941	33610	10967
1942	41338	26056
1943	41644	26231
Total	123,737	63,254

Grand total 186,994

Capacity – Wolfen 40,000 tons per year
Leuna 65,000 tons per year

Table 3

Price Development for Mersol D

	RM/100 kg. Selling price	Cost price
1940	95	50
1941	65	42
1942	60	38
1943	58	37
1944	56	–

Table 4

Use of Mersol in the border-states

	Tons per year
Belgium	3600
General Government (Poland)	2700
Holland	3600
Protectorate (Bohemia and Moravia)	2300
Norway	1130

Total 13,000 tons per year

C.I.O.S. ref. no. FD 6616/45

Synopsis of cold-resistant lubricants

According to the present state of knowledge, one should preferably use the follo ing cold-resistant lubricants for Air Force equipment as laid down in the statement from GL5 (Dr. Weltintzlei)

Purpose	Lubricant	Manufacturer
Instruments	Oils: Spindelölgrun Inteva 2069	Shell Inteva Arbeitsgemeinschaft, Hamburg
	greases Flugzeugfett blau	Inteva U Kalypsolgesellschaft Shell
	Fl - Instrumentenfett	Inteva
	(Kalypsol 129)	Kalypsolgesellschaft
Bearings which remain cold, including ball bearings	Flugzeugfett blau Fl - Instrumentenfett	Inteva etc.
For bearings taking heavy loads and running hot, including ball bearings	Fl - transformer grease blue	Kalypsolgesellschaft
For weapon parts	Flugzeugfett blau Mg-öl40 (Waffenöl blau)	Inteva to be ordered from RLM
Protection against corrosion	Schutzöl 39 Fl 4400 Schutzfett 40 Fl 44420	Shell - Inteva, Rhenania Schliemann

Spindelöl grün is the new designation of what has been called Shell AB 11
Flugzeugfett blau is the class name for the greases :-
Inteva 141b, Kalypsol K and Shell Aero-Fett blau
Fl - Instrumentenfett is the designation for Inteva 1417
One should avoid using transformer oil T 166, Kalypsol 3, Kalypsol 142, grease AT 10 and X 22.
The lubricants bracketed above (Kalypsol 129 and Waffenöl blau) have not finally been introduced.

Grease lubrication for Air-Force equipment

Front designation	Purpose	Manufacturer	Remarks
Verstellpropellerfett VIN 42	Mounting and periodic greasing of slide shafts and wire cable cores in flexible shafts for remote control and gears of any kind	Calypsol	Only in tube packings TL $\frac{147-902}{1}$
Flugzeugfett	In the grease gun and for hand greasing: packing all mobile swivel joints and ball bearings, sounding frames and other bearings of the aeroplane equipment	Calypsol Intava Rhenania-Ossag	Miscible with one another
Fl Instrumentenfett	For lubricating, packing and conserving of all instrument parts on board	Intava	
Fl Transformer grease	For lubricating and mounting of bearings and driving propeller of FT generators and transformers	Calypsol	Only packed in tubes, tested
Schutzfett 40	a) cold: packing and greasing of accumulator terminals and bases, polishing of naked, burnished and anodised steel and light-metal surfaces. b) made fluid by warming Against the effect of sea-water accumulates acid and acid fumes	Intava Rhenania-Ossag Schliemann	the cold and hot states are miscible. Replaces vaseline and other greases as a protective grease. TL $\frac{147-901}{1}$

Deutsche Calypsolgesellschaft

Calypsol lubricants were introduced to the industry at home and abroad more than 35 years ago and have proved themselves to be of high quality. They are manufactured in our works at the Dusseldorf post. The number of types and properties of Calypsol lubricants are so large that they cannot all be mentioned in this short prospectus. The types are conditioned by the most varied factors affecting general engine lubrication, such as heat, cold, humidity, load, etc.

We shall confine ourselves to some main types and its chemico-physical properties as well as some of the possible applications. We do however provide Calypsol lubricants for every kind of application such as foundries and rolling mills, the industry of stones and earth, the cement industry, fire clay and lime industry, the industries of paper, wood, cellulose and textiles, the chemical industry, the sugar industry, in food industry, in optics and precision mechanics, and the whole of the engineering and metallurgical industries.

Type (T): 1. Calypsol W1

Chemico-physical properties: drop point ca. 160°C: ash content ca. 1%, water content: traces only.
Description: strong doughlike structure, therefore lubricating film of high tensile strength, even for higher loads.
Bearing and type of application: plain bearing: central grease guns: Stauffer can
Examples of application: For plain bearings up to the largest dimensions and highest loads, with not very high speeds. For mill bearings, for crusher bearings of every kind, where considerable shocks often occur, for rolling gear, trunions of helical gear, "hollander" bearings, felt roller crushing mills with vertical runners, eccentric bearings, rope pulley bearings, etc.

T: Calypsol W1

C.P.E.: as above Calypsol W1
D: block grease 240 x 75 x 75 mm may easily be cut to the suitable size
B: plain bearing, grease boxes
E: As for Calypsol W1, but only for bearings with box-like grooves in the upper bearing cover (Calypso bearing). Ideal lubrication, very small consumption

T: Calypsol ER1

C.P.E: Drop point ca 180°C, Ash point ca 1.7%. Only traces of water
D: Very tough, strong consistency, stronger than above qualities
B: Plain bearings, Stauffer can
E: Trying cylinder, pulley bearings on rotary furnaces, hot roller bearings and other bearings in roller mills, bearings of drying drums, tube dryers of the lignite industry. Also all bearings which are exposed to external heating

T: Calypsol ERlu

C.P.E.: as above Calypsol ER1
D: grease blocks 240 x 75 x 75 mm., may be easily cut to suitable size
B: plain bearing, grease boxes
E: as for Calypsol ERI, but only for boxlike groove in the cover

T: Calypsol hot bearing and sealing grease

C.P.E: Drop point ca 190°C, ash content ca 3.5
D: very tough grease
B: Plain bearing, Stauffer can
E: For bearings which are exposed to higher temper than the lubricating points mentioned under 3. Instead of felt-rings in engine anti-friction bearings, as sealing grease for stuffing boxes.

T: Calypsol Briketts

C.P.E: Drop point ca 190°C: Ash content ca 3.5%, only traces of water
D: Grease blocs, 240 x 75 x 75 mm may easily be cut to a suitable size: very strong lardaceous structure
B: Plain bearing, grease boxes
E: Particularly for drying cylinder units with high vapour entry temperatures; pulley bearings in the sinter region, bearings on which gases impinge at very high temperatures, the hottest rolling gear of rolling mills, etc.

T: Calypsol WIK

C.P.E: Drop point ca 150°C, Ash content ca 1.2%, only traces of water.
D: Soft and supple, structure consists of long fibres
B: Small ball and roller bearings, plain bearing
E: For smaller electrical instruments, electric drills, house-hold machines, vacuum cleaners, polishing machines, grinding machines, etc.; often as general grease for bearings and gears of small machines.

8. T: Calypsol WIA

C.P.E: Drop point ca 156°C, Ash content ca 1%, only traces of water
D: A supple grease of very homogeneous structure. It still has lubricating properties at 40°C and freezes only at -60°C
B: Anti-friction bearing: high pressure grease gun: plain bearing: Zentral grease gun: Stauffer cans
E: Axle bearing on rail and automotive vehicles. Anti-friction bearing in turn-tables, revolving stages, machines of every kind, e.g. electric motors, transport units, etc. Calypsol is also the standard substance for Stauffer and screwpressure cans as well as for automatic Zentral grease guns. For temperatures from -40°C - +80°C

9. T: Calypsol WIA 137

D: A grease of more solid consistency than Calypsol WIA, with a very high flowing point
C.P.E: Drop point ca 176°C, Ash content 2% ca, only traces of water
B: Anti-friction bearing, plain bearing, lubrication as under 8.
E: For anti-friction bearings with temperatures above 80°C to 135°C as for electric motors in rail vehicles, pit locomotives, for plain bearings for inbriquette presses, also for feeding by Zentral grease guns

T: Calypsol WIA 135

C.P.E: Drop point ca 176°C, Ash content ca 2%, only traces of water
D: Grease blocs of semi-solid consistency
B: Plain bearing, box bearing
E: As for Calypsol WIA, as far as higher temperatures are concerned

T: Calypsol WL water resistant

C.P.E: Drop point ca 98°C, Ash content ca 2%, water content ca 1%
D: Very supple material which is not wetted by water, very economical lubricant
B: Anti-friction bearing, plain bearing, type of lubrication as under 8.
E: For watercooled ball and roller bearings as well as plain bearings, bearings of pumps, water turbine bearings. For all bearings which come into contact with water, e.g. roller pivots

T: Calypsol HWPN

C.P.E: Drop point ca 104°, water content ca 1.8%
D: Is not affected by hot water
B: Anti-friction bearing, plain bearing, stuffing boxes

E: For plain bearings in contact with warm or hot water, anti-friction bearings in pumps, centrifuges, textile machinery, dyeing machinery. Is resistant to weak acids and also prevents the entry of water into the bearing, grease for labyrinth packing

T: Druckluft-Calypsol

C.P.E: Drop point ca 150°C, Ash content ca 0.5%, only traces of water
D: A semi-liquid grease which may easily be dispersed in an air jet and has a great adhesive strength
B: Lubrication pump, oil feeder, special application
E: In mining for working hammers, charcoal saws, spiral drills, hammer drills, coal cutting machines, sliding motors, herringbone gear motors, windlass motors, etc. For all tools driven by compressed air in quarries and road making as well as in the iron industry. In place of mineral oils

T: a) Getriebe Calypsol, b) Getriebe Calypsol 000, c) Getriebe Calypsol Sch

C.P.E: a) Drop point ca 147°C, b) Drop point 150°C. c) Drop point 150°
D: Highly viscous but still flowing, great adhesive capacity
B: Drives, trough filling, splash lubrication
E: Lubrication of encased drives. Getriebe Calypsol is supplied in various consistencies, the decisive factors being number of revs., pressure, etc. When ordering it it is necessary to make exact specifications about the drives. If necessary one should ask for our questionnaire.

T: Liquid Calypsol-greases

C.P.E: a) Calypsol WIK 260x Viscosity a 100°C ca 20 Engler degrees
b " WIK 150 " a 50°C ca 15 " "
" WIK 700 " a 50°C ca 7 " "
" WIK 600 " a 50°C ca 3.5 " "
D: Liquid grease lubricant, highly resistant against heat, against cold and fatigue, as well as ageing.
B: Plain bearing, trough filling, splash lubrication, pressure lubrication, bearing with annular lubrication
E: Calypsol WIK 260x for drives which are highly loaded in place of the so-called gear oils. It is astonishingly resistent against wear and fatigue. Great heat resistance, good flowing properties at normal temperatures, great resistance against cold.
Calypsol IK 150 for gears and bearings with annular lubrication at high temperatures
700 for gears and annular lubrication bearings at medium temperatures
600 for gears and annular lubrication bearings at low temperatures.
Very resistent to cold

16. Auto-Calypsol	Chemico-physical properties	Description	Point of lubrication and application
	Drop point ca 150°C Ash content ca 1.4% Only traces of water	Consistency very tough but supple highly resistent to pressure	plain bearing and differential trough- and capsule filling

To be used in all types of vehicles whose toothed wheel gears do not have bearings into which the oil must be introduced by centrifugal action and through narrow channels. It facilitates easy gearing, has sealing action, tends to reduce noise, is strongly adhesive and is therefore not squeezed out by the tooth flank pressure.

Auto-Calyspol II	Drop point ca 156°C	Soft and supple	

	Chemico-physical properties	Description	Point of lubrication and application
Auto-Calypsol II	Ash content ca 1% Only traces of water	Seals against dust, does not form crusts, high kilometre efficiency	Anti-friction bearing carriages, grease presses, Stauffer cans
	For lubrication of all lubrication points of the carriage ball or roller bearings of the nave hub.		
Auto-calypsol III N	Drop point ca 104°C Water content ca 1.8%	special lubricant, supple structure unaffected by boiling water	Waterpump grease press Stauffer can
	For water pumps on automotive vehicles, tractors, diesel engines Does not penetrate into the cooling water and thus avoids any trouble connected therewith. No leaking of the pump.		
19. Auto-Calypsol IVx and Caliedo lubricants	These are liquid lubricants which can do justice to the highest demands, as shown when they are used in autocar gears, such as Hypoid-gears etc., differentials. They permit extremely rapid, smooth gear changing both in summer and winter. No ageing effect on the lubricating power is noticed even after 6000 hrs.		
20. Walzengapfen-Calypsol Wacal III and Wacal IIw	Lubricants which have been successfully used in recent years in bearings of drum pivots of hot and cold rolling mills, in bearings having intricate contact with water, especially artificial resins and substitute bearings.		
Calypsol for artificial resin bearings	Our customers using artificial resins have so far arrived at the most favourable operational conditions by using one or the other of our normal Calypsol types. We shall give free advice if special lubricants should become necessary in some cases		

Structure Inspectorate of the R.L.M.

From
Rhenania-Ossag
Mineralölwerk A.G.

Re: "Flugzeugfett blau" and "Fett-Shell Aero blau B 2"

With reference to your letter ZMI Rs/G of 1.2.1943, the above Inspectorate has received the grease sample Shell Aero blau B 2 which you reffered to in your letter. Delays were caused by the illness of Mr. Böklow and by air raids on Barmen. Freezing experiments with the grease could therefore only be undertaken in the beginning of October. You are herewith informed that the experiments completely confirm your findings viz. the gear shows a low temperature behaviour better by at least 20°C when "Shell Aero blau" was used. In the meantime freezing experiments have been carried out by Cyclo in Munich with a grease which is there called "Fliegerfett B 2". Probably this is the same as "Shell Aero blau B 2". The Munich experiments show almost the same favourable result. For your information we mention that the Testing station Travemünde E2II has been commissioned by the RLM GL/A-M to carry out the testing. Mr. Graser is conducting the research.

The following points are to be elucidated:

1. Whether one should use the grease "Shell Aero blau B 2" or the "Instrumentenfett neu".

2. The cause of the solidification observed of the grease which is also known to you by correspondence and by discussion. It appears that this solidification of "Shell Aero blau " after four months occurs even in drives where ball bearings have definitely been washed before mounting.

Since the characteristics of the greases are not known here we ask for the viscosity curves of

Shell Aero blau
Flugzeugfett blau
Shell Aero blau B 2
Instrumentenfett blau

We further ask for information on the aviation oil. It was found in the course of experiments with pressure-oil pumps that bubbles are formed behind throttles in the suction line and that at a pressure of 350 mm Hg abs. these bubbles continue up to the pump itself. Since the drawing in of air is impossible these bubbles must be filled with oil vapours which recondense at 100 atm. pressure on the pressure side. As it may be that various troubles occurring with pressure oil pumps may be explained by the characteristics of the aviation oil the above Inspectorate would like answers to the following questions:

1. What is the course of the vapour pressure curve of the aviation oil

2. Is it possible to favour the evaporation i.e. increase the vapour pressure by causing a turbulent flow of the oil through a throttle.

3. Is it likely that a condensation delay may be responsible for the fact that vapour bubbles can exist at 360 mm Hg abs. since the vapour pressure is probably below 360 mm Hg.

4. Can the condensation delay i.e. the vapour pressure be influenced by floating particles of steel or bronze (originated by wear).

O.D.C. Unit No. 10 Serial 10,105
German Academy of Aeronautical Research, 1939
Vol. 9, pps. 133-168

The physico-chemical basis of combustion in engines

Wilhelm Jost

The desirable course of combustion in the gasoline engine is the spreading of a flame from the ignition spark in the adiabatically compressed hot mixture of fuel and air. As an undesirable phenomenon so-called knocking may occur. This consists in an extraordinary acceleration of combustion towards the end of the reaction, together with the occurrence of abnormally high local pressures and the generation of pressure waves. According to recent research the cause of knocking is the following: spontaneously progressing oxydation-reactions occur in hot unburnt residual gas which has been compressed first by the movement of the piston and subsequently by the spreading flame. These reactions may under certain circumstances lead to the practically instantaneous ignition of a residual part of the mixture. The same reactions between fuel and the oxygen of the air play a part in the progress of ignition of the Diesel engine. In this engine however, the processes of solid injection and atomization as also of evaporation of the fuel droplets are of considerable importance. The knocking reactions have been very thoroughly studied because of their unfavourable influence on engine operation. The greater part of this lecture will therefore deal with these reactions. The significance of the normal processes of the spreading of the flame should however also be mentioned, since it is not always fully appreciated. As the associated phenomena are both of practical importance and of theoretical interest we shall deal with them also.

1) The oxydation reactions of hydrocarbons and the knock process in engines

Knocking in engines may be described as the practically instantaneous combustion of the residual part of the charge in the combustion chamber. The possibility of this may easily be explained. With a compression ratio of from 6 to 7 the temperature of the charge at the end of the compression, may (depending on the initial temperature) have been raised to 400°C. The real temperature of that fraction which burns last would be ~ 50% higher still on account of further compression by the progressing flame. If heat conduction were eliminated the temperature could be well above 500°C. At these temperatures and at the pressures obtaining in the engine all fuels react vigorously with oxygen; so vigorously that after a definite period of induction combustion would change to self-ignition. In fig. 1 this has been represented diagrammatically for the ideal case of a fuel-air mixture in which the piston has been arrested at the point of maximum compression.

Fig. 1a represents the percentage combustion of the spontaneous reaction as a function of time. Fig. 1b (continuous curve) represents the percentage combustion ensuing from the spreading flame with spark ignition. In the steady engine operation the percentage combustion due to the spontaneous reaction must lag far enough behind that due to spark ignition as not to introduce any disturbance. One can now easily picture two cases of abnormal course of combustion. Fig. 1c: the spontaneous reaction may set in at such an early stage that one obtains pre-ignition, i.e. before the passing of the ignition spark. The case of Fig. 1d is more important: combustion starts normally, but the reaction in the flame front is overtaken by the spontaneous reaction in the unburnt part of the charge, the last fraction burning practically instantaneously. This constitutes knocking. That this is actually what occurs during knocking may be established by many data obtained on engines as well as on experimental apparatus.

It may be pointed out here that all the undesirable phenomena occurring in knocking may be deduced simply from the above conception. If the last fraction of the charge, having been further compressed by the spreading flame, burns off "instantaneously" i.e. more quickly than the change in volume is able to keep pace with the combustion, then appreciably higher peak-pressure should be obtained in this part of the charge than should occur if the whole mixture would burn uniformly.[1] On the one hand this entails high local mechanical stresses, on the other hand the pressure discontinuity must be communicated to the mass of the gas in the form of pressure waves which in turn may give rise to multiple reflections. This pressure-wave is responsible for the "gasoscillations" found in the indicator diagram. It may be observed directly in flame photographs of combustion with knocking. Further it produces an increased heat transfer to the walls and thus makes greater thermal demands on the engine.

We shall show below that knocking is a consequence of the spontaneous reactions in the unburnt mixture. This we shall do by means of our own quantitative experiments. Here we shall only point to the numerous qualitative and semiquantative considerations favouring this conception. It has been found by many authors that there is a far-reaching parallelism between the behaviour of hydrocarbons in slow oxydation and in knocking. Similarly there are connections between spontaneous ignition and knocking characteristics of hydrocarbons. Further it can be shown in the engine itself that knocking is preceded by a reaction in the unburnt mixture. Evidence is obtained from spectroscopic observations (e.g. Rassweiler and Withrow) or by direct analysis. Fundamental experiments in this direction have been made, particularly by Egerton.

Before entering on our own experiments, a few remarks may here be made on the nature of the reactions occurring and the possibility of the development of an explosion. Every exothermic reaction may lead to spontaneous ignition and an explosion, provided the liberation of heat is greater than the loss of heat to the surroundings (van't Hoff, Taffanel and le Foch, Semenoff). One then uses the term "heat-explosion". In the case of a heat explosion simple expressions are obtainable for the limits of the explosion from the known formula for the reaction velocity. This gives a relation between critical explosion pressure and temperature or in other words the ignition temperature as a function of the pressure (and composition). Footnote: it should be noted that the ignition temperature is not absolute but is significant only for a given experimental set-up. From the instant the gaseous mixture has been raised to the experimental temperature, e.g. by bringing it into a heated reaction vessel, a certain period of induction t elapses before the explosion takes place. Thus for a given experimental arrangement the ignition temperature has a definite physical significance only in connection with the corresponding period of induction. If for instance the gaseous mixture has been heated to a temperature higher than the lowest ignition temperature, then spontaneous ignition leading to knocking will occur only if the gas is kept at that temperature for longer than the period of induction.

In the case of an adiabatic explosion one can enunciate an approximate formula for t if one makes some (legitimate) approximations (Todes) viz.

$$t = \frac{e^{E/RT_o} \cdot RT_o^2 \bar{C_v}}{kE \cdot Q}$$

where E is the apparent heat of activation of the reaction
T^o is the initial temperature
$\bar{C_v}$ and Q are specific heat and heat of reaction
k is the velocity constant of the reaction
In reactions which still have a measurable velocity at several hundred °C, E is of the order of 30 to 50 Kcal.

Now "heat explosion" is not the only mechanism which can lead to spontaneous ignition. The oxydation of hydrocarbons, like many other reactions, is a chain reaction, of such a kind as to show branched chains. A chain reaction is such that certain active primary products enter into the reaction and are thereby continually regenerated so that starting from a few such active primary products a considerable total of transformations may be achieved. This continues until the chains are broken by reactions which use up the primary products.

The classical exmple of this is the explosive chlorine-hydrogen reaction which has been studied particularly by Bodenstein and which follows the following course.

$$Cl_2 \rightarrow 2Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$

After the primary steps up to 10^6 chain members follow the active atoms are then destroyed, e.g. by the oxygen which is mostly present as an impurity or by diffusion at the wall. Chain reactions are therefore characteristically sensitive to a number of substances at low concentration which can either make or destroy the active centres. They are also sensitive to the state of the wall and the dimensions of the containing vessel. These determine whether or not the chain carriers are deactivated at the wall and the speed of their getting to the wall respectively. The sensitivity of the oxydation of hydrocarbons to additions such as lead tetraethyl is relevant in this connection.

Another process may occur in chain reactions. Let this be illustrated by some reactions occurring in hydrogen combustion at higher temperatures. If only few H- atoms are present, reactions occur thus:

$$1.\ H_2 + O_2 \rightarrow OH + O$$
$$2.\ O + H_2 \rightarrow OH + H$$
$$3.\ OH + H_2 \rightarrow H_2O + H$$

Here again is the form of a chain reaction but in the stages 1 and 2 one activated nucleus entering into reaction produces two new ones and what is called branching of the chain occurs. Thus even if only very few active nuclei were available at the beginning yet their number and with it the velocity of reaction increase steadily. This may amount to an explosion even if the temperature is at first kept constant. A necessary consequence of the increase of reaction velocity is an eventual increase in temperature. The increase in temperature is not however the cause of the increase in reaction velocity. Whether or not a reaction with chain branching results in an explosion depends on whether the chain branching (formation of active nuclei) preponderates over the chain breaking (deactivation of nuclei) or not. Since low pressures favour the diffusion of active nuclei to the wall and thus chain breaking, there always is a lower explosion limit. Chain breaking however is frequently favoured by increasing pressure in the gaseous phase so that one is left with a characteristic circular range of explosion. At still higher pressures the range of the simple heat explosion will join on to this, fig. 2 and 3. Such ranges of explosion have very repeatedly been observed with hydrocarbons and not only at low pressures a range in which to one temperature there correspond two (or three) critical explosion-pressure limits (Townsend and co-workers), fig. 4. These phenomena and the many statements to the effect that many substances at low concentrations accelerate the slow oxidation of hydrocarbons enormously (aldehyde, peroxide, ozone) or retard it (aniline, lead tetraethyl, iron carbonyl) alone prove that the oxidation of hydrocarbons proceeds by a chain reaction and leads to an explosion by chain branching.

An additional factor is the considerable dependence on the state of the wall and the dimensions of the vessel. The peculiar phenomenon of the cold flame also can only be understood in terms of an explosion through chain branching. It consists of an explosive combination, accompanied by luminescence of hydrocarbon-air mixtures in the range of temperature between 250 and 350°C. All the characteristics of an explosion are present (also a certain temperature rise of the order of 100°C.). The reaction does not however reach complete combustion. It is arrested in the main at the stage of the aldehydes and their derivative and decomposition products (CO, H_2O). Increase of pressure (and also of concentration of fuel) may make cold flames change into regular ignition.

There are well defined connections between the temperatures at which cold flames appear and the knock properties of hydrocarbons.

All the same it must be assumed that the course of the oxidation in the engine preceding the knocking is considerably simpler than, e.g. under the Townsend conditi
The latter introduces a fuel-air mixture into heated reaction vessels and observes the ignition, the period of induction varying from seconds and minutes up to hours. Under these conditions the processes occurring on the wall of the vessel play a considerable part. This is distinct from the engine where the periods available are so short (~ 1/100th sec) that no time is available for any appreciable diffusion from the gas chamber to the wall or vice versa. Furthermore in the engine the wall is colder than the compressed gases; the initiation of chains at the wall is therefore excluded for this reason alone (disturbances due to hot exhaust valves and similar things will not be considered here).

At the time of the commencement of our investigations the only experiments comparable to engine conditions were Tizard and Pye's measurements on the ignition of fuel-air mixtures by adiabatic compression. It is found that the ignition delays measured at various temperatures show a very simple course, not exhibiting the anomalies observed by Townsend. The temperature dependence is approximately exponential. The ignition temperatures also lie fairly low, in the range where cold flames have been observed. It would appear quite plausible that the branched chain reactions of the cold flame may, under engine conditions where the heat exchanger is relatively small, change into normal ignition through a pure heat process. From the ignition delays measured by Tizard and Pye on n-Heptane, one may even estimate that this substance should start knocking at a compression ratio of 3:4, which is confirmed by experience.

A continuation of experiments in the direction taken by Tizard and Pye therefor seemed to us to hold good prospects, in spite of considerable experimental difficulties. A report on these experiments which had been begun in collaboration with W. Rohrmann, L.V. Müffling and R. Maass will now be presented. Both the final experimental arrangement, and all the experiments communicated below were carried out in collaboration with H. Teichmann. The problems of heat transfer which arose were dealt with by H. Hogener; when a gas is cooled in a closed vessel, the cooling, even if only a part of the space is involved in the heat transfer, is observed throughout the whole gas, on account of the adiabatic changes in volume. The experiments were commissioned by the "German Experimental Station for Aviation".

2) Experiments on self-ignition and knocking combustion in adiabatically compressed gaseous mixtures.

Fig.5 gives a diagram of an experimental apparatus suitable for the investigation of both self ignition by adiabatic compression and also knocking combustion using external ignition. In the figure all the relevant features are shown. In an experimental cylinder (vol. ~ 1.5 litres) the gas is compressed by means of a falling weight (compression ratio variable between [illegible] and 20; in practice 15 was not exceeded — time taken for compression ~ 0.05 to 0.1 secs.). The piston is arrested at the point of maximum compression. At the lower end of the cylinder reaction vessels of different shapes may be mounted, compact vessels with small heat loss for spontaneous ignition and long cylindrical vessels for external ignition and knocking. It was found possible to register the pressure with piezoquart. Generally, however, the development of the flame was registered photographically through an observation window, on account of the disturbances set up by the falling weight and also of the increased sensitivity attainable.

Initial difficulties were experienced with reliable light fittings which had to be secured without introducing complications due to grease. Other difficulties were found in attaining a sufficiently rapid compression yet allowing of a quick and sure means of arresting the piston at its lowest point. These difficulties were, however, overcome. It may be mentioned that the inertia of the piston before coming to rest is so great that a brass bolt 15 mm. thick was torn through in spite of the counter balance gas pressure equivalent to a force of several hundred kilograms at the end of the compression. The whole apparatus could be heated to a maximum temperature of 180°C. On account of sealing the working temperature was generally kept lower.

In this apparatus it was possible to obtain knocking with all relevant substances, even those whose octane number is considerably above 100. Thus the spontaneous ignition characteristics of all substances of interest were secured. In this case it was found opportune to work with a period of induction of 1/10th to 1/100th secs; in this way the experiments were not yet affected by too much heat conduction (as happens with longer periods of induction) or by the finite duration of the compression. The latter has a disturbing influence only with still shorter ignition delays, because during the greater part of the compression stroke the temperature is so low that any reactions in the gas may be neglected.

Typical photographs taken in the apparatus are reproduced in fig. 6, 7, 8. The flame velocities in normal combustion are of the order of magnitude of 5 m/sec. In combustion with knocking photographs the order of magnitude is two higher, i.e. the residual mixture may be regarded as reacting practically instantaneously. Moreover one can always distinguish a reflected wave shock in the burnt gas with knocking combustion. The combustion may, however, as a consequence of small temperature differences start from one or several points in the unburnt portion. If still larger temperature differences are present ignition may occur at individual points of the unburnt gas, a normal flame then spreading from these points - spontaneous ignition. All these phenomena are known in similar forms in the engine.

The flame photographs of an adiabatic compression are quite similar to those obtained of knocking combustion. The small temperature differences in the gas (a few degrees) have a greater effect with longer ignition delays and ignition may then proceed from several points. Shorter ignition delays result in practically instantaneous ignition in the whole tube and a flame picture analogous to that of knocking combustion. The objection, advanced frequently, that spontaneous ignition of the residual mixture could not produce the forceful effects of knocking, cannot be upheld.

The effect of temperature on ignition delay compares well with the values observed by Tizard and Pye. Strictly, a correction should be applied for the cooling of the gases. Reliable experimental data for this are not available. We therefore leave out the correction for the present and mention the uncorrected values. This may be done without serious error because of the small value of the correction (10-15°C) and also because a correction which affects all the experiments to the same extent will have little influence on deductions from them.

Fig 9 is a diagram of a series of measured ignition delays; log τ is plotted against $\frac{1}{T}$ giving straight lines to a sufficient degree of approximation. The gradient of the curves indicates an apparent heat energy of activation of from 30 to 40 kcal for Paraffins and of more than 50 Kcal for Benzene. It is interesting that the range of temperature within which the various substances ignite is relatively small. As an example of a Diesel fuel, cetane was also investigated. It shows a behaviour similar to that of n-Heptane but at still lower temperatures. The steeper temperature-curve with aromatic compounds corresponds to experience gained in engines, viz. the relative worsening of knocking behaviour of these substances with increasing operating temperature.

It is of fundamental importance that one should succeed in evaluating the knock behaviour of a substance from the observed spontaneous ignition in the same apparatus, i.e. to calculate the knock behaviour from the spontaneous ignition process. The determination of knocking assumes a knowledge not only of the spontaneous ignition characteristics but also of the flame movement. This will give the position of the plane of the flame at any given moment and also the compression of the unburnt gas by the progressing flame. The data may be taken from flame photographs of the region just below the knocking limit.

Fig.10 left, simply represents the picture of the flame-front, as seen by photographic registration on a moving film. Since the motion of the film is proportional to time this is a time-motion diagram of the flame-front. The representation is such that the value of the ordinate at any point gives the time required by the flame to reach the other end of the vessel. We would have to compare this with the time taken at any particular moment for an explosion to develop in the residual mixture. However the latter is less than the time taken by the flame, knocking must certainly occur (in practice it occurs earlier). For this reason the periods of induction for the residual gas, as obtained from our measurements have also been entered in fig.10. This required a knowledge of the temperatures of the residual gas for every point on the flame front. For this reason the percentage combustion corresponding to every position of the flame front has been entered in fig.10 together with the relative temperature rises of the fresh gas(2) due to compression by the spreading flame corresponding to these percentages of combustion. Losses incurred by conduction of heat have been neglected; this may be done without introducing uncertainty, because any corrections which might be applied would affect knocking and spontaneous ignition experiments to the same extent. For a more accurate determination one should realise that with knocking the temperature of the fresh gas is being continually raised by compression. Here fundamental difficulties are met with: the reaction velocity in explosions in which chain branching plays a part need not be a definite function of the temperature. All the same we have integrated over the temperatures using the temperature function obtained in the spontaneous ignition experiments. One can show both directly and by calculation that in a heat explosion(3) the rapid increase in velocity sets in after but a few percent of the mixture has reacted. For spontaneous ignition under normal conditions it is consequently justifiable to assume that the gaseous mixture has a constant temperature during the greater part of the induction period; during spontaneous ignition leading to knocking, however, the initial combustion has occurred in a rather narrow temperature range (below its lower limit combustion is negligible, above its upper limit it is "infinitely" fast). It seems justifiable under these conditions to determine the times of induction for increasing compression by graphical integration. The calculated point in the left of fig.10 was obtained in this way. It indicates the point at which knocking combustion of the residual mixture should take place. The arrow beneath it shows the interval during which knocking combustion occurred during the actual experiments) (E = 5.5, To = 52°, Ts = 302°C). The agrement is good as may be expected.

The dependence of spontaneous ignition on pressure and composition of the mixture is also, in agreement with results of Tizard and Pye, relatively small. It is much smaller than might be thought in the light of the known dependence of knocking in the engine on composition of mixture and supercharge. Since, however, in the engine alteration in mixture composition and boosts has a considerable effect on the temperatures - an indirectly on those of the unburnt portion of the mixture - the more pronounced effects encountered in the engine are understandable.

It is of course possible in principle, and even desirable, to attempt a quantitative translation of our results to the engine. The main obstacle to this at the present moment is our lack of knowledge of the temperatures of the unburnt gas in the engine at any particular time. But in spite of the great difficulties which the determination of these temperatures offers, it may be hoped that progress may be achieved in a reasonable period of time. Our method would then provide a method of classifying the knocking characteristics of fuels absolutely independently of accidental conditions obtaining in the test engine.

3. Observations on the lead-sensitivity of different fuels on the basis of reaction kinetics, and the behaviour in blends. 3a)

The known results of knock-rating determination were: the anti-knock value of the n-paraffins decreases with increasing length of chain; it increases, at a constant number of C-atoms, with increased branching of the molecule. On the average olefines have a higher anti-knock value (and a greater resistance to oxidation) than paraffins. On the other hand, the anti-knock value of saturated hydrocarbons is increased to a greater extent by the addition of anti-knock additives than is that of unsaturated hydrocarbons.

Speaking quite generally the velocity of a chain reaction (which is proportional to the knock tendency) increases:

1. with increasing probability of processes which start chain reactions.
2. with increasing probability of chain-branching processes.
3. with decreasing probability of chain breaking processes.

The experience concerning knock behaviour of different hydrocarbons summarized above and the behaviour on slow oxidation may be reconciled from the point of view of chain mechanism with the apparently opposite experience of organic chemistry to the extent that paraffins are the least reactive and olefines the most reactive (which is the opposite with knock) under the following assumptions.
I Inspite of the low reactivity (low probability of starting chain reactions) of the single molecule, the large susceptibility to oxidation of the paraffins arises from chain breaking being very improbable, thus allowing of long reaction chains.
II Olefines, in general, do not have a small reactivity of the single molecule and therefore not a small probability of initiating chain reactions. To explain the relative anti-knock value a large probability must be assumed for chain breaking reactions resulting in relatively short reaction chains. This may quite plausibly be imagined to be caused by combination of the reaction chain-forming linkage with the double bond of the original molecule.

Moreover we can define an antiknock additive as one with chain-breaking properties (this does not necessarily assume that it is the additive as such which possesses these properties, but possibly its decomposition products, e.g. lead or lead oxides in the case of Pb (eth)$_4$; iron or iron oxides in the case of Fe(CO)$_5$. Then obviously the addition of such a substance will show a greater effect if chain breaking without it occurs but rarely. One consequently expects a greater antiknock effect of a given additive in the case of a paraffin or saturated naphthene than with the corresponding unsaturated compound. Extensive data are available on the effect of additives only in the case of lead tetraethyl, mainly from the work of Boyd and co-workers. These completely confirm our expectations.

Just as lead tetraethyl has less effect the more chains are broken without its presence, so a second addition of lead tetraethyl should have a decreased effect if the antiknock value has already been increased by a previous addition. This is also confirmed by experiment.

On the average therefore unsaturated hydrocarbons appear to have a higher antiknock value than the corresponding saturated ones (paraffins and naphthenes). The explanation is given by the chain breaking antiknock action of the multiple bond. Roughly speaking then, unsaturated hydrocarbons behave like saturated ones with an addition of an antiknock agent. In both cases further addition of antiknock agent must be less effectual than for saturated hydrocarbons without any previous addition.

We have the statement: a fuel has a high antiknock value because fewer chains arise in it or because many chains are broken in it. These allow conclusions to be drawn as to the probable behaviour of these substances in blends. If to a fuel of low antiknock value such as n-heptane one of a higher antiknock value is added, it may have two effects. First, it will dilute the fuel of low antiknock value but it may also influence the course of the combustion. It should be possible to calculate the first effect on the assumption of a rational measuring unit; the octane number cannot be taken to be such without investigation. The second influence may produce either a favourable or unfavourable change in the antiknock value. The mixture will be expected to have a higher antiknock value than that calculated from the law of mixtures if the fuel added has a strong chain breaking effect. The octane number which would have to be ascribed to the added fuel in order to make the observed octane number of the mixture agree with the one calculated is called the blending octane number. If the ideas on the different groups of fuels, developed earlier, are correct then those of group I (low probability of chain breakage and high lead sensitivity) should in general have a lower blending octane number in the pure form than those of group II (high probability of chain breaking and low lead sensitivity) of the same antiknock value. This is also confirmed by experience from a wide field.

It is also possible to derive a quantitative expression for the relation between antiknock value and its increase through lead addition for a group of substances whose reaction velocities are affected similarly by the addition of lead. After a number of simplifying assumptions(4) the increase ΔK of the critical compression ratio K is given by $\Delta K = \text{const}\; K^k$. This relation is entered in fig.11 (broken line). It gives a good account of the behaviour of paraffin and naphthene in the limiting case.

The above observations on the basis of the kinetics of reaction represent a first attempt. Finer details have so far been omitted. On the average the results have been very well confirmed by experience. Thus in spite of the need of detailed corrections there is hardly any doubt as to the fundamental correctness of the results.

4. The mechanism of the flame propagation

The "normal combustion velocity" of benzene hydrocarbons in stoichiometric mixture with air is only a few decimetres per sec. (30÷40 cm/sec.). The normal combustion velocity Vn is taken to be that velocity with which a flame front would move relatively to the fresh gas which is assumed to be at rest(5). In practice it is almost impossible to make an arrangement such that the gas is really at rest before the flame front. It is always possible however to determine the combustion velocity. This may be done using a Bunsen burner, the inner cone representing the flame front; the Gouy relation is here used, which states that the amount of gas flowing in per unit time is equal to the amount reacting during the same time and also in turn equal to the product of area of flame front and normal combustion velocity. Another method is according to Stevens. In this, the mixture of gases is enclosed in a soap bubble and ignited in its centre. The velocity of propagation of the flame, determined, say, photographically, is found from the expansion of the burnt gases, as is also the normal combustion velocity. The influence of the expansion may be eliminated and Vn may then be determined.

We shall mention below the factors influencing the normal combustion velocity and the additional factors involved in the normal propagation of the flame. First we should mention another interrelation, with the aid of the simplified fig.13. There are, as is well known, certain ignition limits for combustible substances in air or oxygen. These are limits of composition of the mixture, outside of which limits an externally initiated explosion at a point (e.g. by a sufficiently great spark, a flame, etc.) will not be propagated under set conditions. Accordingly we find in fig.13 that the normal combustion velocity as a function of the composition of the mixture approaches zero in the neighbourhood of the upper (Zu) and the lower ignition limits (Zo)(6). Obviously an explosion cannot be propagated if its velocity of propagation no longer has a finite value. Thus the problem of narrowing the ignition limits (diminishing the danger of an explosion) or of widening them is directly related to the question of flame velocity. The second problem also, that of increasing the combustion velocity and widening the ignition limits, may attain practical importance.

It must be realised that the thermodynamic efficiency (as opposed to power) increases with increasing excess of air. Because, with increase of the latter the mean temperatures become lower and K, the ratio of the specific heat, increases. The latter, as is well known, determines the efficiency of the gasoline engine η

according to $\eta = 1 - \frac{1}{\varepsilon^{k-1}}$ where ε is the compression ratio. The use of weak mixtures in engines must be weighed up against the comparative narrowness of the limits of ignition for petroleum hydrocarbons in air. An increase in Vn, accompanied probably by a widening of the ignition limits, may also be of practical interest. If the flame in the engine travelled with the normal combustion velocity of ~ 30 cm/sec then the course of the combustion would take perhaps ½ sec. in a larger cylinder of diameter ~ 150 cm. The operation of a high speed engine would be impossible with such slow combustion. In reality flame velocities 20 to 100 times the above are observed in the engine. These large flame velocities arise from the presence of currents in the gas, - turbulence - which may be artificially multiplied by suitable arrangement of valves and shaping of the combustion chamber. It is obvious that an increased flame velocity may not be caused simply by a stronger gas current carrying the flame front, which is little disturbed, much more quickly from the point of ignition through the combustion chamber. For in this case a burning gas sphere would reach the other wall much more quickly, but the amount of gas burnt would not be any greater because this depends solely on the product of flame area and the normal combustion velocity. A more rapid combustion can therefore be achieved in one way only: viz. as a consequence of an increase in the flame area by cleavages as a result of current and turbulences. The truth of this may be seen directly from instantaneous photographs of wave-fronts in engines and also in wide tubes. Serious difficulties on account of too small combustion velocities have not so far been met with (except in the neighbourhood of the ignition limits). This is due to the fact that with increasing engine speed the velocity of the gas and the turbulences also increase.

It is not, however, impossible, that on further stepping up of the engine speed a decrease of the efficiency on account of too slow a combustion velocity may occur. This situation could be met with only by an increase in Vn if this is at all possible.

There is a peculiar current in the fresh gas in the case of the propagation of a flame in a tube fitted with a gas at rest, and it plays an important part. Since changes in pressure and current in the fresh gas as a whole do not arise we consider as the simplest case ignition at the open end of a tube closed at one end. This current ensures that the velocity of flame propagation is always larger than Vn, twice as large or more. The shape of the flame front in moderately wide tubes is, according to experience, that of a hemisphere if gravitational influences are neglected, fig.14a. The combustion should progress along the surfaces of concentric spheres approximating more and more closely to a plane (broken lines of fig.14a) since the flame front progresses in the direction of its normal (7) at the speed Vn, if all currents are excluded. This would amount to a decreasing area of the flame and with it of the flame velocity. This however contradicts experience: a hemispherical flame front appears to be relatively stable. This can be the result only of the action of currents whose axial components have been entered in fig.14a. The figure refers to the ideal case in which the cooling effect of the walls may be neglected and the flame front thus touches the wall. It then becomes necessary to assume that the flame front meets the wall at a finite angle. Otherwise an infinitely large oppositely directed current would have to be postulated in the proximity of the wall. The advance of the flame front at a velocity above Vn is explained by a current derived from experiment according to fig.14b. This also explains that it is possible to determine the normal combustion velocity correctly, as a quotient of burnt gas and area of flame front, i.e. according to Gouy (Coward and co-workers) from observations of flame velocity and simultaneous photographic registration of the size of the flame front.

It has not yet been shown how the current shown in fig.14b arises. It may be mentioned that in connection with the theory of radiometer forces Hethner showed that currents completely identical to those shown in fig.14b could be obtained as a consequence of thermal diffusion according to Kundsen. The condition for this is an axial temperature gradient in a tube (in the gas as well as at the wall). Applying Hethner's formula to our case, an enormously steep temperature gradient in the combustion zone $\sim 10^5$ °C/cm. proportional to the diffusion, gives a current in a direction opposite to that of the hot gas going along the wall at a speed of $\sim 10^2$ cm/sec. and a corresponding current of opposite velocity in the middle of the tube. One would thus obtain a straightforward explanation of the observed effect and also an explanation of the curved flame front if such a thermal diffusion were the cause of the current. It is unfortunately difficult to tell whether Hethner's results may be used for our purpose: firstly the temperature gradient in the wall of the tube is absent and secondly the combustion zone does not touch the wall on account of the latter's cooling action, the conditions in the intermediate zone being very difficult to evaluate. We therefore do no more than to draw attention to this similarity between the empirical current diagram and Hethner's result.

The old ideas do not suffice to give an explanation of the observed normal combustion velocities. According to the former, heat conduction from the burnt gas to the fresh gas heated the fresh gas to its ignition temperature, causing it to react; the process of conduction and ignition then repeated itself. All the same, heat conduction is of course one of the decisive factors for the propagation of flames. Against this explanation objections come first of all from theory: the introduction of an "ignition temperature" in this connection is meaningless. One can further show quite generally that diffusion from the fresh to the burnt gas and in many flames the diffusion of active particles free atoms or radicals are at least as important as conduction from the burnt to the fresh gas. Free atoms or radicals may already be present in the burning zone in considerable numbers at thermal equilibrium. During an exothermic reaction however free radicals may be formed at a considerably higher concentration than corresponds to the equilibrium of the end products. In the case of the oxy-hydrogen reaction this has been shown directly with the aid of para-hydrogen.

Experiments also show directly that heat conduction cannot be the sole or preponderant factor in the propagation of flames.

This is shown thus: if one inert gas is replaced by another of the same specific heat (e.g. Argon by Helium) the velocity of the flame in no way alters, contrary to expectations on the basis of the change in heat conduction (Coward and co-workers).

The structure of the zone of combustion (whose thickness according to theoretical calculations and direct observation (Wacke) is of the order of magnitude of 10^2 cm.) must therefore be imagined as in fig.15. One assumption would be that the fresh gas flows to the right with speed Vn so that the region of combustion remains stationary at the zero point of the co-ordinate system.

From T_o there is a continuous rise in temperature (over a distance of $\sim 10^2$cm.) up to the temperature of the burnt gas T_e. Correspondingly the concentration of the end products c_e rises and the concentration of the initial products c_a decreases. It is certain that the concentration of active particles rises rapidly. If during the reaction the concentration exceeds the equilibrium value corresponding to the end-state, then the concentration of active particles passes through a maximum. The simplified representation of fig.15 allows of several qualitative conclusions. One can also deduce the extent to which the flame velocity may be expected to be influenced by additives. Let us take the case of the combustion of hydrogen, for which most experience is available. The mobility of hydrogen exceeds that of the other reactants by so much that diffusion of hydrogen from the fresh gas to the combustion zone plays an important part. It is obvious that this diffusion of additional hydrogen into the zone of combustion can hardly have any influence on combustion where excess of hydrogen already exists. Consequently effects caused mainly by this diffusion are known only in the region of the lower ignition limit (deficiency of H_2). Clusius worked with a vertical tube and found that the lower ignition limit for the ignition of H_2 is lower if the gas is ignited from below than when it is ignited from above. Also that, on the other hand, the ignition limit for hydrogen is considerably lower than that for deuterium, especially with ignition from below. This is explained by the difference in diffusion velocity of the two substances from the fresh gas to the combustion zone, combined with the fact that if ignition proceeds from below a ball of burning gas rises upwards from the point of ignition, thus getting into contact with new regions of fresh gas and allowing the diffusion of more H_2 into itself.

The diffusion of active particles from the combustion zone to the fresh and with it the importance of the part they play in the propagation of the flame can only be indirectly inferred (e.g. Jost and Müffling)(8). There are a number of experimental results which support this view. For instance, the flame velocity of oxy-hydrogen mixtures is halved by the addition of 1% of acetylene. In consideration of the finding of Bonhoeffer that acetylene catalyses the recombination of hydrogen atoms this must surely be based on the fact that small amounts of acetylene capture hydrogen atoms and any other active particles, such as -OH radicals, diffusing into the combustion zone from the fresh gas. The action of a number of additives mentioned by Jorissen and Japanese authors should be similarly explained, these additives greatly lowering the ignitability of hydrogen especially at the upper ignition limit.

The following general statements may be made on the extent to which velocity of combustion and the limits of ignition can be influenced. The velocity of combustion will always be decreased by a sufficiently high concentration of an inert gas if only for the reason that the flame temperature and with it the velocity of reaction are decreased indirectly. The heat transfer to the fresh gas by conduction cannot be influenced appreciably by small additives. Reactions in the unburnt gas as a consequence of diffusion of active particles may however be influenced by additives, even if these additives are combustible (acetylene in the case of oxy-hydrogen). A strong effect on flame velocity and ignition limits may however be obtained only when the diffusion of fresh gas into the combustion zone is not the preponderant factor. Thus, in agreement with experience, the upper ignition limit may be lowered considerably, but the lower one not raised correspondingly by such additives.

Even when the velocity of combustion and the ignition limits are influenced by inert gases (N_2 and CO_2) the influence seems to be considerably greater at higher fuel concentrations than at lower ones. This fits well into our hypothesis, fig.16.

Discussion

Broeze

I should like to refer to only one point in Mr. Jost's paper. This point, already touched by Mr. Jost deals with the connection between scientific investigation and technology. I think it is a task of this conference to clarify this connection very particularly.

Mr. Jost mentions "an absolute classification of the knock characteristics of an engine, independent that is of the chance conditions in the test engine". One might remark that a classification of knock characteristics independent of the engine does not exist. Knock has such an essential connection with the engine and the operation of it, that knock apart from the engine does not really have any meaning.

The words "chance conditions of the test engine" I take as indicating that these conditions gave rise to results differing from day-to-day and that this made it necessary to become independent of these conditions. It should however be realised that these conditions do actually exist. Furthermore it is of great importance that a certain fuel does give different results in a certain engine or type of engine under one set of engine conditions, temperature, load, speed, etc., from those under other conditions.

We cannot avoid this by leaving out the engines and reverting to a piece of apparatus. The only possibility would be if this apparatus were used to cover the entire field. Since, however, there are a number of variables, viz. temperature, pressure, time (time entering as a complicated function because the compression may increase either slowly or quickly), mixture ratio, admixture of residual gases, etc., the absolute classification of a fuel would be neither a point, nor a line, and we have arrived at a stage where we could do with one, but a three- or four-dimensional structure. It would surely be too slow a process to plot out this; we would have to return to the engine to make at least those plots which are felt to be of importance at the present stage of engineering.

Today it is required that certain engines under certain conditions derived from the operational considerations should give the result. Perhaps Mr. Jost would like to explain in greater detail as I may not have understood his intention perfectly.

Jost

I would not give rise to the misunderstanding that I favour the immediate abolition of the test engine, and instead advocate the use of my method for the purpose of classification. I do believe, however, that there is need for a method independent of the test engine and permitting of prediction of the behaviour of the fuel based on a knowledge of the particular conditions of the test engine.

As to the sensitivity of knock to changes in pressure and time this is quite as practicable with my method as with a test engine. It is however quicker and cheaper since less fuel is consumed. It will of course not be possible to make the measurement in exactly the same way as if they were done on the test engine which itself gives the standard. Measurements relating to the pure reaction occurring in the unburnt mixture are made, this being the process at the basis of knock; the fuel is tested over a wide range of temperature, over the required ranges of pressure and composition of mixture; then it should be theoretically possible to calculate in advance the knock characteristic for any engine. This assumes that I know the following data for the engine; the law according to which the flame is propagated (theoretically to be found from the indicator diagram) and the temperature of the unburnt mixture at any time. This again is theoretically possible but does of course present difficulties.

Buschmann

In the latter part of Mr. Jost's paper, mention was made of physical and chemical experiments on oxy-hydrogen combustions and explosions for comparison with the propagation of flames. In recent years one has heared and read occasionally of the use of electrolytic gas of hydrogen in practice, sometimes as main fuel mixed with air, sometimes added in larger or smaller quantities as fuel addition during operation.

I have myself worked with small additions of electrolytic gas and hydrogen in engines. I observed increased performance and decreased consumption, i.e. better combustion and a more favourable thermal efficiency for a carburettor engine even if additions amounted to only a few percent by weight. The gases mentioned had a distinctly better effect when evolved electrolytically at the moment of use than if taken from the storage bottle. My hypothesis that the status nascendi plays a part should be tested by chemists. I would recall ideas proposed by Erren and Levaczec.

English journals have repeatedly given reports during the past years on gasoline and recently on Diesel engines as well in which additives of hydrogen or electrolytic gas were made. These reports gave a favourable picture. I should like to suggest that the experiences from this field of ideas should be exchanged and evaluated in co-operation between all those who have been intimately associated with it. They should thrash out whether or not it is worth while to advance these prospects and to apply them to engine development on a larger scale. I am conscious that these things do not belong to the immediate programme. It was said this morning that things farther afield should not be mentioned today. Since however the president asked that everything appertaining to this subject and of some value to it should be brought forward I took the liberty of making this point.

Ernst Schmidt

As has been done by Mr. Jost in his paper knock has usually been regarded as a process caused by the instantaneous ignition of the unburnt gas. I do think, however, that this conception which is not quite correct physically should be made somewhat more precise. For it is only the increase of pressure in the unburnt gas caused by the combustion that leads to an increase in temperature culminating in self-ignition.

Now increases of pressure progress only at the velocity of sound or (what amounts to the same to a factor near to one) with mean molecular velocity. The velocity of ignition throughout the unburnt gas being attained is thus bound up with the velocity of sound. Under certain conditions only could a really instantaneous ignition of the whole gas be imagined. That is in case the temperature increases in the direction of propagation of the pressure in such a fashion that at more distant points a somewhat smaller increase of pressure is sufficient to induce spontaneous ignition on account of the higher temperature. Only for some definite distribution of temperature could complete instantaneous ignition be imagined.

If temperature differences occur then ignition is possible at a somewhat more distant point accidentally having a higher temperature, as was also mentioned in Mr. Jost's paper. This ignition may even cause a reverse velocity of flame propagation. If however the velocity of sound represents the upper limit of the speed of ignition, a fact which also emerged from experiment, then one can ask why detonation does not occur then. Referring also to the remarks by Mr. Eucken, the latest experiments, those of Wolfhard especially, who has measured the increase of the ionisation currents with real detonations and in knocking combustion would appear to show that knock in the engine is not a true detonation: the increase of the ionisation current in a knocking engine is not much more rapid than in combustion without knocking.

Then arises the following question: why, if the carrier of the ignition is the pressure wave proceeding at the velocity of sound, is there no true detonation. It is probably to be ascribed to the insufficiently rapid development of the reaction. In the engine the combustible mixture is highly diluted by nitrogen so that only a very small fraction of the molecular collisions lead to reaction. Moreover the insufficient uniformity of the mixture may slow up the reaction to such an extent that detonation cannot come about. For we know that the carburettor action is that of an atomizer and that evaporation does not occur to a large extent till afterwards, during the compression. In the short time available I do not believe that a perfect mixture, which could only be attained by diffusion and turbulent motion can actually be established. During combustion irregularities will occur, i.e. richer and leaner region will persist in the mixture and these will slow down the reaction in the practical engine.

Jost

May I briefly make clear my position to the fundamental question of detonation. I agree of course completely with Mr. E. Schmidt in his statement that none of the experiments up to date, excepting those of Schelik and Voinov which have also been criticized in Mr. Boeze's paper, give any experimental indication of a detonation occurring in the knocking of the gasoline engine.

We have never endeavoured to make a more accurate determination of the flame velocity. The maximum velocity may thus be 700 or 1000 or 1200m/s; it might be called the effective flame velocity. The latter must be of the order of magnitude given which is half the velocity corresponding to a detonation.

Eucken

The problem does not seem to me to have been unambiguously explained so far. I would therefore give expression to scepticism as I have already done in my paper. I shall confine myself to two points.

1. Scrutiny of the well-known flame photographs by Dixon allows the observation in several cases, of a detonation gradually developing from the slow advancing flame. According to this a continuous transition from normal flame propagation to detonation must exist.

2. One finds some difficulty in finding any cause for the space-explosion proper, i.e. the first ignition within a homogeneous, explosive gaseous mixture. In reality however we already have a hot front where everything is ready for a reaction at least during combustion in the gasoline engine. Why then, one can now ask, does the detonation not proceed from this point. Can it really be taken as experimentally ascertained that the detonation or the knocking do not fundamentally start at the flame front, in the case, that is, of a perfectly homogeneous compression of the unburnt gas? In practical experiments, it is true that it does not seem possible to avoid temperature differences as a consequence of pressure waves in the unburnt gas: the space-explosion would then set in at points at which there is an accidentally high temperature.

The experiments discussed in the reports of the Messrs. Broeze, van Driel and Rietler (pps. 19ff. etc. undoubtedly show that the bulk explosion does not really proceed homogeneously. Rather it usually proceeds from a single or at least a limited number of centres. But why then should it not amount to a kind of detonation?

In any case the expression bulk explosion seems somewhat misleading since according to the experimental results available up to date the explosion is certainly not homogeneous but proceeds from definite centres.

Jost

I agree of course that even before ignition a strongly accelerated flame might proceed from the normal flame front; for this the mixture may have been sufficiently prepared by having been kept at the high temperature after adiabatic compression.

In knock photographs one does not exclusively observe pictures in which knocking sets in at a distance from the flame front. It may start practically at the flame front. On the other hand, I have seen ignition setting in at the wall farthest from the sparking plug. In this case I would imagine that a pressure wave set up previously, obtained an especially large amplitude on reflection and then caused ignition. I should like to say the following about Dixon's photographs: in general there is an accelerated flame which turns into detonation, simultaneously there is a receding wave. The latter is necessary for the conservation of momentum. In the photographs of knocking combustion there will, however, probably always be receding waves, these arise only after combustion has reached the wall. Thus one never sees the waves proceeding backwards and forwards from the point where knocking sets in, as one should in the case of a detonation. It has not been seen on any photographs except those of Sokolik and Voinov which we have never recognised as conclusive. I was glad to learn from Mr. Broeze's paper that he has judged them similarly.

Ernst Schmidt

Mr. Eucken has just been asking how knocking phenomena could already begin in the unburnt portion although they are much more probable at the advancing flame front. We must not forget that the valves are extremely hot in the practical engine. It is my opinion that knock phenomena are often brought about by the valves and any other parts of the wall at a high temperature.

In the practical engine we do have to take into consideration additional circumstances which are consciously eliminated in physical experiments carried out under very clean conditions.

Eucken

I should like to add that the wave reflected at the wall does not completely contradict the assumption of a detonation. I refer to the pressure wave mentioned by Mr. Schmidt which causes ignition at the point of its reflection from the wall. This wave need not have proceeded from the flame front. It may have originated somewhere else.

Jost

To this I should like to reply that I did not regard this as a criterion. As a criterion I do regard the lack of a receding wave arising simultaneously with the detonation.

Eucken

On this I should like to remark that the flame front is not very sharply defined. You have mentioned in your paper that every thing there is in turbulent motion. In consequence a number of reflected waves will spread out, the individual ones being relatively weak. Since they are not exactly in phase the whole picture becomes badly defined, a reflected wave not being distinguishable.

Even this argument then would not seem definitely to contradict the possibilit of a detonation wave. On the other hand I should like to stress explicitly that at the present time there is no basis on which I could make out a substantial case for the existence of a real detonation wave. In any case the point is so important that its clarification should by all means be attempted. It is therefore worth while to have a more thoroughgoing discussion here.

Jost

According to the experiments available at present, disregarding those of Sckolik and Voinov, the following would argue against a detonation:

1. A velocity equal to the velocity of detonation has never been observed. A the minimum this would have to be 2000 m/s. Normally we never exceed 1000 m/s.

2. The receding wave has never definitely been observed, in any case no defini observation in favour of a detonation has been recorded.

We cannot of course absolutely deny the occurrence of a detonation. For that further experiments would have to be made. Our apparatus would incidentally be suitable for such an experiment.

I could imagine that detonation would be most likely to occur in cases of extreme knocking. We made the following observations during spontaneous ignition experiments. The burning of the mixture becomes uniform, the intensity of the flame increases and the afterglow decreases, as the ignition lag increases.

This may be an indication of something else happening under extreme conditions. The meaning of this would be (I would, however, leave the question open): under extreme conditions we may suppose that a real detonation occurs: what is observed normally however is not a detonation.

I would not deny it 100% but confine myself to the statement: up to now, apart from perhaps a few special cases, there is no cogent reason for assuming a detonation.

Eucken

Surely the positive result of our discussion is this: we should all be glad if Mr. Jost would check the matter with his beautiful apparatus. It would be very much worth while. At any rate it would be a most decisive experiment for us. For as I have said in my paper in order to reach an explanation of the knock phenomenon, we need a working hypothesis: the question of whether or not we are dealing with a bulk explosion is of decisive importance for this working hypothesis. We may have to ask which conditions would have to obtain to effect a change from combustion to detonation. As was shown in my report I am inclined for the time being to believe that your conception and that of Mr. Schmidt are essentially correct. But we do need a further investigation in order to rest on a sure foundation.

Macho

I should like to say a few words in regard to the fourth part of Mr. Jost's report. This dealt with the physical mechanism of flame propagation. Mr. Jost concludes that for the latter diffusion is at least as important as heat conduction. This may give rise to a misunderstanding.

Certainly diffusion is a very lively process at high temperatures. If, for instance, a bead of common salt is held in the flame of a Bunsen burner, a luminescent yellow paraboloid is formed with the bead as the focus. The sodium atoms thus appear to be able to diffuse against the full gas current underneath the bead. The velocity of diffusion is greater than the flow velocity of the gas as a consequence of the high concentration gradient and the high temperature conditions in the area or rather the layer of combustion of a flame are different. There the high temperature flame gas meets the low temperature fresh gas; if a molecule, e.g. a molecule of water, at a high temperature, wants to pass out of the flame gas through the area of combustion into the unburnt gaseous mixture, then it will have lost its velocity through a few collisions on the way.

In other words: the area of combustion is such that continuity of temperature and concentration gradient is maintained over the distance of a few free paths. It is true that both heat conduction and diffusion are decisive factors for the passage of heat through the area of combustion itself. There I agree with Mr. Jost. Accordingly the velocity of combustion is also decisively determined by the diffusion processes in the area of combustion. For the further progress of combustion in the unburnt mixture however it is solely the heat conduction that is responsible. One can keep Le Chatelier's definition: The velocity of combustion is the velocity at which the unburnt mixture must move towards the combustion surface so that it may be heated to the ignition temperature by conduction from the latter, where the temperature of ignition is fixed by the given conditions. The equation of heat transfer in moving bodies is applicable to this process. To the area of combustion itself the differential equations of heat and of diffusion are not applicable. Only gas-kinetic considerations may here be used.

Jost

According to direct experiment the velocity of combustion does not change as the heat conductivity or the root of the heat conductivity if one refers to the usual equations. One can immediately draw the conclusion that the transfer of heat is not exclusively decisive. Further by quite general methods one can show theoretically that mean velocity of diffusion in the gas and the heat conductivity are closely related processes and that their effects must be equally important.

I further agree with Mr. Mache that the heat transfer is mainly effected by conduction. Heat transfer is not the only factor decisive for the propagation of the ignition. For instance if one has got hot gas and cold gas in contact with it then there will be a steep concentration gradient of the initial substances from the fresh gas to the burnt gas. The fresh gas will diffuse into the unburnt gases with a considerable velocity under the influence of this steep gradient. It will then react very quickly. This process alone would afford an explanation for a velocity of combustion of the order of magnitude actually observed leaving out things such as conduction of heat, etc.

The following however is still to be added: in hydrogen flames for instance one certainly has a considerable concentration of hydrogen atoms. The velocity of diffusion of hydrogen atoms is extremely large, much larger than the mean coefficien of diffusion for the whole mixture. The heat conductivity may of course be compared with the mean coefficient of diffusion for the total mixture. It is thus that one obtains an effect of heat conduction in dissociating mixtures: hydrogen atoms of high energy diffuse into the cold mixture and take their heat of reaction with them. Apart from this there is a transfer of active particles into the cold mixture. One can make the following argument: if the transfer of energy of these active particles were only of the order of magnitude of the conduction of heat then its effect on flame propagation should all the same be much greater. For, out of the mean thermal energy only a small fraction is effective as activation energy for the reaction. Only molecules with energies above a rather high limit are capable of undergoing a reaction. The energy which the hydrogen atoms carry with them is available as energy of activation.

Eucken

I would only mention very briefly that Mr. Jost's report has really seemed very convincing to me and that this attitude seems to be shared by other gentlemen.

Schneuffer.

In the expositions made so far it has been stated that there is detonation combustion as well as spontaneous ignition. It has, however, never been clearly defined under which conditions these two kinds of combustion can occur. If you refer to the literature you will find that all research workers who have succeeded in bringing about a detonating combustion have worked either with tubes or vessels essentially differing in shape from an engine cylinder. From this emerges the fact that in order to obtain a detonating combustion one needs a certain size of the combustion chamber, i.e. a certain initial distance is necessary for the detonation wave to be built up.

Since I was not able to realize a detonation wave during my knock experiments the subject was approached by my co-worker at the D.V.L. Mr. Cherlinsky who carried out the relevant experiments. These experiments did show that an initial distance of from 1,5 - 2 m. was necessary to produce detonating combustion. We went even further: the D.V.L. high speed recorder was developed which allows the satisfactory recording of such rapid combustion processes. Whereas in the tube we obtained detonating combustions continually with the corresponding velocities in engines of even the largest dimensions we never obtained velocities above 300 m/s. That means that far from reaching a detonation velocity, the velocity of combustion in an engine does not even reach the velocity of sound.

If these questions are approached not from the point of view of the physicist but that of the engine designer, then this result appears quite obvious. For a detonating combustion one simply needs a certain run-up which the engine designer cannot afford. Any remains of doubt have by the way been eliminated by Weinhart who measured the change with time of the ionisation current during detonating and non-detonating combustion. Contradicting measurements on engines can be disproved without difficulty as has been shown by Broeze.

Eucken

There is yet another hypothesis feasible: that in knock we do not have a genuine detonation but that stage of transition already mentioned between combustion and detonation. One could classify it as a detonation not fully developed. In this case it would be quite understandable that a receding wave does not appear. Only under the extreme condition of an instantaneously started detonation, which is not generally the case, in the engine, would this occur.

Jost

The receding wave is always present. To the question whether knocking develops at or before the flame front I would answer: both cases may be found. This is not, however, an argument against detonation. Bone has made pictures in which detonation started up in the detonating mixture 6.5 cm. in front of the flame front in a cylindrical tube. These are dimensions which are not even exceeded in the engine. In this respect also there is to be found no fundamental difference.

Lindner

I should like to observe the following with regard to the influence of diffusion on the velocity of flame propagation in a combustible mixture of gases. Here velocities of diffusion are so low that an effect at higher velocities of combustion cannot be observed. The process of diffusion gains in importance in the neighbourhood of the limits of ignition where the velocities of propagation are less than 1 m/s.

A good understanding is obtained of these things by an examination of the motion of the flame in the neighbourhood of the igniting spark according to the Schlieren method. If the flame paths proceeding from the ignition spark are plotted against time something like the following picture is obtained from Benzene-air mixtures. Curve "a" applies to the lower limit of ignition, curve "b" to the upper limit, i.e. deficiency of air.

The flame front is strongly accelerated in the immediate proximity of the point of ignition by reason of the thermal or even electrical effects (ionisation) of the ignition spark. At the lower ignition limit (curve a) an immediate strong retarding of the flame front occurs after ignition. At the upper limit we find a continuous transition to the constant velocity of propagation which characterises the further progress. The only explanation of the retarding at the lower limit is that the large Benzene-molecules available in too small a number in that region have too low a velocity of diffusion. A mixture capable of being ignited must be available for the further propagation of the flame, and to attain this the benzene molecules must find time to diffuse into the bubble of hot gases, set up by the igniting spark.

The conditions in hydrogen air mixtures are exactly the reverse. The retardation (curve a) is observed at the upper limit, i.e. with deficiency of air. For here the molecule of the oxygen of the air is the larger relative to the hydrogen molecule. The former thus has the smaller velocity of diffusion. The retardation comes into greater prominence the higher the values chosen for the initial pressure during ignition. This fact favours an explanation on the basis of a diffusion process for the diffusion constant varies inversely as the pressure.

Jost

I should like to mention that this is not really my theory but rather that of Clusius. It was he who determined the lower ignition limits of hydrogen and deuterium. He showed that the positions of this limit for H_2 and D_2 are determined by the different diffusion velocities. Especially if one ignites the gas at the lower end of a vertical tube the limit is much lower for hydrogen than for deuterium. This is due to the fact that hydrogen diffuses from the outside into the rising glowing ball of gas, the combustion zone, where there is a hydrogen deficiency. This is the explanation given by Clusius,

Eucken

If I remember rightly this is the case of the so-called cold flames,

Jost

Yes, that was in the case of hydrogen where the type of cold flame was different from that observed in the combustion of hydrocarbons. I suppose it is similar to the findings of Mr. Lindner which make it apparent that they are diffusion phenomena. Fundamentally one takes into account both heat conduction and diffusion. By a somewhat arbitrary method one eliminates the heat conduction so that it does not appear explicitly. Implicitly it is contained in the calculation.

Footnotes

1. As has been shown quantitatively by Brown (e.g. Chem. Rev. Z 1938) and also by G. Damköhler.
2. Compare G. Damköhler, Jahrb. 1939 for German aeronautical research II 62-75.
3. And under the conditions of combustion in the engine the essential conditions for heat explosion will exist in spite of chain branching.

3a. W. Jost and L.V. Müffling, Journal Electrochemie, 45, (1939) 93.

4. W. Jost, L.v.Müffling, W. Rohrmann, Zeitschrift Electrochemie 42 (1936) 488.
5. The term "ignition velocity" is commonly used. This term may bring about associations, not existing in reality, with the ignitability of the various substances. We shall therefore not use the expression.
6. In practice one does not succeed in observing velocities of combustion below a certain finite value (10 cm.).
7. Here we disregard disturbances from the cooling action of the wall. These are also responsible for the fact that the flame front does not in reality touch the wall.
8. W. Jost and L.v Müffling, Ztschr. physikal chemie, part A, vol.181, 1938, p 208.

Figures

1. Diagrams of combustion in the Engine.
2. Region of Heat Explosion as a function of Pressure p and Temperature T
3. Explosion region for chain explosion at low pressure.
4. Typical region of explosion (shaded)
   Curve a: 1-2-3 chain explosion
   3-4 Heat explosion
   Curve b: diagrammatic course for hydrocarbons according to Townend.
6. Normal combustion with external ignition
7.,8. Knocking combustion with external ignition
9. Ignition delays with self-ignition of stoichometric fuel-air mixtures.
10. Calculation of knock from the Effect of Temperature on Self-ignition
11. Increase of critical compression ratio by addition of $Pb(C_2H_5)_4$ according to Lovell, Campbell and Boyd
12. Blending octane number and critical compression ratio
13. Combustion speed in terms of concentration.

Fig. 14. Flame Travel in Cylindrical Tube.
15. Temperature and concentration in the combustion zone
16. Normal velocity of combustion of hydrogen mixed with atmospheres of constant compositions according to Hehn

GDC 10/10,228.

Deutsche Akademie der Luftfahrtforschung.

ATOMIC-PHYSICAL CHANGES IN THE SLIDING OF METAL SURFACES

By Richard Glocker

From experiments carried out in conjunction with
H. Richter and H. Hendus.

The fundamental question as to whether, in polishing, the production of an amorphous layer (Beilby layer) is brought about merely by smoothing the an-
surface, or also by changes in the atomic order, has not been clearly
swered by applying the electron diffraction method. Owing to the extremely shallow depth of penetration of the rays, the diffraction picture is completely altered by layers, a mere few molecules thick, of organic substances (fats, hydrocarbons) adhering thereto.

A renewed investigation into this question held out some hopes of success when it became possible to develop a polishing process in which the participation of organic molecules could be excluded. Soft metals such as tin and lead are polished by hand in their own grindings on a finest grained glass plate. For polishing harder metals, use was made of a glass disc rotating at high speed in a vacuum.

The arrangement used for the electron diffraction photographs is shown in Figure 1.[1]. The pencil of rays which is intercepted by two shutters each 0.1 mm in diameter passes through the chamber from right to left; the preparation is placed in the central cubical part. One great advantage of the mechanical shutter system is the ease of adjustment and the low current consumption, which makes it possible to keep the tensions of 60 kV constant within ±1% by very simple means.

The fundamental difference between the photographs of a crystalline and an amorphous substance may be seen from Figures 2a and 2b. There are a number of sharp diffraction rings with crystalline selenium (Figure 2b), but with amorphous selenium (Figure 2a) the rings are not very many but wide, and the innermost is the most intensive[2].

(Figure 1)
Electron diffraction camera by Seemann

In Figures 3a and 3b two photographs on a crystalline and a polished tin surface are placed together for the sake of comparison. In the first case, the diffraction picture is that of the well-known crystal space lattice of "white" tin and in the second case a picture similar to that of amorphous selenium. Proof that this is an arrangement of tin atoms similar to a liquid is afforded by a comparison with the picture of a piece of tin foil, which was heated above the melting temperature while the photograph was taken (Figure 4a). The conditions of the ring dia-
ameters are the same; the absolute values nevertheless differ by 8% and
show that the atoms of tin on the polished surface are rather further apart, a circumstance that is very likely due to the insertion of gas atoms.

It is worthy of note that an "amorphous" dispersion picture is likewise produced if a rolled crystalline sheet is corroded or heated for a short time above the melting point, and is then quenched (Figure 4b). This can be restored to the crystalline form by annealing for half an hour at a temperature just below the melting point, and in a
vacuum. The reciprocal change from the amorphous state into the

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1) Manufacturer; Seemann-Laboratory, Freiburg i.Br.
2) Cf. the irradiation photographs, Figures 4a/b. With reflection
photographs (Figure 3b) the intensity of the inner ring is much weakened by absorption.

crystalline and vice-versa shows that the "amorphous" arrangement is a true structure of elementary tin. Beilby's theory, that on being polished, the amorphous state is brought about by rapid cooling of the smallest fused areas, thereby gains considerably in probability. In the same order of ideas is the observation that amorphous polished layers can be obtained most easily with metals having a low melting point, such as tin, lead, bismuth and likewise antimony. Binary, ternary and quaternary alloys of these elements, which are well-known as bearing metals, provided typical, amorphous polished structures. The position of the rings varied here according to the space requirements of the types of atoms concerned.

Figure 2a - Vitreous selenium. Figure 2b - Crystalline selenium.

Figure 3a - Crystalline tin. Figure 3b - Polished tin surface.

Figure 4a - Tin heated above melting temperature. Figure 4b - Tin quenched from a temperature above the melting point.

An extension of the investigations to sliding processes in bearings with oil lubrication first of all encountered the difficulty of finding a solvent that dissolves the layer of oil and does not itself leave any residue on the surface of the metal. The most suitable solvent was finally found to be very pure petrol benzine1) distilled over charcoal. The form of the test-pieces for running-in experiments on bearings, which were carried out on a wear machine of the State Material Testing Institute, Stuttgart, by Mr. Brockstedt, may be seen from Figure 5.

(Figure 5)
Form of the sliding rings for the experiments with bearings.

They consisted of three 12 mm long sector-shaped arc pieces, while a complete ring of chromium steel formed the counter-bearing. The most favourable load conditions for the formation of amorphous surface layers are shown in Table 1; the bearing pressure was gradually increased in the manner indicated. Nickel requires greater loads and longer running times than tin. The amorphous layer develops particularly rapidly with Rose metal, which melts at 94°C. and consists of 2 parts Bi and 1 part each of Sn and Pb. The photographs of a dry, polished sample (Figure 6a) of Rose metal and an originally crystalline sample2) (Figure 6b) treated in the wear machine, are practically identical. The existence of amorphous layers was also detected in white bearing metal. In all cases, these were confined to small areas surrounded by larger crystalline areas. The investigation with electron rays was carried out immediately following on the wear experiment, as a crystallisation of the amorphous surface points could be observed even after standing for one day.

1) I should like to take this opportunity of thanking Mr. Fricke.

2) The samples were lapped before insertion with feldspar of 10 µ. Both the polished samples and those lapped with feldspar furnished a crystalline dispersion picture.

Metal	Load kg/sq mm	Time hrs.	Speed m/sec.	Temp. of oil °C.
Nickel	20	6		
	40	14	2	70
	90	150		
Tin	30	30	2	50
	45	180		
White bearing metal	40	0.05	8	
	40	0.05	6	40
	40	12	4	
Rose metal	15	0.75		
	30	4	2	35

Table 1

Amorphous layers during the running-in process for bearings.

In order to confirm these findings, further processes were developed for producing amorphous layers. Amorphous antimony could be obtained in four different ways: by evaporating in a vacuum, decomposition of $SbCl_3$, electrolytic precipitation, and polishing. Proof of the genuineness of these structures was afforded by converting into the crystalline phase (brief heating to 100°C.). Thin foils with a noncrystalline atomic arrangement could be obtained with a large number of elements, e.g., B, Si, P.S.Te, As, Tl etc., particularly by evaporating in a vacuum. In the case of 13 elements it was possible to reconvert into the crystalline form.

Particularly worthy of note are evaporation experiments with alloys, because they confirm the results of the polishing and running-in experiments with alloys. If a mixed crystal with 50% Sb and 50% As is evaporated in a vacuum, and if the precipitate forming on a film of collodion is examined, we have the photograph in Figure 7a. The two types of atom have completely merged and form a common atomic arrangement resembling a fluid. The same applies to alloys of Sb and Se or Ga and In. On the other hand, in a photograph of the alloy Ga-Sb, the amorphous ring systems of both components overlap (Figure 7b); here a separation into groups of atoms of the same nature takes place in very small areas.

In order to check the electron diffraction findings and to obtain details of the atomic order of amorphous solids, amorphous antimony and vitreous selenium were thoroughly investigated by Mr. Hendus with monochromatic X-rays. The photograph of amorphous selenium will be seen from Figure 8; for the sake of comparison, a picture of crystalline selenium (Figure 9) obtained by the usual method is also given. As will be seen from Table 2, the interference periods with electron and X-rays agree very well, and do not show any appreciable differences between the amorphous solid state and the molten state of the selenium1).

1) Fused selenium after J.A.Prins, Trans.Faraday Soc.33 (1937) 110.

State	Phot. process	$d_{1A^{\circ}}$	d_2/d_1	d_3d_2
vitreous	X-radiation	3.32	0.54	0.63
vitreous	Electr.rad.	3.33	0.54	0.64
liquid	X-radiation	3.38	0.55	0.64

Table 2

Interferences of vitreous and liquid selenium.

Figure 10 contains a comparison of the values of the interference periods of the innermost-ring, as obtained by electron diffraction on amorphous layers in the course of these experiments, and with the X-ray values of metal in the molten state as given in technical literature and Hendus' determinations with solid amorphous antimony and selenium. On the whole, agreement is good, while a large part of the figures given in literature for polished structures deviates considerably from the corresponding figures for the liquid state. For the magnitude of the interference periods, the atomic volume is primarily the determining factor, and this is plotted in Figure 10 as a curve; an exception is formed by elements having low atomic weight. This comparison of the figures for amorphous layers obtained with electron rays and the X-ray figures for fused metallic masses affords fresh proof of the identity of the two atomic arrangements.

Figure 6a - Rose metal after polishing on glass.

Figure 6b - Rose metal after running in on the wear testing machine.

Figure 7a - As-Sb alloy with uniform "amorphous" atomic arrangement.

Figure 7b - Ga-Sb alloy with overlapping of the amorphous atomic arrangement of Ga and Sb.

Figure 8
Fine X-ray structure photograph of vitreous selenium.

Figure 9
Fine X-ray structure photograph of crystalline selenium.

Figure 10
Interference periods of the innermost diffraction ring of elements in the molten and amorphous state.
X Electron rays ○ X-rays

Further characteristics of an amorphous atomic arrangement have to be obtained. By analysing the X-ray photographs of antimony and selenium by Fourier's analysis[1], the number of nearest neighbours of an atom (co-ordination number) and the distances between the atoms were determined. The differences compared with the corresponding values for the respective crystal space lattice were trifling. The atomic arrangement of an amorphous solid thus has a certain order, but the latter is very much smaller than in the crystal lattice. The basic difference can be elucidated by means of a two-dimensional point system (Figure 11).

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1) H. Hendus, Zs. f. Phys. 119 (1942) p. 265.

Figure 11
Two-dimensional model of the atomic arrangement

A) of a crystalline substance
B) of an amorphous substance

In both drawings, each point is surrounded by a group of four atoms at a certain distance. If to system A a further degree of order is added so that all the points lie at the angles[1] of a quadratic network, i.e., they assume an orientated position in respect of determined directions, an arrangement is produced as would correspond to a crystalline substance on a model scale. This is characterised by the property that the whole net arrangement can be built up by the periodic repetition of one structural unit, the lattice cell[2].

Now that the existence of amorphous metal layers in the polishing and sliding process has been proved beyond all doubt[3], the next task must be to clarify their importance for the adhesive ability of the oil molecules.

Thanks to the support of the Research Department of the R.L.M., the investigations, which stretch over several years, were able to be concluded, although under difficult external conditions.

[1] Only every second line is drawn.

[2] In Figure 11, the lattice cell is the smallest square confined by the lines shown.

[3] H. Richter, Zs. f. Phys. (1943), in the press.

GDC.10/10,314.

PHYSICO-MOLECULAR PROCESSES IN LUBRICATION*

BY: Lothar Wolf, Halle, as guest.

The Problem.

Scientific research into lubrication is in a position similar to that of electro-chemistry shortly before the introduction of the ionic theory. In view of this circumstance, the aim of present-day lubricants research may be characterised by the task of imparting to the term "lubricating property"** the same accurate and concise degree of significance as the term "electrolytic conductivity" for the ionic theory.

If we attempt to portray the position in regard to lubricants research, as it presented itself about 10 years ago, we obtain the following picture: In the range of complete lubrication **, the mechanically descriptive treatment developed by Sommerfeld, Gumbel, Reynolds, Michell etc. and based on the hydrodynamic continuum theory, appeared to be adequate in regard to the physical side of the process; nevertheless, despite a number of attempts, the material side of the problem, i.e. the relationship between the material nature of the substance concerned and the lubricant on the one hand and its suitability for lubricating on the other hand, remained to a very large extent unsolved. In the domain of boundary lubrication, the continuum theory based on considerations of flow technique was insufficient to describe even the physical process; as increasingly higher demands were made by technique ***, this found expression in the fact that it was believed possible to deal with the difficulties that kept on arising by the use of such vague and picturesque terms as oiliness unctuosity or slipperiness.

We have reason to suppose that these difficulties - in great measure at least - are to be sought in the neglect of the discontinuous (i.e. molecular) structure of the material. From the point of view of the molecular theory, the question of lubrication is one of the arrangement of the molecules inside the lubricating fluid and on the boundary surface between the lubricant and the material on the one hand and of the energetic reciprocal actions on the other hand, existing between the molecules of the lubricating fluid, between the atoms of the material (which here is always assumed to be metallic) and its molecules, and between the atoms of metal. The problem is therefore that of establishing in every individual case a quite definite arrangement of the molecules of the metallic surfaces - which are probably sliding on one another - and of keeping this arrangement sufficiently stable and mobile at the same time. Viewed from this angle, lubricants research therefore implies primarily an investigation of the intermolecular forces and arrangement inside the fluid lubricant (problem of liquid or complete lubrication) and on its boundary surfaces with the metal (problem of boundary lubrication). The state of mixed or partial lubrication, in which complete and boundary lubrication overlap and are simultaneously active, does not therefore require at the moment special treatment of its underlying principles.

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* The same subject is reported on in partly enlarged, partly abbreviated form in the 1942 volume of the journal "Die Chemie".

** In our use of the terms lubricating property, complete lubrication, boundary lubrication and mixed lubrication, we have adopted the terminology issued by the DVL.

*** As an example of an attempt to overcome these difficulties in practice by avoiding traditional ideas, reference is made to a Russian investigation of 1940 (E.G. Semenido, Petrol. Ind. USSR (1940), 60).

Complete Lubrication

The state of complete lubrication is, as has been stated, mastered from the flow technique standpoint by the hydrodynamic continuum theory*. Of the macroscopical-material properties, which are taken for granted in this theory, the one which chiefly determines this state is the viscosity of the lubricating fluid and it dependence on pressure and temperature. The question as to the relationship between the lubricant's suitability and the chemical constitution is in this domain primarily a question as to the relationship between chemical constitution and viscosity, or in more general terms, the mechanical properties of the fluids. This question has often been asked but has never received an adequate reply, even in the simplest cases. We recognised that the reason for this is that the manner in which the problem is put, (provided that by chemical constitution is meant only the formal composition and structure of the free individual molecules), is too narrow. The properties of fluid substances are indeed determined not only by the arrangement and linkage of the elementary atoms in molecular union, as usually meant by the term "constitution", but to an equal extent by the arrangement and reciprocal linkage of the molecules in the space occupied by the fluid. To give an example, this means in the present connection: The molecule of a fatty acid is characterised by the formula $R.C^{O}_{OH}$ and that of its methyl ester by the formula: $R.C^{O}_{OCH_3}$. The great difference - amounting to about one order of magnitude in viscosity - between the mechanical properties of a high fatty acid and its methyl ester should therefore, if the chemical constitution in the above narrower sense were the only determining factor, be caused by a relatively slight material change, scarcely affecting the structure of the individual molecule. As a matter of fact, more accurate investigation shows that the smallest particles, carrying out their heat transfer independently inside the fluid, in the case of the ester, are those of composition and form $R.C^{O}_{OCH_3}$, but in the case of (not too dilute) acids are twofold super-molecules, i.e. double molecules having the form $R.C^{O}_{O}H_{2}{}^{O}_{O}C.R$. In comparing an acid with its methyl ester, one is not really comparing materials whose constituents (in the sense of the kinetic theory) are approximately of the same magnitude and shape. Conditions are similar for the comparison of an alcohol $R.OH$ with its methyl ester $R.OCH_3$, where in the non-diluted fluid in one case there is a complicated mixture of super-molecules $(ROH)_f$ of different degree of association f and different form**, and the other case exclusively the simplest molecules of the form $R.O.CH_3$. A comparative morphological investigation cannot, therefore, achieve the object unless allowance be made for the supermolecular structure of the fluids.

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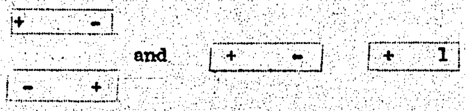
* Investigations as to the scope of the hydrodynamic theory have been carried out in Germany by E. Heidebrook in association with W. Nuecker, W. Peppler and others.

** Similar cases of the formation of super-molecules (or association) occur in other types of material. In alcohols in particular, the variants as regards number and structure of the molecules (type and degree of association) are specially remarkable. See in this connection K.L.Wolf and H.G. Trieschmann, Praktische Einführung in die physikalische Chemie, part 1, Brunswick 1937, p.107 et.seq. For literature and new results see H.Dunken, F.Judenberg and K.L.Wolf, Zeitschrift für physikalische Chemie (B) 49 (1941) 43 and K.L.Wolf, Theoretische Chemie, part 2, Leipzig 1941, p.220 and 347 and particularly part 3 (in the press-).

Of the various forms of supermolecule isomers, the difference between polar and non-polar supermolecule formation is of importance; if we simplify supermolecule formation diagrammatically by the picture of the juxtaposition of two molecular dipoles, we may show this by the types



continued at foot of page 3.

This influence makes itself most felt when, on being diluted and with rising temperature, the supermolecules break up to an increasing extent into supermolecules of lower degree of association, which may be observed in mixtures of liquids and in temperature changes. If to this be added the fact that in fluid mixtures, the formation of supermolecules or association overlaps the reciprocal action with the molecules of the solvent (phenomenon of solvation), and that both solvation and association affect viscosity in the same sense, and if it be further observed that when an associative substance is diluted, association decreases while solvation increases, also that the temperature coefficients of association and solvation often deviate considerably from one another, and that corresponding phenomena in the case of large molecules may also occur inter-molecularly*, the diversity of the material conditions to be satisfied will be appreciated when it is a question of proceeding systematically e.g. in an attempt to make fluid lubricants which are to have constant viscosity over a wide temperature range and a low pour point.

Boundary lubrication

Still more diversified and irritating is the physico-molecular treatment of boundary lubrication. We speak of boundary lubrication when - e.g, with a small bearing gap or low sliding speed - the friction is independent of the macroscopic viscosity η **. If the coefficient of friction μ (for sliding friction) be examined for this case at the same lubrication point, using different lubricating fluids, we have the picture shown in Table I, where, in addition to indenendence of the viscosity coefficient η which is of course called for in the domain of boundary friction, it should be observed that saturated hydrocarbons produce the lowest friction and that in homologous series friction decreases with increasing molecular size. The higher friction coefficients of acids, compared with those found for hydrocarbons, are striking, as it is well known that in practice the lubricating quality of paraffin oils is often improved precisely by the addition of fatty acids. This induced us to investigate the effect of additions of acids on the friction coefficient of saturated hydrocarbons. We were able to make the observation (elucidated in Fig. 1 by one of many examples), that by the addition of minute quantities of fatty acids, the friction is at first greatly increased, and is only improved when the acid concentration is further raised. The surprising question hereby arises as to whether the customary addition of acid in practice does not partially restore to its former quality an oil that has previously been spoiled by traces of acid. It would therefore be desirable for technical experiments to be carried out as quickly as possible with chemically uniform oils of great purity. In other solvents, this effect is less in evidence; as Fig. 2 shows, it does not exist in the case of benzol; the addition of acid here has the effect of increasing friction.

The question as to the cause of the action of additions of acid, which sometimes increase and sometimes reduce friction cannot be answered from friction measurements alone.

To complete the friction measurements, we therefore made use of measurements of the boundary surface tension against metal, especially as we had found in experiments on alcohols carried out recently by H. Dunken, a

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**continued from Page 2.
Regarding the question, which should also be discussed in this connection, of the packing of molecules and supermolecules in fluids, vide K.L.Wolf and R.Grafe, Kolloid-Zeitschrift 98 (257) 1942. Experiments are in progress for making use of the respective results of lubricant research.

* The case seems to be realised in a few recently tested lubricants.

**For further details in this connection, vide H.Dunken, I.Fredenhagen and K.L.Wolf, Kolloid-Zeitschrift 100 (1942) in the press.

simple ratio between the boundary surface tension of the alcohols against metal* and the value of the static friction coefficient u for metal surfaces. Measurements in the homologous series of the undiluted fatty acids at first showed that in the case of acids as well there is a simple ratio between the boundary surface tension and the coefficient of friction u. Also, from measurements with solutions of fatty acids in hydrocarbons, an analogy was evident between friction and boundary surface tension, albeit in the form that in a concentration c, where the friction coefficient exhibits a sharp maximum, the boundary surface tension has a pronounced and equally sharp minimum. (Fig. 3.)

An explanation for this curve of the boundary surface tension with concentration may be found, if the acid active at the boundary surface contains a boundary surface active component which with higher acid concentration is less in evidence, i.e. the acid solutions are mixtures of three, not two substances. Now acids in very dilute solutions in dipole-free substances consist exclusively of single molecules. As the concentration increases, these combine - in accordance with the law of mass action - rapidly to form double molecules, so that even in solutions of moderate concentration, there are no longer any single molecules present. The single molecules, which have a large, free, permanent electric dipole moment, however, alter the boundary surface tension of the solvents very much more vigorously than double molecules. This great activity of the single molecules is responsible for the great drop in the boundary surface tension with a low acid concentration; with high concentrations it disappears again just as do the polar single molecules. By assessing the measurements of the boundary surface tensions with the Gibbs adsorption isotherm, we were able to determine the extent of preferential adsorption of the single molecules over the double molecules; the relevant data will be found in Table 2.

Substances, which do not form any non-polar double or super molecules, do not show minima of this kind, as shown, for instance, by investigations with mixtures of benzol and heptane, CCl_4 with paraffin oil, or halogen benzenes with cyclohexane or heptane. On the other hand, here too, there exists selective absorption, as shown by two examples in Tables 3 and 4.

Further information regarding the behaviour of the coefficients of friction should be provided by current experiments with the foregoing and with further mixtures of liquids**. Investigations into boundary surface tensions, on the other hand, have fared so well that we are able to make a few more detailed statements here.

Boundary surface tension, adhesiveness and tensile strength.

The adhesion of a liquid to a boundary surface is denoted by giving its adhesiveness H, measurable in erg/cm^2, i.e. the effort required to pull a layer of liquid 1 sq.cm in cross section from the boundary surface. This adhesiveness may be determined by the equation given by Duprée

$$H = \sigma_1 + \sigma_2 - \gamma_{12} \qquad (1)$$

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* For technical measuring reasons, the boundary surface tensions were measured against mercury and the friction coefficients against brass. Comparative experiments show that the conditions are similar in the two metals. For the measuring process, vide I. Fredenhagen, Diss. Halle 1942.

** In these subsequent experiments, reference will be made to the observations by T.P.Hughes and G. Wittingham, Transact. Far. Soc.38 (1942) 9.

from the boundary surface tension $_{12}$ and the surface tensions $_1$ and $_2$ of the two boundary surface partners. Adhesive effort obtained in this manner is collated in Tables 5 and 6. These reveal the following facts:

1 - The adhesive effort increases with the polarisibility of the molecules.

2 - The adhesive effort of fatty acids is greater than that of alcohols.

3 - The adhesive effort increases in the homologous series of the alcohols and esters with increasing carbon number; in the homologous acids series it remains constant.

4 - The adhesive effort decreases (in the case of alcohols and acids) with branched chains.

From the adhesive effort H (from the ratio Force = Work/Distance), the relevant adhesivenesses Z_{adh} (in dyn/cm^2 or in kg/cm^2) can be determined, while as distance (owing to the rapid drop in the intermolecular forces with distance), a distance of 10^{-8} cm may be regarded as adequate. The adhesive strengths, which provide a standard for the forces required to remove a boundary surface 1 sq. cm. in cross-section, correspond inside the fluid or the metal to their tensile strengths (likewise to be given in dyn/cm^2 or kg/cm^2). The latter are obtained from the breaking strength H_z, which is analogous to the adhesive strength and is in turn determined indirectly for fluids from measurements of the surface tension in accordance with the equation corresponding to (1)

$$H_z = 2 \qquad (2)$$

and for metals directly by technical experiments. Table 7 shows a compilation of the figures in question. From this table it will be seen that on pulling apart two metal plates held together by a layer of fluid, however sharp the pull so that flowing cannot take place, it can be reckoned that the metal represents the point of lowest resistance to the tensile strain. It is thus understandable how and why lubricants. e.g. in high speed piston engines and gear wheels can have a corrosive action, as has been observed by von Heidebroek*.

On the theory of boundary surface adhesion

The above findings are to a great extent supplemented by theoretical considerations. It must, however, be expressly pointed out that the following considerations only apply when one of the boundary surface partners is a metal and the other contains molecules representing permanent electric dipoles. Table 8 shows by way of provisional information **, how different conditions are with aqueous boundary surfaces, for which alone, in the past, experimental material was available to any extent.

We studied - and this must suffice as a first approximation - the reciprocal electrostatic action of a metal-insoluble dipole molecule with the metal. If a dipole molecule comes into the vicinity of a metal surface, it is subjected to a force of attraction, which can be understood as that

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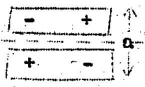
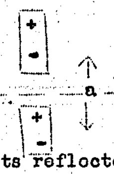
* E. Heidenbroek and E. Pietsch, Forschungen auf dem Gebiet des Ingenieurwesens, 12 (1941) p.4 and Zeitschrift für angewandte Chemie 1941.

** We hope to make a subsequent report on how these considerations vary for non-metallic boundary surfaces, and how they may be supplemented with metal surfaces by allowing for the action of non-static forces.

between the permanent dipole and its image (reflected on the conducting surface, the charges being reversed). This force is of the same nature and order of magnitude as the reciprocal action between two real dipoles, already referred to, causing the formation of double molecules. In both places, a distinction must be made between two extreme possibilities: the tangential



and the normal



- arrangement of the two dipoles, or of the dipole and its reflected image. The opinion is now widespread - evidently being influenced by Jaquet's calculations - that polar molecules are adsorbed on metallic boundary surfaces always, or for preference, in the normal (= vertical) position. Jaquet based his calculation on the fiction of the dipole length zero. However, a check of the calculation by H. Dunken, with exact calculation, produced the following result: Let l be the length of dipole and a the shortest distance between the two dipoles on both sides of the boundary surface, $q = l/a$ (the "reduced" dipole length) the ratio of both, Ψ_t the potential of the tangential position and Ψ_n the potential of the normal position. The quotient Ψ_t / Ψ_n, which we term the "position factor" ϕ for short, measuring the preference given to tangential over the normal position, depends on the reduced length of dipole, in the manner shown in Fig. 4. From this, the following will be seen: ϕ is for all $q > 0.32 > s$, when $q = 0.32$ it equals s, and for all values of $q < 0.32$ is in its turn $< s$. This means to say that as long as the distance a is at least three times greater than that of the length of dipole l, the normal position is given preference in relation to the metal boundary surface, otherwise, however, the tangential position. If $q = 0.32$, both positions are of equal value; in this case, there is a kind of degeneration in regard to the orientation of the dipole on the boundary surface. In the extreme cases where $q = 0$ and (this was Jaquet's special case) $q = \infty$, each favoured position is occupied with double the energy gain ($\phi = 1 : 2$ or $2 : 1$) of the non-favoured position. Calculation shows further that the potentials depend on the angle, which the dipole orientation forms with the metal surface, in various ways, viz. minor deflections from the tangential position lay claim to a considerable part of the total amount of energy Ψ_t, while the potential Ψ_n is quite insensitive to deflection. This signifies that the tangential orientation can be imagined as being relatively rigid, while the normal position - the binding strength being the same - is relatively mobile. It appears from this that according to whether the dipole, as in alcohols, lies near the molecular surface or, as with ketones or ethers, it lies further inside the molecule, there will be a strong possibility of variations in the mechanical properties of the layers adsorbed on metal surfaces, determining boundary lubrication. For cases where conditions may vary through action other than dipole action, Figure 5, which shows the result of the corresponding calculation for quadrupole molecules, provides a preliminary example. However, the variety of possibilities is determined, not only by the nature of the forces, but also by the nature of the density of the packing (itself dependent on the molecular structure; /Fig.6/) of the molecules in the boundary layer. Since these possibilities can be surveyed today on the basis of our knowledge of molecular structure, we hope that it will now be feasible to pursue the problem of the structure of desired layers of lubricant in the sense of our introductory remarks, and thereby tackle questions of substitutes for and the improvement of lubricants logically from the material side. In principle, the only question requiring further elucidation is that of determining friction and wear by the various forms of the adsorption layer.

Read before the German Aeronautical Research Academy, 7th May, 1942.

TABLE I

Material	Coeff. of Friction.	100
Cyclohexan	0.12 ± 0.005	0.96
Heptare	0.135 ± 0.005	0.40
Benzol	0.13 ± 0.005	0.65
Methane Tetrachloride	0.19	0.95
Methanol	0.32	0.59
Ethanol	0.22	1.72
n-Propanol	0.20	2.10
n-Butanol	0.18	2.8
n-Hexanol	0.14	5.3
Propionic Acid	0.40	1.15
Butyric Acid	0.35	1.59
Valerianic Acid	0.30	2.3
Caproic Acid	0.25	32
Heptylic Acid	0.22_5	44
Monylic Acid	0.15_5	8.1

TABLE II

Out of a Total of 10,000 Molecules there are apportioned:

Inside			On the boundary surface		
To Single Molecules	To Double Molecules	To Cyclo-hexane	To Single Molecules	To Double Molecules	To cyclo-hexane
1	0.3	9999	9275	607	118
6	13	9981	6830	3152	18
23	203	9774	3566	6433	1
40	664	9296	2335	7665	0
99	3274	6627	1315	8685	0
94	9904	0	455	9545	0

Distribution of the molecules in the interior and on thenboundary surface, in respect of mercury, for mixtures of valerianic acid with cyclohexane under various conditions of mixing. (mass action constant inside the solution 2.10^{-3}, on the boundary surface $8.5.10^{-3}$).

TABLE III

Out of a total of 10,000 molecules there are apportioned:

Inside		On the boundary surface.	
To iodobenzene	To Heptane	To iodobenzene	To Heptane
1	99	14	86
4	96	34	66
12	88	65	35
64	36	96	4
82	18	98	2

Distribution of the molecules inside and on the boundary surface in respect of mercury for solutions of iodobenzene in heptane.

TABLE IV.

Out of a total of 10,000 molecules there are apportioned:

Inside		On the boundary surface.	
To cyclohexane	To acetone	To cyclohexane	To acetone
4	96	24	76
15	85	59	41
32	68	80	20
74	26	96	4
87	13	98	2

Distribution of the molecules inside and on the boundary surface in respect of mercury for mixtures of cyclohexane and acetone.

TABLE V

Material	Surface Tension	Boundary Surface Tension	Adhesive Effort.
Hexane	19.5	380	120
Cyclohexane	24.7	377	128
Benzol	28.6	366	143
CCl_4	27.3	358	149
CS_2	31	341	170
Dioxane	33.0	377	136
Chlorobenzene	33.2	350	163
Bromobenzene	36.3	340	176
Iodobenzene	39.5	306	214
Ethyl Acetate	23.8	384	120
Ethyl Tartrate	39.3	346	173
Phenyl Acetate	37.3	353.7	164
Cyclohexyl Acetate	25.3	360.4	145
Water	72.3	385	167
Ethyl Alcohol	22.4	382	120
Octanol	27.0	367	140
Cylopentanol	33.	365	148
Acetic Acid	27.4	331	176
Octylic Acid.	28.7	334	175

Adhesive effort H_{Hg} of various materials in respect of mercury (at 22°C)

TABLE VI

Material	Surface Tension	Boundary-Surface Tension	Adhesive Effort
Alcohols			
Methanol	22.5	384	119
Ethanol	22.4	382	120
n-Propanol	23.7	379	125
i-Propanol	23.7	384	117
n-Butanol	24.8	377	128
t-Butanol	20	384	116
n-Hexanol	26.4	372	134
n-Octanol	27	367	140
Acids			
Formic Acid	37.4	393	124
Acetic	27.4	331	176
Propionic	26.5	333	174
n-Butyric	26.6	335	172
n-Valerianic	27.4	333	174
n-Hexylic	28.1	334	174
n-Heptylic	28.3	335	173
n-Octylic	28.7	334	175
n-Nonylic	29.9	332	178

TABLE V CONTINUED

Material	Surface Tension	Boundary—Surface Tension	Adhesive Effort.
Esters.			
Methylacetate	24.9	388	117
Ethyl Acetate	23.8	384	120
n-Propylacetate	24.3	380	124
i-Propylacetate	23.1	369	134
n-Butylacetate	24.5	374	131
sec-Butylacetate	23.5	354	150
i-Butylacetate	22.8	355	148
n-Amylacetate	25.5	365	141
i-Amylacetate	24.8	345	160
n-Hexylacetate	26.3	365	141
n-Heptylacetate	27.1	357	150
n-Decylacetate	28.7	343	166
n-Dodecylacetate	29.1	341	168

Adhesive effort in respect of mercury in homologous series. (at 22°C)

TABLE VII

Material	Tensile Strength	Adhesive Strength.
Cyclohexane	4 900	12 500
Benzol	5 600	14 300
CCl_4	5 600	15 000
Ethyl Alcohol	4 500	12 000
Propanol	4 700	12 500
Butanol	5 000	12 800
Hexanol	5 300	13 400
Propionic Acid	5 300	17 400
Butyric Acid	5 300	17 200
Hexylic Acid	5 600	17 400
Heptylic Acid	5 700	17 400
Water	14 400	16 700
Mercury	96 000	96 000
Brass	5 000	
Iron	4 000-7 000	

Tensile strength and adhesive strength

TABLE VIII

Material	Boundary Surface Tension in respect of		Adhesive Effort in respect of	
	Water	Mercury	Water	Mercury
Hexane	51.25	380	40.0	120
Octane	50.81			
Benzol	35.03	366	66.6	143
CCl_4	43.26	358	56.1	149
C_6H_5Cl	37.41	350	68.5	163
CS_2	48.36	341	55.8	170
Acetone	-	369	-	134
Mercaptan	26.12	340	68.5	160
Ethanol	-	382	95	120
Octanol	8.52	367	90.8	140
Acetic Acid	-	331	-	176
Heptylic Acid	6.56	335	94.6	173
Ester	about 25	about 350	about 75	about 150

Differences with aqueous and metallic boundary surfaces.

3979/105

Berichtsammlung des Versuchslaboratoriums
Report No. 448

Examination of Austrian Petroleum

Dr. Hargmann, Dr. Ebender

Index:

A. Introduction

We had been commissioned to make a chemical examination of Austrian crude oils. These have assumed increasing importance within the frame of the German petroleum sources. Statements were wanted about the components of the various crude oils so that this valuable new source of crude oil might be fitted into the German economic system in the most useful way, also from the chemical point of view. Continuous supervision of the various oil sources should also be instituted so that one can follow qualitatively any changes or variations in the composition of the crude oils produced.

These investigations naturally extend over a long period of time. All the same we think it expedient to set down at this time the results of the tests on the raw oil samples produced so far; this attitude is supported by the fact that no further raw oil samples have come in lately. We want to try and undertake a classification according to quality.

Our work covers both the crude oils proper as well as the gasoline and middle oil fractions in particular. (Special investigations of the lubricating oil fractions were undertaken by the department of Dr. Zorn).

B. The test samples

For our investigations we have so far received three deliveries with samples of the crude oils listed below :-

1st Batch (received 26.8.1943)

BA. 2	Asphalt	Neusiedl	van Sickle
BA. 8	Sonde G 39	Feld	RAG Zistersdorf
BA. 21	" ST.U.6	Sarmat	DEA Neusiedl
BA. 28		Schlier	von Sickle
BA. 35	" ST.U.18	"	DEA Neusiedl
BA. 40	" ST.U. 7	"	" "
BA. 41		Torton	van Sickle Neusiedl
BA. 51	" G 19	Mischöl	RAG Zistersdorf
BA. 55	" G 9	"	" "
BA. 59	" G 33	Asphalt	" "
BA. 67	" G 14	Mischöl	" "
BA. 68	" G 26	"	" "
BA. 70	" G 8	"	" "
BA. 76	" G 38	"	" "
BA. 77	" G 18	"	" "
BA. 78	" G 5	"	" "
EPG 54	" G 12	Horizont 3,4	EPG Gösting
EPG 57	" G 12 A	" 2	" "
EPG 62	" G 23	" 4	" "
EPG 65		Mischtank 7/8 43	"