Attachment V

The Ethylene-Lubricating Oil Process
Its Development and Industrial Application

(Report by Dr. H. Zorn and co-workers, I. G. Leuna, 1943)

Part I of the present report describes the discovery of and laboratory work pertaining to the ethylene-lubricating oil synthesis. The experimental work undertaken in the Ammonia Laboratory at Oppau in cooperation with Dr. Gerhard Hofmann and Dr. Wolfgang Haag during the period of 1934-1937 formed the basis for deciding on June 10, 1936, upon the construction of the semi-industrial plant which was designed for the production in Leuna of 700 Jato* lubricating oil SS 903.

This plant was constructed in the MTA Ludwigshafen by Chief Engineer Futterer in cooperation with Dr. Lauhe who also erected the plant in Leuna under the supervision of chief engineer Hasselblatt. Operation of the plant started in August 1937 under the jurisdiction of the Organic Division headed by the Director, Dr. Giesen. Dr. Gerhard Hofmann was appointed plant manager.

The second part of this report describes the operation of this plant and its expansion to the present day production. The following gentlemen participated under the direction of Dr. Giesen in obtaining these results:

Dr. Gerhard Hofmann, Dr. Hermann Metzger, Dr. Paul Hofmann, Dr. Sackmann, Dr. Hanisch, Dr. Lauhe, Chief Engineer Hasselblatt and engineer Mayer.

On the basis of experience gained at Leuna it was decided in 1941 to build additional ethylene-lubricating oil plants in Schkopau, Heydebreck, Moosbierbaum and to expand the Leuna plant.

The conclusion of this report coincides with the departure of the manager, Dr. Gerhard Hofmann, to Heydebreck at which time Dr. Gericke took over the direction.

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* Jato = Metric tons per year

Part I

Development Work 1934-1937

p.1 The work on the polymerization of ethylene developed from previous work on the action of mixtures of gaseous olefins, in the presence of aluminum chloride, on hydrogenated tar oils boiling above 250°, carried out in the period of 1927-1929 in the Ammonia Laboratory at Oppau by Dr. Freese and Dr. Zorn in the group working under Dr. Pangs and Dr. Galle. This work was based on the discovery of Allenet (Ger.Pat. 402,990) according to which gaseous olefins are readily polymerized to liquid hydrocarbon mixtures when treated under pressure in the presence of anhydrous aluminum chloride suspended in petroleum ether. This method was used by McAffee (U.S. Pat. 1,608,329) who attempted for the first time to produce lubricating oil by passing cracking gas olefins into petroleum fractions in the presence of aluminum chloride. He further recommended adding hydrogen to the cracking gas in order to prolong the activity of the aluminum chloride since hydrogen presumably retards the formation of tarry carbonaceous products. The McAffee process was extended by the Chem. Fabrik Weyl & Co. (Ger.Pat. 341,686) to coal tar fractions. In an analogous way the Oppau work was an extension to pressure-hydrogenated oils.

The experimental work in Oppau led to the construction of a semi-industrial plant in Leuna in 1929. The olefins required were obtained by dehydrogenation of hydrogenation waste gases in a Cowper oven heated to 800°. Gas engine oils were obtained having the following properties;

Sp. gr./20°	0.947	V.I.	-18
Visc. at 20°	90.4 E°	m	4.37
" " 38	20.5	VP	4.61
" " 50	9.3	Flash pt.	193
" " 99	1.8	Setting pt.*	-19
		Coke test	0.08

* Solidification point.

In 1931 this work was discontinued for reasons of economy.

The conversion of gaseous olefins to lubricating oils was resumed several times in 1932-1934. At that time we were engaged in the vapor phase cracking of paraffin and attempted to convert into lubricating oils the gaseous olefins which were necessarily formed in conjunction with the liquid cracking products. The experiments were carried out by passing the cracking gases without pressure through a three-necked glass flask provided with an agitator, and in which anhydrous $AlCl_3$ p.2 was suspended in ligroin. The gas was introduced at an internal temperature of + 50°.

Table 1 *

Date 1932	Exp. No. K.V.	Charge Ligroin g	Charge $AlCl_3$ g	°C	Duration hrs.	Crack. gas lit.	Resid. gas lit.	Increase in wt.
11.15	9	200	50	80	3 1/2	151	114	41
11.3	7	200	50	70	4	153	94	47
10.28	5	200	50	50	4	150	105	59
11.1	6	200	50	50	6 1/2	150	103	61
12.21	12	200	50	40	2 1/4	152	112	59
12.19	11	200	50	30	4 3/4	150	110	57
11.11	8	200	50	70	5 1/4	156	119	29

The above table shows the quantities of gas absorbed. For example, in Exp. No. 6, with 150 lit. of cracking gas introduced, 103 lit. of residual gas was obtained which was reintroduced without further absorption.

* Exp. K.V. 9: C_nH_{2n} in the intake gas 53.4%, in the outlet gas 33.35%.
After the reaction had started, no additional heat was supplied.
" 12: C_nH_{2n} in intake gas 55.2%, in outlet gas 35.0%.
" 8: The $AlCl_3$ was added in portions during one half hour.

p.3 As will be seen from Table 2, propylene and butylene are the gases chiefly absorbed from the olefins contained in the cracking gas. Of the ethylene contained in the cracking gas, only about 1/3 was copolymerized.

Table 2

	Exp. 6: Inlet Gas (150 lit.)			Outlet Gas (103 lit.)		
CO_2	0.00	Vol.%		0.00	Vol.%	
O_2	0.00	"		0.00	"	
CO	0.41	"		0.11	"	
H_2	3.14	"		4.41	"	
C_2H_4	35.50	"	52.15%	24.30	"	30.01%
C_3H_6	12.10	"		3.79	"	
C_4H_8	4.20	"		1.07	"	
C_5H_{10}	0.35	"		0.85	"	
CH_4	23.15	"	44.22%	31.00	"	65.46%
C_2H_6	16.33	"		24.50	"	
C_3H_8	3.67	"		7.30	"	
C_4H_{10}	1.01	"		1.81	"	
C_5H_{12}	0.06	"		0.85	"	

Absorbed

C_2H_4:	18.3 l = 22.9 g	Approx. 34% of the C_2H_4 present
C_3H_6:	14.3 l = 26.8 g	" 79% " " C_3H_6 "
C_4H_8:	5.2 l = 13.0 g	" 83% " " C_4H_8 "

Absorbed, calc.: 62.7 g ; found 61 g.

Table 3

Exp. No.	Taken Ligroin lit.	AlCl₃ g	Press. atm.	Duration hours.	Gas amt.	t °C	Total Prod. g	Product 170° at 1 mm °E₉₉	V.I.
90	7.6	1000	2	16	720	70	2450	1.69	67.4
87	10	1000	2	10	500	80	1920	1.59	39.2
88	10	1000	2	6	400	80	1550	1.49	29.3
89	8.9	1000	2	6	4000	70	1300	1.44	17.2

p.4 Table 3 shows a few experimental results obtained in 1934 in a somewhat larger apparatus operating under a slight pressure (2 atm.). The figures show that oils of a relatively low viscosity are obtained with very divergent properties (V.I.). These large differences prompted us to investigate the polymerization of individual pure olefins.

Polymerization of Propylene

We started with a study of the polymerization of propylene since this olefin can be very easily obtained in a pure form. It was supplied as a 99% pure gas in cylinders from the butadiene plant Lu 286. The work was conducted as illustrated in the next diagram.

p.5 The volume of the agitator flask was 2 liters. The V_2A-metal stirrer was introduced through a mercury seal. The speed of agitation, 700 r.p.m., was the same in all experiments. The propylene gas was introduced at the bottom of the flask. When no other data are given in the subsequent tables, the operation was carried out under the following conditions;

Temperature	60 - 65°C
Rate of Flow	32 lit./hr
Solvent	300 g
$AlCl_3$	30 g

In the first experiment carried out in June, 1934 the solvent was commercial decalin. The resulting propylene polymerizate had a V.I. of -11.2. The experiment was repeated with the decalin that had been used in the first experiment and a polymerizate was now obtained having a V.I. of + 1. The properties of the resulting polymerizate were found to be dependent on the nature of the solvent, as will be seen from Table 4. (See next page).

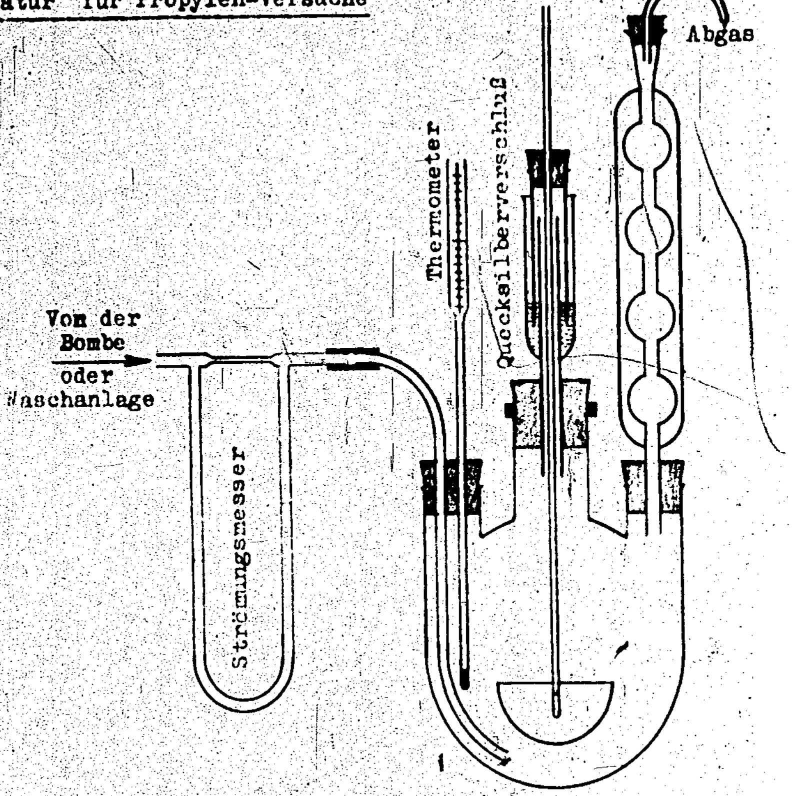
p.6 In considering these results it is remarkable that when a mixture of hydrocarbons is used as solvent, this mixture gives better V.I. the higher its boiling range. The V.I. increases in the order petether, ligroin, kerosene, hydrogenation product 60-130, hydrogenation product 200° from 5.8,10.1,29.7, 31.4 to 75.0. The favorable effect of melted hard paraffin is also of interest. As will be seen from experiments 45 and 142, polymerizates affect the V.I. unfavorably, a fact particularly evident from a comparison of unused and once used hydrogenation products boiling above 200°C; Exp. 58 and 58 a. A comparison of experiments 70-73 is also very interesting. In this case pairs of chemically pure C_8 and C_{12} hydrocarbons which had the same molecular weights but a different constitution, normal and iso-compounds, were used as solvents. It will be seen that the V.I. of the polymerizate is better with the dodecanes than with the octanes, and higher with the normal than with the iso-hydrocarbons.

Table 4 *

Exp. No.	Type of Solvent Used	Viscosity in E°		
		38°	99°	V.I.
25	Ligroin	51.2	2.54	10.1
46	Kerosene	52.5	2.70	29.7
47	Pet.ether	51.2	2.52	5.8
48	Light naphtha 'Normalbenzin'	96.2	3.35	10.7
27	Nitrobenzene	9.28	1.58	28.0
120	Dichlorobenzene	93.2	3.34	16.0
	Hydrog'd paraffin cracking prod.			
24	b.60 - 130°C	85	3.37	31.4
45	" boiling>200°C	27.4	2.37	75.0
52	Hard paraffin, m.p. 52°	27.5	2.30	65.5
	Cracked hydrog'd paraffin			
37	cracking prod.>200°	78.1	3.39	45.2
142	Polymerizate of No. 45	122	4.26	46.3
124	Propylene Polymerization light overhd.	80.5	3.66	60
70	n-Octane	90.3	3.53	37.4
71	i-Octane	79.5	3.25	29.8
72a	n-Dodecane	100	3.83	45.2
73	i-Dodecane	91.5	3.58	40.0
58	Hydrog'd paraffin cracking prod.>150°	28.2	2.32	65.2
58a	Solvent distilled from 58	54.0	2.94	54.0
58b	" " " 58a	74.0	3.41	54.0

* The V.I. values were calculated by the Dean and Davis method (Chem.Met.Eng.36, 618 (1929) from the viscosities of the polymerizate boiling above 170°C at 1 mm Hg. as measured in the Vogel-Ossag apparatus.

Apparatur für Propylen-Versuche



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The reasons for these experimental results must be sought in a copolymerization of the solvent. According to the work of Ipatieff*, a so-called "conjunctive" polymerization takes place between paraffins and olefins in the presence of $AlCl_3$. The iso-paraffin hydrocarbons, in this case, react more easily than the n-compounds. In accordance with the work of Dr. Nienburg and Dr. Zorn (Lab. Report 1570 from the Oppau Ammon.Laboratory) the V.I. of a hydrocarbon of a given molecular weight is higher, the less the hydrocarbon molecule is branched; for branched molecules the V.I. is higher, the longer the side chains. For this reason the V.I. increases in the above order of solvents from pet. ether to a hydrogenation product boiling above 200°, and from n-octane to n-dodecane; and decreases on transition from n-hydrocarbon to i-hydrocarbon since in that case branching of the C-chain of the polymerizate is increased; likewise, it decreases when polymerizates (Exp. 142) and repeatedly used solvents (58a and b) are used since these contain branched hydrocarbons. The influence of the following factors on the quality of the resulting propylene polymerizates will also be shown: the rate of gas flow, the quantity of $AlCl_3$, the amount of solvent and the temperature. All experiments were carried out in the same solvent which was a fraction of a hydrogenated paraffin cracking product boiling above 125° that had already been used once in previous experiments and recovered by fractionation and refining.

p.7 Table 5a shows the rate at which the propylene was being introduced. The V.I. of the resulting polymerizates (constituents boiling above 170°/1 mm) is not influenced by this factor.

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* Jour. Amer. Chem. Soc. 58, 913 (1936)

Effect of
Table 5a; Change in the Rate of Gas Flow

Exp. No.	Solvent cc	Temp. °C	$AlCl_3$ g	Amt. of Gas Lit./hr.	Amt. of Polymerizate in 6 hrs.	Viscosity in E°		
						38°	99°	V.I.
43	300	65	30	16	140	34.8	2.52	64.5
58	"	"	"	32	320	28.2	2.32	65.2
44	"	"	"	50	385	30.2	2.37	62.6
101	"	"	"	150	1250	31.3	2.45	69.6

Effect of
Table 5b; Change in the Quantity of $AlCl_3$

Exp. No.	Solvent cc	Temp. °C	$AlCl_3$ g	Amt. of Gas Lit./hr.	Amt. of Polymerizate in 6 hrs.	Viscosity in E°		
						38°	99°	V.I.
40	300	65	15	32	300	30.6	2.45	72.7
51	"	"	30	"	325	27.4	2.37	75.0
41	"	"	45	"	310	42.3	2.68	58.9

This table shows that the V.I. drops with an excessive amount of $AlCl_3$.

Effect of
Table 5c; Change in the Quantity of Solvent

Exp. No.	Solvent cc	Temp. °C	$AlCl_3$ g	Amt. of Gas Lit./hr.	Amt. of Polymerizate in 6 hrs.	Viscosity in E°		
						38°	99°	V.I.
56a	150	65	30	32	300	44.7	2.68	51.8
58	300	"	"	"	320	28.2	2.32	65.2
57a	600	"	"	"	313	31.4	2.41	63.5

This table shows that after reaching a certain quantity, the amount of solvent has no effect on the V.I.

Effect of

Table 5d; Change in Temperature

Exp. No.	Solvent cc	Temp. °C	$AlCl_3$ g	Amt. of Gas Lit./hr.	Amt. of Polymerizate in 6 hrs.	Viscosity in E° 38°	99°	V.I.
75	300	20	30	32	337	—	17.3	72
74	"	38	"	"	328	612	11.75	65
76	"	50	"	"	314	190	5.39	41
86	"	60	"	"	350	126	4.37	47.2
77	""	70	"	"	329	71	3.15	36.7
78	"	80	"	"	206	44.6	2.56	36.8
79	"	90	"	"	228	32.9	2.24	28.0
		1/2 hr. 5 1/2 hr.						
91	"	40°	30	"	281	280	6.88	46
94	"	90°	30	"	186	49.5	2.68	36.3

This table shows that the V.I. decreases with increasing temperature and that the oils simultaneously become less viscous. With increasing temperature the quantity of polymerizate produced per unit of time also decreases.

p.8 Consequently, the temperature is the only significant factor which definitely influences the propylene polymerization process. Thermodynamically this is quite understandable since polymerization is a strongly exothermic process. The polymerization process, however, is not only influenced by temperature but also by the catalyst.

Table 6 shows experimental results indicating the effect of additives on the $AlCl_3$ catalyst. The same solvent (300 cc) was used as in the previous experiments. The rate of flow was 32 lit./hr.

Among the additives listed there is none that has any particularly favorable effect. Some of them such as $ZnCl_2$, particularly at higher temperatures, as well as $SiCl_4$, $TiCl_4$, $FeCl_3$, FeS, and Tonsil AC have a definitely harmful effect.

In connection with these experiments the effect of water on the catalytic action of $AlCl_3$ was also investigated. The results are given in Table 7.

Table 6

Exp. No.	$AlCl_3$ g	Type of Additive	Amt. g	Temp. °C	Polymerizate Amt. in 6 hrs.	Viscosity E° 38°	99°	V.I.
80	30	Anhydrous $ZnCl_2$	6	40	303	810	14.5	71
84	"	" "	15	40	311	263	7.21	65
89	"	" "	15	60	253	101	3.43	12.6
83	"	NaCl	10	40	330	202	6.43	66
85	"	NaCl	80	40	327	248	6.94	65
102	"	$SiCl_4$	1.5	60	279	98.6	3.61	31.4
103	"	$TiCl_4$	1.5	60	259	117	4.04	38.7
96	"	Anhydrous $FeCl_3$	1	60	268	107	3.83	36.2
121	"	" "	15	60	262	170	5.02	41.0
106	"	Iron Powder	30	260	201	101	4.04	55.4
200	"	"	10	60	216	117	4.48	63.0
204	"	FeS	1	60	204	78.6	3.37	25.9
155	"	"Tonsil" AC (Active clay)	5	60	127	64.8	2.92	26.5
131	"	Mercury	5	60	328	103.4	3.85	42.2

Table 7

p,9

Exp. No.	$AlCl_3$ g	H_2O g	Temp. °C	Time hrs.	Polymerizate g	Viscosity E° 38°	99°	V.I.	Remarks
86	30	–	60	6	350	126.2	4.37	47.2	After long standing the oils from these polymerizates became cloudy, due to a precipitate of a substance of 1800 mol. wt.
69	"	Na X)	"	6	288	122.5	4.04	32.4	
68	"	0.1	"	6	318	94	3.72	46.8	
87	"	1.0	"	6	296	134	4.53	50.0	
88	"	2	"	6	271	88.1	3.88	63.5	
122	"	3	"	6	276	97.5	3.88	52.5	
123	"	4	"	6	268	94.5	3.61	36.1	
128	"	5	"	4 1/4	183	77.1	3.27	36.6	

X = The solvent was dried with metallic Na.

It can be seen (Exp. No. 69, 68, 87 and 88) that a small amount of water favorably influences the polymerization process. An absolutely water-free solvent, dried over Na, is the least effective. Up to 2g = 0.67% of H_2O, the V.I. increases; on addition of more water it then drops and a very interesting phenomenon takes place; after long standing (several days) the polymerizate becomes cloudy and an oil separates which could be isolated (mol. wt. of 1800). This formation of very high-molecular polymerizates was brought about by the addition of water.

The effect of an addition of water is also evident in operations carried out under pressure.

p.10

Table 8

Exp. No.	Autoclave Type	Amount and Nature of Solvent cc.	$AlCl_3$ g	Temp. °C	Press. atm.	Yield cc	Viscosity of Polymerizate 170°/1 mm Hg E^o_{99}	V.I.
24	5 l. V2A	2000 Used	125	20-70	-	2810	4.64	43.0
27	" "	2000 "	125	60	4.5	4600	3.82	37.3
35	" "	2000 "	125	20-70	11	4800	4.46	33.7
39	" "	2000 "	125	20-70	18	4860	4.81	31.0
29	" "	2000 Unused	125	20-70	4.5	4250	6.66	50
34	" "	2000 "	125	20-70	10	4850	5.32	50
37	" "	2000 " And moist	125	20-70	15	4100	7.24	60
41	2.5 l. Iron	1000 Used	100	50-70	-	2650	5.23	36
43	" "	1000 "	100	50-70	21	2380	2.57	25
47	" "	1000 Unused	100	50-70	18	2200	2.52	48

In all other experiments the solvent was a hydrogenated cracked paraffin boiling at 180-250°, partly unused and partly used, that is, containing products of a previous polymerization. Just as in the experiments carried out without pressure (See Table) a used solvent does not give as good V.I. as an unused solvent (compare Exp. 27, 35 and 39 with 29, 34 and 43 with 47). If we compare experiments 24 and 41 carried out without pressure with 39 and 43 it will be seen that the polymerization of propylene under pressure gives thinner oils with a lower V.I. The wall material of the autoclave has no effect on the V.I. of the propylene polymerizates. An investigation was now made of how other organic substances dissolved in the 300 g of solvent might influence the polymerization. The following table shows the results obtained.

Table 9

Exp. No.	AlCl$_3$ g	Type of Additive	Amount of Additive g	Time in hrs.	Amount of Polymerizate g	Viscosity E° 38°	99°	V.I.
82	30	Stearic acid	3	6	315	303	7.40	55
p.11 95	30	Methanol	2	6	260	85.3	3.43	40.4
107	30	Butanol	8	6	75	26.4	2.06	24.8
118	30	Conc. HCl	2	6	321	102	3.76	37.1
162	30	HCl gas introduced		5 1/4	237	92.8	3.68	44.9
156	30	n-Butylchloride				80	3.32	35.9
153	30	Ethyl acetate	2	5	128	87.5	3.56	43.6
154	30	Acetaldehyde	2	5	156	119	4.04	36.4
159	30	C S$_2$	1	4	189	117	4.11	42.8

It can be seen that the polymerization process of propylene is, on the whole, little influenced by these additions. The polymerization is only affected after large amounts have been added, e.g. 8 g. of butanol.

Table 10

Exp. No.	Solvent g	AlCl$_3$ g	Liquid Olefins g	Propylene g	Temp. °C	Viscosity E° 38°	99°	V.I.
18	300	30	0	240	60	30.9	2.28	45.8
98	0	15	80	240	100	44.4	2.97	78
				cf. No. 18				
103	0	30	100 prep.)*	260	65	99.5	4.64	82
104	300	30	100 "	350	65	32.9	2.76	93
100	300	30	91 "	274	65	18.9	2.14	89
105	300	30	110 n) **	330	65	25.5	2.43	92
108	300	30	108	345	65	11.7	1.84	94)
99	300	30	78	309	65	28.0	2.37	72)

Here the liq. olefins were introduced together with the propylene.

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* prep.) = liquid olefins pre-polymerized and propylene then introduced.
** n.)= added after introduction of propylene.

p.12 —— Let us compare Exp. No. 18 with 98, for example. In this experiment the propylene polymerizate from Exp. No. 18 was subsequently treated with liquid olefins and the V.I. increased thereby from 45.8 to 48. In Exp. 103 and 104 the procedure was reversed. In this case the olefins were first prepolymerized and the propylene then introduced, the liquid olefins in No. 104 being prepolymerized in a solvent and in No. 103 polymerized without solvent. In the latter case a more viscous oil is obtained with a lower V.I. than in the former case.

A comparison of the results of Exp. 100, 105, 108 teaches that it is immaterial whether the liquid olefins are prepolymerized or added to the propylene polymerizate, or introduced as a gas with the propylene and then polymerized together. In all cases a V.I. of about 90 is obtained. In all these experiments the weight ratio of liquid olefins to propylene is 1:3; in Exp. No. 99, carried out under the same conditions as Exp. No. 108, the ratio is 1:4; in this case the V.I. dropped to 72.

Table 11

Exp. No.	Olefin Type	$AlCl_3$ g	Temp. °C	Time hrs.	Viscosity E° 38°	99°	V.I.	Sp.gr.	Mol.wt.	Coke No.	Flash Point °C
86	Propylene	30	60	5.7	126	4.34	+44	0.851	649	0.12	244
78	α-Butylene	30	60	5	74.6	3.34	+43.2	0.857	654	0.11	-
5	β-Butylene	30	60	5	23.4	1.76	-83	0.865	426	0.24	173
4	Iso-Butylene	30	60	5	25.6	1.77	-107	0.876	406	0.35	175
164	n-Amylene	30	60	4	43.3	2.84	+73.4	0.868	527	0.12	215
1	n-Octylene	30	69	5	38.7	3.56	+114	0.851			
3	n-Octadecylene	30	60	5	10.8	1.94	+125	0.848			

In Table 11 the properties of the propylene polymerizates boiling above 150°C./1 mm Hg are compared with those of α-, β- and isobutylene and with those of higher n-olefins.

The difference in the properties of the polymerizates of straight chain olefins with a terminal double bond from those of the iso-compounds is apparent. The former give products with a positive V.I. which increases with lengthening carbon chain. They also have the highest mol. wts. and flash points and the lowest specific gravities and coke numbers. β- and isobutylene behave inversely*.

p.13 The behavior of the propylene polymerizates toward Oppanol is also of interest. The latter product is very soluble in these polymerizates. The resulting solution has the same V.I. as the original oil but the viscosity is higher, as may be seen from the following data:

	E^{o}_{38}	E^{o}_{99}	V.I.
Propylene polymerizate without additive	18.9	2.14	88.8
Propylene polymerizate + 1% Oppanol	48.5	3.27	88.0

It is probable that Oppanol is dissolved melecularly and not colloidally in the C_3H_6 polymerizate which has a similar constitution.

p.13a **Polymerization of Ethylene**

The first one to catalytically convert ethylene into a liquid viscous oil was Balsohn (Bull. soc. chim. 2, 31, 539 (1879)). He used $AlCl_3$ as catalyst. One year later Gustavsohn reported in the same journal (34, 322-25, (1880)) that ethylene also reacts with $AlBr_3$. For two decades no further study was made of the catalytic polymerization of gaseous olefins. In 1902 Aschan (1), and in 1911 Ipatieff attacked the problem again. The latter first tried to polymerize ethylene thermally (2) and found that the polymerization of ethylene starts above 325°C.

* A detailed investigation of the relations between constitution of the olefins, their polymerization tendency and the properties of their polymerizates is contained in the Laboratory Report 1543 by Dr. Haag and Dr. Zorn of the Oppau Amm. Laboratory.

(1) Ann. 324, 23
(2) Ber. 44, 2978.

Two years later (3) he noticed that polymerization begins at 230°C in the presence of anhydrous zinc chloride, and at 180° in the presence of anhydrous aluminum chloride. He obtained a mixture consisting of olefinic, naphthenic and paraffinic hydrocarbons. The formation of a similar hydrocarbon mixture was observed by De Montmollin (4) in the dehydration of ethyl alcohol in the presence of phosphoric acid as catalyst. Concentrated sulfuric acid to which cupric oxide or mercuric sulfate has been added is suitable for the polymerization of ethylene to liquid hydrocarbon mixtures, according to Damiens (5). Not only $ZnCl_2$, $AlCl_3$, H_3PO_4 and H_2SO_4 were used as catalysts, but Dr. Hoffmann and Otto (6) showed that boron fluoride, particularly in the presence of nickel, is a polymerization catalyst for ethylene. It is also of interest that azomethane is capable of initiating the polymerization of ethylene at 300°, as was shown by Rice and Sickmann (7). A comprehensive review of the literature has been made by Dr. Hauber and Drl Hagen in Oppau (8) which includes those investigations pertaining to the production of synthetic polymerizates from ethylene.

p.13b The problem of manufacturing lubricating oils by the polymerization of ethylene was taken up for the first time by A. W. Nash and co-workers (Jour. Inst. Pet. Techn. vol. 16, 830-69 (1930); Petrol. Times 24, 799, No. 618 (1930)) in 1929 and 1930.

They introduced 100 g. of finely powdered $AlCl_3$ into 100 g. of petroleum ether in a two liter steel autoclave and forced in ethylene at +5° to+10° under a pressure of 35-55 atm. The pressure dropped about 15 atm. daily and finally 10 atm. daily. In the course of 23 days they obtained 219 g. of Oil A and 68 g. of Oil B.

(3) Ber. 46, 1748
(4) Bull. soc. chim. 1916 vol. 19, p. 242
(5) Bull. soc. chim. 1923 vol. 33, p. 71
(6) Ger. Pat. 505,265 and 512,959.
(7) Jour. Am. Chem. Soc. 57, 1384 (1935)
(8) Report 37 of 5/1/39
" 54 " 4/20/40

The Oil A is the polymerizate which is combined with the $AlCl_3$, and the Oil B the product obtained by decomposing the $AlCl_3$ - hydrocarbon sludge.

Table 12

	A	B
Spec. Grav.	0.8332	0.8636
n_D	1.4622	1.4863
Mol. wt.	384	380
g.H/100 g.C	17.04	15.58
Visc. 38°	13.8 E°	34.5 E°
" 99°	1.55	1.79
V. I.	-104	-194
Iodine No.	-	32

Table 12 shows the properties of the fractions of these oils boiling at 225-250° C at 100 mm Hg.

These figures distinctly show the characteristic differences between these two oils. The Oil B obtained by decomposing the $AlCl_3$ sludge with water is characterized by a low H content and a much poorer V.I. than the Oil A. It is interesting to note that both oils have the same average mol. wt. Oil B. was much darker than Oil A and much less resistant to attack by oxygen and a solution of $KMnO_4$.

p.14 When the polymerization is carried out at a higher temperature, the oils become less viscous and their temperature viscosity relation poorer.

In summary, Nash arrives at the conclusion that these synthetic C_2H_4 oils do not compare with natural lubricating oils, particularly because of their oxidation tendency. He points out that it is possible to improve them by adding inhibitors, even though these, as their name implies, can only have an "inhibiting" effect. The problem still remained of producing synthetic lubricating oils equal in quality to naturally occurring oils. With respect to the mechanism by which these ethylene polymerizates are formed, the authors make the following statement:

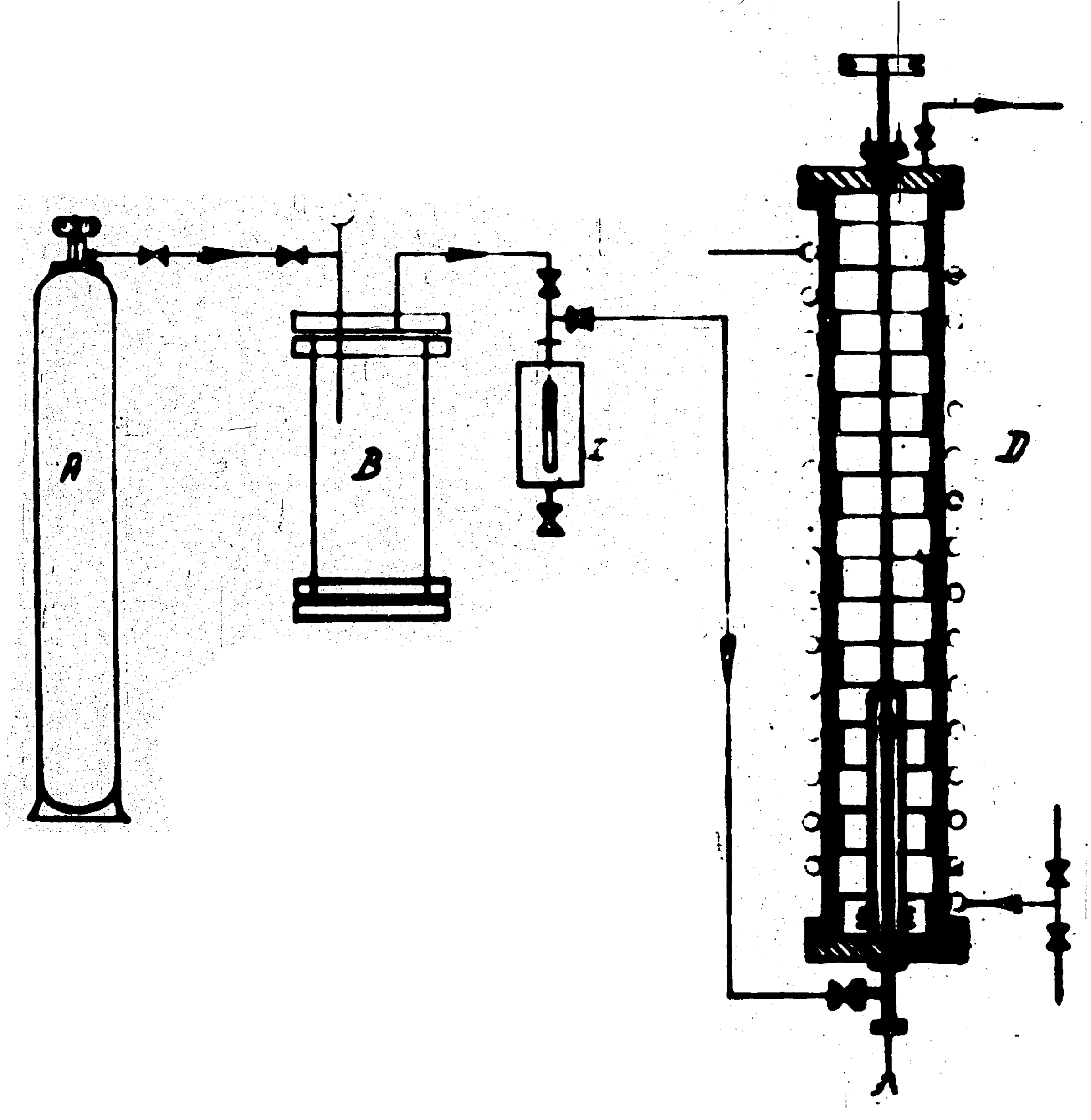
they assume that higher olefins $(C_2H_4)_n$ are first formed from the C_2H_4. These olefins are then isomerized to cycloparafffins by means of the $AlCl_3$. According to thermo-dynamic investigations of Francis and Kleinschmidt this ring closure to cycloparaffins is thermodynamically possible at all temperatures below 400°. The cycloparaffin molecule is saturated and, therefore, no longer capable of forming a solid molecular compound with $AlCl_3$. It becomes a constituent of Oil A.

The liberated $AlCl_3$ molecule can then combine with a new C_2H_4 molecule, convert it into a higher olefin, and then again transform this olefin into a cycloparaffin. Finally, the $AlCl_3$ can also react with hydrocarbon molecules bonded to it as a complex (e.g. the higher olefins), by splitting off a paraffin hydrocarbon with simultaneous formation of a multi-nuclear aromatic hydrocarbon. In this manner are formed the hydrogen-poor unsaturated hydrocarbons of Oil B which being very tightly bound to $AlCl_3$, rapidly reduce the activity of the catalyst.

The findings of A. W. Nash and co-workers were confirmed in 1933 by Watermann and Tulleners (Chimie et Industrie June, 1933, Special Number p. 496-505). These authors experimented in an iron autoclave and used ethylene prepared from alcohol. They obtained almost the same results as A. W. Nash and his co-workers. They also ascertained the characteristic differences of the two types of Oil, A and B, and confirmed the fact that beside the simple polymerization of ethylene, isomerization, hydrogenation and dehydrogenation processes simultaneously take place. The V.I. of their highest boiling products varies between -56 and +2. These values are consequently somewhat better than those of Nash and co-workers, which were all below -100. It seems especially noteworthy that Watermann obtained the value +2 even once. This result made us believe that through a more careful study of this $AlCl_3$-catalyzed ethylene polymerization it might be possible to in-

А.Э 1

26.9.34



crease the V.I. still further. We were reminded of the admonition so often expressed by A. Mittasch: "In catalytic processes, use only the most chemically pure materials." So on September 26, 1934 we started preliminary experiments on p.15 the catalytic polymerization of pure ethylene. We used an ethylene supplied from Holten which, on the basis of its gas analysis and odor, was really pure. In the course of our work the odor test was found to be the safest means of evaluating the usefulness of the ethylene.

Experiment A.P. 1: (See attached diagram)

A 5 liter V2A autoclave with a V2A agitator was charged with 2 liters of a previously hydrogenated cracked paraffin (fraction 225-305°) and 300 g. of powdered $AlCl_3$ added. Ethylene from a storage cylinder A was passed through a paraffin vessel B and a look box C filled with paraffin oil into the autoclave D, with agitation. The internal temperature thereby rose from 24 to 38°. Ethylene was then introduced without external heating until after 10 hours absorption apparently ceased. The pressure in the autoclave had now increased to 16 atm. After stopping the agitator and releasing the pressure, 2340 cc. of a liquid, dark-brown product and a very viscous residue were obtained. The two were decomposed separately with water. The solvent was steam distilled from the liquid portion to 260° and the remaining oil further distilled to 170° under 1 mm. Hg pressure. There remained 254 g. of newly formed high-boiling oil which was treated with 2% of "Tonsil" yielding a pale yellow oil having the following viscosity.

$$11.57\ E^{o}_{38} \qquad \underline{1.82^{o}E_{99} \qquad + 90.8\ V.I.}$$

From the residue, treated in the same manner, there was obtained 209 g. of oil of $51.3\ E^{o}_{38}$, $2.99\ E^{o}_{99}$ and a V.I. of +64.3. This was the first time that a polymerizate having a high V.I. was obtained from ethylene. In a repeat experiment, AP 2, the temperature increased to 57°, measured within the autoclave. The resulting oils, boiling above 170°, had the following properties:

Oil	From Liquid Prod.	From $AlCl_3$-Residue
Sp. Gr. + 20°	0.844	0.887
E^o38	16.95	30.90
E^o_{99}	1.93	2.32
V.I.	62.3	53.2
Coke No.	0.01	0.89
Mol. wt.	557	508

p.16 A.P. A third operation was performed with only 200 g of $AlCl_3$. In order to accelerate the absorption of ethylene by applying higher temperatures, the autoclave was then supplied with a steam coil. While 45 minutes were required to absorb 20 liters of ethylene at an internal temperature of 40°, the time could be reduced to 15 minutes by increasing the internal temperature to 70°. At 70° the pressure in the autoclave dropped from 58 to 30 atm. and remained at this figure in spite of a plentiful supply of gas. A total of 2540 cc. of liquid products including solvent and 518 g. of residue were obtained. From the liquid portion 496 g. of oil was obtained on vacuum distillation, of 216 E^o_{99} and a V.I. of 78.8 (Brit. Oxid. Test: 0, no asphalt). The oil from the residue had a viscosity of 8.05 E^o_{99} and a V.I. of 61.

After these preliminary tests, experiments up to A.P. 23 were made with hydrogenated paraffin cracking product, all with pet. ether as solvent and with varying quantities of $AlCl_3$, and different initial conditions, temperatures, and pressures. Lubricating oil yields of 1400 g. and viscosities up to 8 E^o_{99} were obtained. The V.I. were between 65 and 95.

On October 28, 1943, Exp. A.P. 24 was started with a new shipment of gas obtained from Ludwigshafen. The experiment had to be discontinued after 5 hours when absorption of gas ceased. The experiment was repeated but with the same result. In both experiments the addition compound floated on the clear solvent as a voluminous non-viscid mass from which the solvent could be squeezed out as from a sponge.

An experiment with specially dried pet. ether as solvent gave the same result. The oils boiling above 170° obtained in very poor yield had viscosities of 2 and 2.5 E^{o}_{99} and viscosity indices of -17.6 and -70.4.

An inspection of the ethylene cylinder disclosed a considerable quantity of liquid products: ethyl alcohol, acetaldehyde and ethyl acetate; several cylinders of this shipment contained the same impurities.

In order to eliminate these impurities from the gas, various gas washing processes were investigated. The best purification was obtained with a simple alkaline wash under pressure. In order to prevent future contaminations in the gas supply due to unclean cylinders, an alkali wash tower with Raschig rings was installed between the ethylene cylinder and the autoclave, connected through a stripper with a $CaCl_2$ drying tower. Although analysis could show no impurities in the washed gas, polymerizates were obtained with V.I. of about 40. The high values of about 80-90 could not be reproduced with this purified ethylene produced from alcohol.

p.17 Further experiments were now made with ethylene supplied from Holten. This ethylene originated from coke oven gas from which it was separated in a Linde plant. This ethylene also gave varying V.I., but among different values, ~~figures~~ of 90 and higher were frequently found. An accurate analytical inspection of the various gas shipments showed that the variations in the V.I. were caused by impurities, which are Co, CO_2, H_2S and O_2.

Table 13 shows the effect of various amounts of harmful gases. Experiments were made with the same ethylene and the same $AlCl_3$. A V_2A autoclave of 5 liters capacity was used, charged with 2 liters of pet. ether and 125 g of $AlCl_3$.

The pure ethylene gave a V.I. of 88. carbon monoxide does not prevent polymerization when present in very small amounts, but a decrease in the yield and in the quality of the oil is experienced on the addition of as little as 0.05% CO.

Table 13

Type of Gas	Quantity Added % vol.	Yield in lit.	E^o_{99}	V.I.
C_2H_4		4.00	7.02	88.8
CO	0.05	4.0	5.45	82.0
CO	0.14	3.5	3.67	69.0
CO	1.0	2.8	2.04	38.4
CO	2.1	2.25	2.18	22.4
CO	10.0	2.00	1.75	-10.5
H_2S	0.2	no reaction		
CO_2	0.1	weak reaction		
CO_2	0.4	no reaction		
CO_2	3.0	" "		
O_2	0.8	" "		

After the effect of impurities in the ethylene had been recognized and gas washing had been adopted, a better V.I. was obtained, but variations often occurred. The reproducibility of the experiments was unsatisfactory. The aluminum chloride was then thoroughly investigated. By using various samples of $AlCl_3$ it was found, as shown in Tables 14 and 15, that a direct relation existed between yield and oil quality and the iron and residue contents* of the aluminum chloride.

The figures in Table 14 show that as the content of anhydrous $FeCl_3$ increases, the V.I. decreases and on comparing experiments made at the same temperature, such as Nos. 164, 149, 134 and 176, it will be seen that the oils become less viscous and the yield decreases with increasing content of iron chloride. Table 15 shows that in addition to iron chloride, the content of non-sublimable residue also has a catalytic effect. In order to determine this more exactly, a practically iron-free $AlCl_3$ was used which had been obtained in the Ludwigshafen $AlCl_3$ plant by treating the iron-containing chloride with metallic Al. It will be seen that the yield decreases** with an increasing residue content and that at the same time the V.I. drops, although more slowly.

* Unsublimable residue in $AlCl_3$ was determined by quickly weighing about 2-3 g of the $AlCl_3$ in a previously weighed porcelain boat. The boat was then placed in a glass tube heated to 250°C through which a small stream of nitrogen wwas flowing. The boat was then taken out and weighed after cooling in a P_2O_5 desiccator. It was then heated once or twice for one hour at 250° to constant weight.

** These experiments were made in an autoclave of V2A steel having a capacity of 45 liters (see Table 15).

p.18

Table 14

% Fe	Exp. No.	T °C	5 lit. V_2A Autoclave Yield in g	Product 170° in vacuo °E_{99}	V.I.
0.04	185	120	3850	5.27	92.0
"	174	110	3200	4.88	92.0
"	173	100	3270	7.21	94.0
"	164	90	3700	6.69	94.0
0.17	152	110	3700	2.99	61.9
"	150	100	3900	3.37	74.4
"	149	90	3770	5.23	74.0
1.20	138	100	3730	2.52	63.7
"	131	100	3250	2.33	64.0
"	131	90	3820	2.57	62.1
1.77	180	110	2975	3.76	53.9
"	176	90	2680	2.63	59.5

p.19

Table 15

% Residue in $AlCl_3$	Exp. No. G V	45 lit. N6 autoclave yield in kg	Lube Oil °E_{99}	V.I.
156	82	33.5	4.61	110.7
	83	34.0	4.26	110.8
	84	34.0	4.76	114.0
2.16	67	33.0	4.90	111.0
	68	33.4	3.44	110.1
	69	30.0	6.38	109.0
	70	31.5	4.40	112.2
3.80	57	30.5	5.80	108.0
	58	28.5	5.44	107.0
	62	28.5	4.26	109.1
4.64	63	28.5	5.52	105.2
	64	29.0	5.57	102.3
5.08	66	27.0	4.90	97.0

p.20

Table 16

Various Materials Added to the $AlCl_3$

The tests were made in a 5 liter V_2A autoclave with 2 liters of pure pet. ether and 125 g of $AlCl_3$ (iron free).

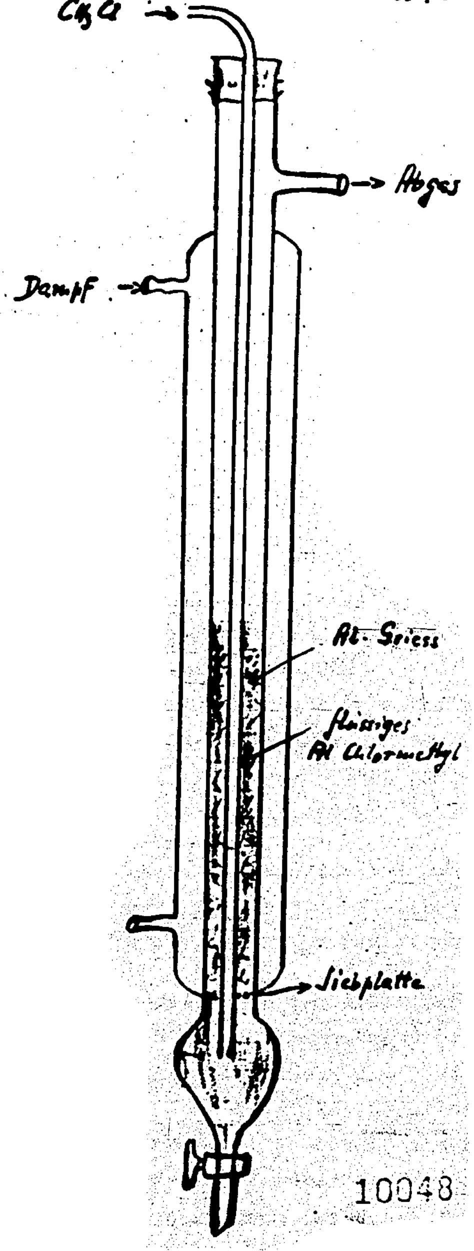
Exp. No.	Additive	Temp. °C	Yield cc	Lube Oil	
				E^0_{99}	V.I.
282	- - -	120	4.20	5.16	86.0
307	- - -	120	4.00	4.47	88.0
295	- - -	130	3.80	3.96	88.4
270	5 g $FeCl_3$	120	2.60	1.82	28.3
301	5 g $TiCl_4$	120	3.90	6.45	75.0
288	5 g $TiCl_4$	130	3.80	2.76	58.1
264	5 g $SiCl_4$	120	3.80	4.41	86.9
286	5 g $HgCl_2$	120	4.00	3.81	80.0
278	2.5g NO_2Cl_2	120	4.20	3.19	75.1
277	1 g Iodine	120	4.20	4.81	76.0
275	5 g $LiCl_2$	120	4.20	3.61	83.3
276	5 g $SbCl_5$	120	3.20	2.18	58.6
330a	5 g $SnCl_4$	120	5.58	2.70	51.6
289	125 g BF_3 without $AlCl_3$	120	4.25	5.01	78.0

Table 16 lists experiments aimed at increasing the catalytic action of the aluminum chloride by the addition of other chlorides.

The results show that these efforts were unsuccessful. Only negative results were obtained. In Experiment 270 the unfavorable action of iron chloride is apparent. Antimony pentachloride and tin tetrachloride also had an unfavorable effect. Silicon and titanium-tetrachlorides have no noticeable effect. The result of Experiment 289 in which the $AlCl_3$ has been replaced by BF_3 is also of interest. Yield, V.I., and viscosity of the resulting polymerizate hardly differ from the values of the $AlCl_3$ polymerizate, except that the V.I. is somewhat lower.

p.21 In connection with this series of experiments, the behavior of an especially interesting product was studied; aluminum chloride-aluminum trimethyl, $AlCl_3.Al(CH_3)_3$. This product melts at 48°, ignites immediately in the air, reacts explosively with water and alcohol but is readily soluble in CCl_4 and in saturated hydrocarbons. It

Abb. 2


CH_3Cl →
→ Abgas
Dampf →
Al-Griess
flüssiges Al Chlormethyl
→ Siebplatte

Im Anschluss an diese Versuchsreihe wurde dann das Verhalten eines besonders interessanten Produktes studiert: das Aluminiumchlorid-Aluminiumtrimethyl $AlCl_3 \cdot Al(CH_3)_3$. Es ist eine bei 48° schmelzende Substanz, die sich an der Luft sofort entzündet, mit Wasser und Alkohol sofort explosionsartig reagiert aber im $C\,Cl_4$ und in gesättigten Kohlenwasserstoffen gut löslich ist. Sie wird dargestellt nach einem Verfahren von I.G. Höchst: P.Anm. I 45 291 IVa/120 vom 9.9.32 und I 49013 IV/120 vom 14.2.34 durch Überleiten von CH_3Cl über mit Jod oder Hg angeätzten, aktivierten Al-Grieß oder Al-Späne. Wir stellten es in folgender Weise dar:

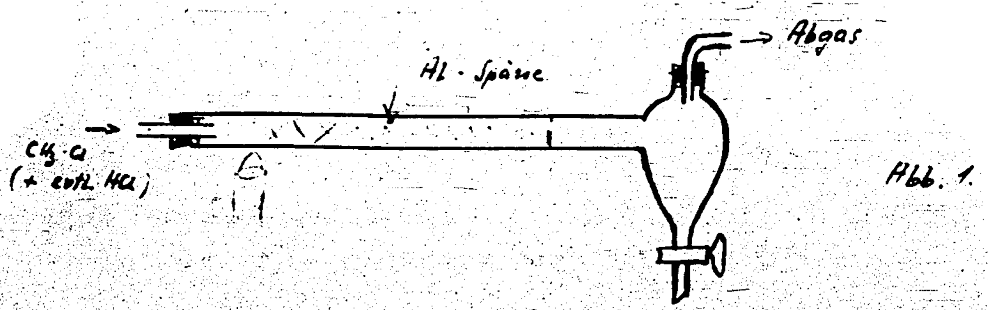


Abb. 1.

Ein Quarzrohr mit angeschmolzener Vorlage (s.ob.Abb.1) wird mit Al-Spänen beschickt, die mit Jod aktiviert sind. Durch das Rohr wird ein langsamer Strom Chlormethyl geleitet, während die Späne an einer Stelle angewärmt werden, um die Reaktion einzuleiten. Der Beginn der Reaktion dauerte oft mehrere Stunden, durch Einleiten von HCl-Gas kann er jedoch abgekürzt werden. Nach Einsetzen der Reaktion muss der Gasstrom gedrosselt werden, um einen zu heftigen Reaktionsverlauf zu vermeiden.

Je nach der Gasströmung, bezw. der dadurch bedingten Reaktionstemperatur, bildeten sich 2 Produkte, bei niederer Temperatur ein flüssiges, bei höherer ein festes. Beide waren meist durch Verunreinigungen des Al braun gefärbt.

Die Hauptschwierigkeit der geschilderten Arbeitsweise war die Abführung der Reaktionswärme. Es wurde deshalb so verfahren, dass die Reaktion in flüssigem Al-Chlormethyl durchgeführt wurde, das von aussen mit nassem Dampf gekühlt wurde. Die nebenstehende Abbildung zeigt das Reaktionsrohr, das etwa zur Hälfte mit Al-Spänen gefüllt ist, zu Anfang mit solchen, die bereits in App. 1 "angesprungen" waren. Bis etwas oberhalb der Späne wurde Al-Chlormethyl in das auf 80-90° geheizte Rohr eingefüllt und nun langsam durch das Einleitungsrohr Chlormethyl zugegeben. Die Reaktion trat rasch ein und das gebildete flüssige Produkt konnte laufend [illegible]lassen werden. Da das Produkt an der Luft unbeständig ist und sich sofort entzündet, wurde es unter Luftabschluss in einem Claisenkolben abgelassen. Unter Normaldruck wurde es dann aus diesem abdestilliert. Bei 40-50° sind die Produkte noch flüssig.

is prepared by a process developed by the I. G. in Höchst: Pat. appl. I 45 291 IVa/ 120 of 9.91932 and I 49013 IV/120 of 2.14.34 by passing CH_3Cl over granular Al or Al shavings activated with iodine or Hg. We prepared it as follows:

A quartz tube with fused-on receiver (see Figure 1) is charged with Al shavings activated with iodine. A slow current of methyl chloride is passed through the tube while the shavings are heated at one spot in order to initiate the reaction. The reaction often required several hours to start but by introducing HCl gas the time can be shortened. Once the reaction has started it must be modified to decrease its violence.

Depending on the flow of gas and the resulting reaction temperature, two products were formed, a liquid product, at low temperature, a solid at higher temperatures. Both were usually colored brown due to impurities in the Al.

The main difficulty of the above procedure was to conduct away the heat of reaction. An attempt was therefore made to carry out the reaction in liquid Al-methyl chloride which was cooled externally with wet steam. Figure 2 shows the reaction tube which is about half filled with Al shavings, previously "primed" in apparatus 1. Al-methyl chloride was introduced to a height somewhat above the shavings in the tube which was heated to about 80-90° and methyl chloride slowly added through the inlet tube. The reaction started rapidly and the resulting liquid product could be drawn off continuously. Since the product is unstable in air and ignites at once, it was drawn off into a Claisen flask in the absence of air. It was then distilled under normal pressure from this flask. The products are still liquid at 40-50°. Dissolved (up to 20%) in a hydrogenated high-boil-
p.22 ing cracking product, the products still fume strongly in the air but do no longer ignite so readily.

Table 17

idition of "Alkyl" to the Solvent

5 liter V_2A autoclave

After charging 2 liters of pet. ether and 125 g of $AlCl_3$, the "Alkyl" was introduced in a current of nitrogen.

Exp. No.	Added	Temp. °C	Yield cc	Lube Oil $^\circ E_{99}$	V.I.
214	- - -	80	4.00	7.83	98.0
313	- - -	100	4.10	7.53	92.0
307	- - -	120	4.00	4.47	88.0
295	- - -	130	3.80	3.96	88.4
324	1 g Alkyl	120	4.00	4.99	95.0
321	2.5 g "	120	3.80	4.41	95.0
311	2.5 g "	130	4.20	4.26	89.4
316	5 g "	80	4.00	6.53	100.0
365	5 g "	90	3.85	6.25	103.0
315	5 g "	100	3.85	5.70	92.0
299	5 g "	120	3.70	5.53	98.0
272	5 g "	130	4.00	4.88	95.0
265	8.3 g "	120	3.40	5.94	91.0
284	8.3 g "	130	3.70	4.93	85.0
266	15 g "	120	3.20	6.08	90.0
355*)	125 g Alkyl, Solid	120	2.65	2.23	47.7
349*)	" " " , Liquid	no reaction			

*) without addition of $AlCl_3$

.23 The experiments summarized in Table 17 were made by adding the "Alkyl" compound, dissolved in one liter of pet. ether, in a current of nitrogen to the charge of one liter of pet. ether and 125 g of $AlCl_3$ (iron free) in the 5 liter V_2A autoclave. It will be seen that on addition of 1-5g of this "Alkyl" compound a small increase in V.I. is obtained, e.g., compare the results of Experiment

307 with Exp. 324, 321. Larger amounts of "Alkyl", however, produce no improvement. The liquid compound $Al(CH_3)_3.AlCl_3$ reacts weakly, as may be seen from Exp. 355. In the liquid compound $Al(CH_3)_3.AlCl_3$ the two free valence electrons of the aluminum chloride, which give rise to its catalytic activity, are saturated or bound to the molecule $Al(CH_3)_3$ which also has two free valence electrons. In the product $Al(CH_3)_3.2AlCl_3$ we probably have a solution of $AlCl_3$ in $Al(CH_3)_3.AlCl_3$ since this product is catalytically active.

Of more interest than the "Alkyl" experiments were those in which powdered Al was added. They were carried out in connection with experiments which had been made in an autoclave lined with aluminum. These experiments had yielded cloudy oils and this cloudiness was caused by precipitated paraffin. The operation was now conducted in such a manner that to 1-20 g of Al bronze was added the usual charge of 2 liters of pet. ether and 125 g of $AlCl_3$, in the 5 liter V_2A autoclave. It was found that with increasing Al the amount of polymerizate formed decreased. With an addition of 20 g of Al bronze to 125 g of $AlCl_3$, about 1 kg of polymerizate was obtained which, in addition to rubbery products, contained as much as 20% of paraffin having mol. wts. of 900-1800 and melting points reaching 115 C. The resulting oils were cloudy even with small quantities of Al-bronze and had poor pour points of about 0°. This method of operation was discontinued.

After having thus investigated the catalytic action of aluminum chloride, the catalytic effect of the wall material of the autoclave will now be described. Experiments were first made in an iron autoclave of 2 1/2 liters capacity.

p.24 The autoclave was charged with one liter of pet. ether and 100 g of $AlCl_3$; ethylene was then forced in and the autoclave heated. In contrast to the experiments in V_2A autoclaves, no strong exothermic reaction developed in the iron autoclaves at the beginning of the polymerization. Moreover, the pressure drop was very slow and the experiments listed in Table 18 were therefore discontinued after 18 hours, although the autoclave was by no means full at that time. For the sake of comparison we may recall that the 5 liter V2A autoclave which was twice as big was filled in 3-4 hours, on the average.

Table 18

2.5 Liter Iron Autoclave

p.24 1000 cc of pet. ether + 100 g of $AlCl_3$. Duration 18 hours.

Exp. No. A P	t °C	Crude prod. cc	Product 170° in vacuo °E_{99}	V.I.
130	to 72°	1770	2.99	69.6
133	" 68°	1060	2.70	52.9
145	" 90°	2030	3.56	54.5
148	" 90°	1180	2.97	53.9
151	" 98°	2050	3.38	58.8

The experimental results show that the polymerizates obtained in the iron autoclave have a lower viscosity and V.I. than the product obtained under similar conditions in V_2A autoclaves, as seen in the comparison summarized in Table 19.

p.26 Table 19 summarizes experimental results which were obtained in a V_2A autoclave using agitators of different materials. In order to afford an exact comparison of the results, only those experiments are given in which the same $AlCl_3$ and the same ethylene were used. It will be seen that a copper agitator is, as a rule, not quite as good as one made of V_2A (Exp. 491 is an unexplained exception). Iron also displays its unfavorable effect in V_2A autoclaves, both with respect to the V.I., yield and viscosity of the polymerizates. For the sake of comparison the experiments made in the iron autoclave with iron agitators are also reported. Nickel as agitator material has no effect on the yield but influences the quality

p.25

Table 19

Effect of Agitator Material

5 liter V_2A Autoclave

	8454				8400				7718				2918				2			
C_2H_4 Cyl.	Exp. No.	Yield lit.	$^{o}E_{99}$	V.I.	Exp. No.	Yield lit.	$^{o}E_{99}$	V.I.	Exp. No.	Yield lit.	$^{o}E_{99}$	V.I.	Exp. No.	Yield lit.	$^{o}E_{99}$	V.I.	Exp. No.	Yield lit.	$^{o}E_{99}$	V.I.
V_2A	498	3.80	4.92	93.4	454	3.73	8.19	103.0	485	3.50	6.07	99.0	482	4.00	6.89	93.8	478	4.00	7.74	92.0
	500	3.30	4.03	93.5																
Cu	496	3.45	3.00	86.3	449	3.70	4.04	96.9					491	4.00	5.90	98.0				
Fe	499	3.00	3.05	82.5					483	2.00	6.52	81.0	487	3.50	4.74	78.7	481	3.70	3.49	75.4
Ni	497	3.80	4.65	79.0	450	3.75	4.74	73.2												
					450a	4.10	6.26	76.0												
Fe-Autoclave with Fe agitator									488	1.70	2.38	42.7	486	2.10	2.44	68.4	479	1.75	2.22	30.5

P.27

Table 20

Comparative Experiments with V2A and N materials

5 Liter V_2A Autoclave

1) V 2 A					2) N_6					3) $N_{5/8}$				
Exp. No. A.P.	t ^{o}C	Yield lit.	${}^{o}E_{99}$	V.I.	Exp. No. A.P.	t ^{o}C	Yield lit.	${}^{o}E_{99}$	V.I.	Exp. No. A.P.	t ^{o}C	Yield lit.	${}^{o}E_{99}$	V.I.
598	150	4.00	3.71	75.2										
601	140	4.15	4.54	89.2	600	140	4.10	5.80	97.0			N5		
					612	130	4.30	4.44	97.5					
596a	120	4.35	5.54	86.0	603	120	4.15	5.98	94.0	619	120	3.5	4.33	92.2
610	120	4.48	5.26	84.0	609	120	4.30	5.49	103.0	626	120	3.6	4.38	90.8
					611	110	4.00	6.41	94.0	618	110	3.7	5.48	98.0
												N8		
604	100	4.30	5.86	78.0	599	100	4.47	7.17	97.0	632	100	3.6	6.49	102.0
					602	100	4.20	8.15	93.0					
594a	80	4.20	6.58	81.0	593	80	4.50	8.38	96.0	616	80	3.7	5.82	100.5

of the polymerizate, causing the V.I. to drop. This fact prompted us to carry out our tests in autoclaves in which the material, in contrast to V_2A contained no nickel, but chromium as the most important constituent. Materials of this type are N_5, N_6, and N_8 steels. Their composition is as follows:

	N_5	N_6	N_8	V_2A
C	0.1	0.2	-	0.1
Cr	3.0	6.0	3.0	18
Ni	-	-	-	8
Mo	0.5	0.35	0.5	
V	-	0.25	0.05	
W	-	-	0.5	

Experimental results obtained with these materials are given in Table 20.

p.28 On comparison of the results obtained in the V_2A material with those in N_5, N_6 and N_8 under identical conditions it will be seen that the elimination in all three N materials of the nickel, which has a catalytically unfavorable effect, produces a substantial increase in the V.I.. Of the three N materials, on the other hand, the N_6 steel was found to be the best inasmuch as the total yield of polymerizates is the highest with that particular steel.

Having reported the effects of aluminum chloride and of the wall material of the autoclave, the influence of the ethylene concentration in the gas will be described in the following. This factor was investigated by admixing varying amounts of other catalytically indifferent gases with pure 99% ethylene.

Such gases are: hydrogen (1), nitrogen (2), methane (3) and ethane (4); the results are given in Tables 21 a-e.

Table 21a

Hydrogen
5 lit. V_2A autoclave

vol.% H_2	Exp. No. A.P.	Yield lit.	Lube Oil °E_{99}	Lube Oil V.I.
2.8	338	4.07	8.46	91.0
5.0	350	4.00	5.27	83.0
7.5	298	3.80	6.45	80.0
10	304	3.70	2.78	66.9
ca.20	340	2.80	2.07	36.3
ca.50	379	no reaction		

Table 21b

Methane
5 lit. V_2A autoclave

vol.% H_2	Exp. No. A.P.	Yield lit.	Lube Oil °E_{99}	Lube Oil V.I.
4.1	359	4.40	3.15	81.0
7.9	322	4.00	3.58	71.6
8.7	287	3.00	2.28	70.6
11.7	290	2.70	2.32	66.4
14.0	357	2.10	3.13	57.7
20.0	306	2.30	2.30	43.1

Table 21c

Nitrogen
5 lit. V_2A autoclave

vol.% N_2	Exp. No.	lit. °C	Yield lit.	Lube Oil °E_{99}	Lube Oil V.I.
5.0	363	80	4.20	6.63	82.0
8.0	322	120	4.00	3.58	74.0
10	267	120	2.80	2.39	68.6
ca.20	261	120	2.35	1.90	64.1
ca.33	257	120	no reaction		

p.29

Tables 21d & 21e

2.0 lit. solvent
125 g $AlCl_3$

12 kg solvent
1.4 kg $AlCl_3$

% C_2H_6	21d Exp. No. A.P.	21d Press. Atm.	21d Yield	21d °E_{99}	21d V.I.	21e Exp. No. G.V.	21e Press. Atm.	21e Yield	21e °E_{99}	21e V.I.
5 %	529	50	4.00	5.95	94.0	85	50	33.0	4.91	111.8
	520	30	4.50	5.92	92.5	84	50	34.0	4.76	114.0
	534	30	3.50	4.73	91.8	83	40	35.0	4.26	110.8
						82	30	33.5	4.61	110.7
20 %	535a	80	3.60	5.47	97.2	96	65	32.0	3.89	106.4
	536	60	3.85	6.56	90.0					
	537	30	3.40	4.64	85.0					
30 %	546	105	2.65	5.49	88.0	106	90	21.3	3.31	94.7
	547	80	2.70	3.11	85.5	105	90	20.9	1.95	92.1
	552	35	2.95	2.02	82.9					
40 %	555	70	2.50	3.16	73.3	108	105	15.3	2.07	90.3

p.30 It will be seen that the V.I. decreases for all four gases with decreasing ethylene concentration, and that the viscosity of the polymerizates is lower with simultaneously decreasing yields. Tables 21 d and e show the results obtained when the variation in the partial pressure of the C_2H_4, resulting from the variation in the C_2H_4 concentration, is taken into account by increasing the total pressure. For an 80% C_2H_4 concentration it is possible to improve the V.I. by increasing the pressure. We may compare Exp. No. 537 with 536 and 535a in Table 21d. For a 70% C_2H_4 concentration an improvement in V.I. and yield is no longer obtainable by increasing the pressure. The yield in polymerizate in both cases is lower than with the 95% gas and is not influenced by an increase in the partial pressure of the C_2H_4. The experiments made in the 5 liter V_2A autoclave were confirmed by tests made in a 45 liter V_2A autoclave. (see Table 21e). The charge in each experiment was 11.9 kg of solvent (pet. ether) and 1.4 kg of $AlCl_3$, a total of 13.3 kg. If this quantity be deducted in Exp. 108, which was carried out with 60% ethylene, it will be seen that in this case only 2 kg of polymerizate is formed in comparison to 20.2 kg for a 95% gas; Exp. No. 82. It should also be borne in mind that in Exp. No. 82, 20.2 kg were obtained in four hours, while 21 hours were required to produce the 2 kg in Exp. No. 108. A dilution of the ethylene thus gives a poorer polymerizate both qualitatively and quantitatively. Consequently, it is necessary to operate with at least 95% ethylene (higher concentrations are preferred) if a polymerizate of high quality is to be obtained economically.

Having discussed the influence of ethylene concentration, the significance of the quantity and the nature of the solvent will now be taken up.

p.31 Table 22 shows the effect of various solvents. The same amount of $AlCl_3$ (125 g) was used in all experiments.

The less solvent taken, the more viscous are the resultant polymerizates and the better their V.I. Here again it should be noted that the polymerizates become less viscous with increasing temperature, as mentioned on page 9. The experiments with a hydrogenated cracked paraffin in Table 23 show the same behavior.

p.31

Table 22

Varying Amounts of Solvent

The experiments were made in a 5 lit. V_2A autoclave. The charges were made up with the quantities of pet. ether stated and 125 g of $AlCl_3$ from the same shipment. The ethylene had to be taken from different shipments.

Exp. No. A.P.	T °C	Crude prod. cc	Prod. 170 in vacuo		
			$^oE_{99}$	V.I.	
192	120	3600	3.68	83.7	3 lit. pet. ether
193	110	3600	3.61	81.5	
194	100	3500	4.31	85.6	
168	90	4080	5.39	89.0	
185	120	3850	5.37	92.0	2 lit. pet. ether
174	110	3200	4.88	92.0	
173	100	3270	7121	94.0	
164	90	3700	6.69	94.0	
196	120	4500	7.15	97.5	1 lit. pet. ether
197	110	4400	7.75	94.0	
178	100	4400	7.76	92.0	
177	90	4600	8.70	96.0	

p.33 In the Table 23 the action of different solvents and additives to the solvents is shown. The experiments were again carried out in a 5 lit. V_2A autoclave with 125 g of $AlCl_3$, with the exception of Exp. No. 142 in which an iron autoclave was used with only 100 g of $AlCl_3$. The experiments made with iso-octane and iso-dodecane are of special interest. They confirm the observation previously made with propylene that i-dodecane gives a polymerizate having a higher V.I. than the one obtained with i-octane. In contrast to the experiments with propylene, the high viscosity of the ethylene polymerizate obtained with i-dodecane is striking.

In Experiment No. 142 carried out with iso-octane in an iron autoclave, the yield and V.I. demonstrate the unfavorable catalytic action of iron.

In Experiments Nos. 385, 386, 389a and 390 which were made with pet. ether to which varying amounts of liquid olefins, i.e. cracked paraffin boiling from 20 to 260°, it can be seen that the latter, which, when polymerized alone, yield lubricating oils having a very high V.I. (110-120), have no effect when added in small quantities; they even have an unfavorable effect when added in large quantities, as in Exp. 390. Apparently, when they are present in large amounts they adversely affect the polymerization of ethylene.

The purpose of Exp. 394, 428, 444 and 445 was to convert the $AlCl_3$ into a liquid form in order to facilitate its introduction into the autoclave. For this purpose $AlCl_3$-hydrocarbon addition compounds were prepared, in one case with liquid olefins,(cracked paraffin Exp. 394 and 428), and in another case with propylene, (Exp. 444 and 445). In both cases the yields and the V.I. were normal. The $AlCl_3$ may be consequently used in this form.

Experiments 325 and 312 are of particular interest. In this case pet. ether with a small amount of Oppanol dissolved in it was used as solvent. Exp. 325 shows that this product does not affect the ethylene polymerization if the operation is

p.32

Table 23

Exp. No.	Type of solvent	Amt. of solvent cc	Temp.	Yield	Viscosities Prod. 170° 1 mm Hg °E$_{99}$	V.I.
411	Pet. ether	2000	80°	4.30	6.69	91.0
400	Hydgd. cracked paraffin 20 - 180°	2000	80°	4.25	6.52	92.0
397	" " 180 - 250°	2000	80°	4.60	7.90	92.0
191	" " " "	2000	100°	4.45	13.9	102
190	" " " "	2000	110°	3.9	11.5	98
187	" " " "	2000	120°	4.7	11.7	102
201	" " " "	2000	130°	4.2	5.1	82
206	" " " "	2000	140°	4.1	3.0	67
144	Iso-octane	2000	90°	3.9	2.5	64
142	" "	1000	90°	1.2	1.97	10)Fe-Autoclave
153	" "	2000	90°	3.5	2.53	64
170	Iso-dodecane	2000	120°	4.7	12.9	102
169	" "	3000	120°	4.5	13.1	101
385	Pet. ether + liq. Olefins[1]	1950+50	80°	4.2	8.1	92
386	" " + " "	1900+100	80°	4.2	8.4	93
389a	" " + " "	1800+200	80°	4.1	8.3	96
390	" " + " "	1600+400	80°	3.9	6.6	85
394*)	Pet. ether+liq.Olefins with $AlCl_3$	1900+100	80°	4.2	8.0	93
428*)	" " " "	1900+100	120°	4.1	6.0	93
444*)	" " + Propylene with $AlCl_3$	2000	80°	3.9	7.4	94
445*)	" " " "	2000	120°	4.0	4.2	96
325	Pet. ether + 15g Oppanol	2000	80°	4.1	8.8	96
312	" " " "	2000	120°	4.2	4.5	77

---

1) Liquid olefins = liquid cracked paraffin boiling between 20 and 260°.

* In these experiments the $AlCl_3$ was converted into a liquid, reddish-brown hydrocarbon addition product by pretreatment with liquid olefins or propylene.

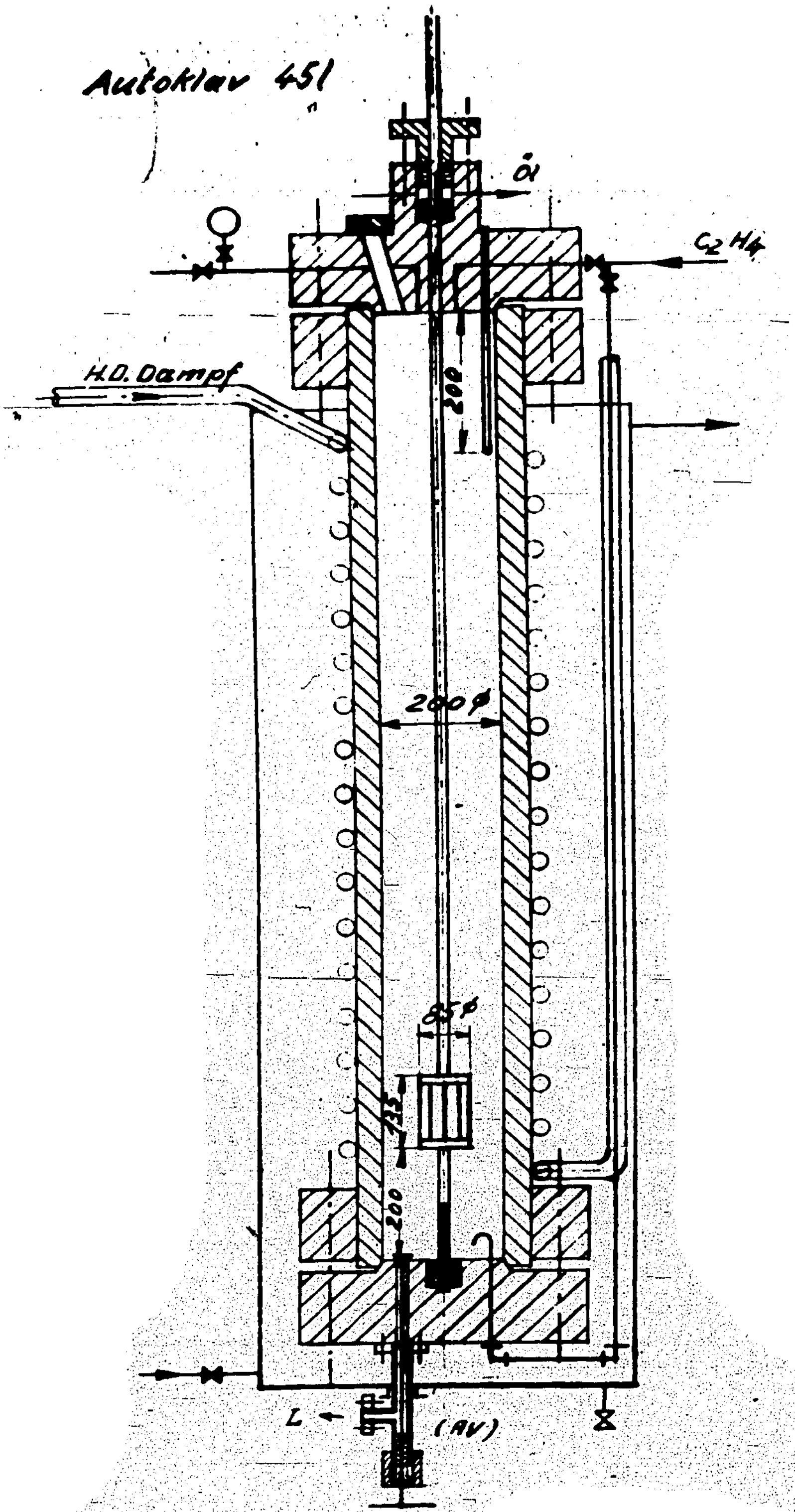
conducted at 80°. When the temperature is increased to 120°, the Oppanol unfavorably influences the quality of the resulting ethylene polymerizate, as may be seen from the results of Exp. 312. At higher temperatures the iso-butylene polymerizate is attacked by $AlCl_3$.

p.34

Table 24

Exp. No.	125 g $AlCl_3$ + 2 lit. solvent	Yield lit.	Lube Oil E^o_{99}	Lube Oil V.I.
	+ Crude prod. from Exp. G.V. 10		4.88	96.0
415	" " " " "	4.40	7.95	93.0
415a	" " " " 415	4.60	11.20	99.0
415b	" " " " 415a	4.65	13.52	103.0
415c	" " " " 415b	4.68	13.52	100.0
415d	" " " " 415c	4.50	13.45	100.0
415e	" " " " 415d	4.80	15.50	100.0

Experiments have been grouped in Table 24 to show the yield and quality to be expected on continuous operation, eventually planned. For this purpose the 5 liter autoclave was not filled as before with 2 liters of pure solvent, e.g. pet. ether, but with 2 liters of crude polymerizate obtained in a previous experiment. This crude polymerizate contained the $AlCl_3$-hydrocarbon compound which had been produced in its formation. The series was started with 2 liters of a product from a large scale experiment, G. V. 10. This product gave after treatment an oil with 4.88 E^o_{99} and 96.0 V.I. After an addition of 125 g of $AlCl_3$ 4.4 liters, another two liters of crude product was removed and used in Experiment 415a, together with 125 g of $AlCl_3$. The remaining 2.4 liters were freed from $AlCl_3$ sludge by decantation and worked up in the usual manner. The fractions boiling above 150° at 1 mm Hg had the properties indicated in the Table. From these data it will be seen that the new yield was normal



30. Juli [illegible]

and constant and that the VI. remained constant, although the oils became increasingly viscous. Up to Exp. 415 c the viscosity also remained constant.

After the important factors governing the polymerization of ethylene had been established by experiments in the 5 lit. autoclave, a V_2A autoclave of 45 lit. capacity was constructed and put in operation. V_2A was selected because N_6 plate was not available at the time. Its construction can be seen from the attached drawing. It will be seen that the gas can be supplied from above into the vapor space as well as from the bottom into the oil. In addition a special valve (AV) is installed in the bottom flange. This conical valve is provided outwardly with a stuffing box and is intended to prevent solid or liquid $AlCl_3$ addition compound from entering the product outlet line and the attached high pressure valve. This construction has also been found suitable for the large autoclaves.

The autoclave was initially provided with a simple paddle agitator operating at about 300 r.p.m. The charge of the autoclave for each experiment consisted of 1.4 kg of $AlCl_3$ and 11-12 kg of solvent. The autoclave was then heated to about 40°C and ethylene forced in at a pressure of 40 atm., after which it was heated to p.35 about 70-80°C. An exothermic reaction then started and the temperature rose to 150-180°C. Upon reaching the maximum temperature the pressure dropped to 20 atm. By cooling with water at 70-80°C, (colder water is harmful since it may terminate the reaction), the contents of the autoclave were brought down to a temperature of 90-100°C. This temperature could then be maintained by further introduction of ethylene until the autoclave was full of liquid, which was indicated by a sudden rise in pressure. When a paddle agitator was used the process was completed in 7-11 hours, after which ethylene was no longer absorbed. The contents of the autoclave then totalled about 25 kg., about 31 lit., indicating that the 45 lit. autoclave was not yet full.

We thought that this incomplete reaction might be due to insufficient agitation. Apparently, the paddle agitator was incapable of stirring up the relatively very heavy aluminum chloride. Dr. Büche, Ludwigshafen, called our attention to the Hoesch agitator. Model tests were made with the assistance of Dr. Büche in a glass apparatus simulating the autoclave. Taking for a model a mixture of sand and water, it was found that for equal speeds the Hoesch agitator had an uncomparably better effect than a paddle agitator. We then built into our 45 lit. autoclave a Hoesch agitator made of V_2A, having a form and dimensions based on the model tests made by Dr. Büche. The result was that the autoclave could be completely filled in about 4-5 hours, the total contents amounting to 31-33 kg. A matter of great significance is the dependence of the time of reaction on the speed of the Hoesch agitator, as is shown in the following Table 25.

Table 25

Influence of the Speed of the Hoesch Agitator

45 lit. V_2A autoclave

Exp. No. G V	r.p.m.	Duration, Hours	Yield, kg	Lube Oil	
				$^oE_{99}$	V.I.
46	300	4 3/4	32.5	5.23	104.8
45	370	3 1/4	32.0	6.18	106.0
47	440	2 1/2	31.5	5.18	108.0
48	500	2 3/4	32.5	5.47	101.0
49	560	2 3/4	29.5	6.11	105.0

p.36 It will be seen that at a speed of 440 r.p.m. the optimum time for the reaction has been reached. Higher speeds, are not necessary. The reaction time is then about the same as in the 5 liter V_2A autoclave. The next item investigated was the amount of $AlCl_3$ necessary to obtain the highest yield in this autoclave, while retaining the best possible quality.

Table 26

Influence of the Amount of $AlCl_3$

45 liter V_2A Autoclave

$AlCl_3$ used	Exp. No.	Yield	Lube Oil °E_{99}	Lube Oil V.I.	% $AlCl_3$, referred to finished oil
800	36	30.0	4.81	88	5.0
1000	35	30.5	5.90	95	6.3
1400	44	33.0	5.47	107	8.0
1600	38	32.0	5.60	104	9.6
2000	50	33.0	5.33	104	11.7

Table 26 shows that the optimum amount is 1400 g (=8% of the finished product). To use more is of no advantage since no increase in yield is obtained, the autoclave being full when 33 kg have been produced. Neither is there any improvement in the quality. When less than 1400 g is used, the yield drops and the quality of the polymerizate is poorer. In this and in the following experiments an aluminum chloride was used having the following composition;

20.10% Al, 0.04% Fe, 0.002% Ti, 0.02% Si, 79.50% Cl, non-sublimable residue 1.4%.

The manner of supplying the ethylene is very important as illustrated in

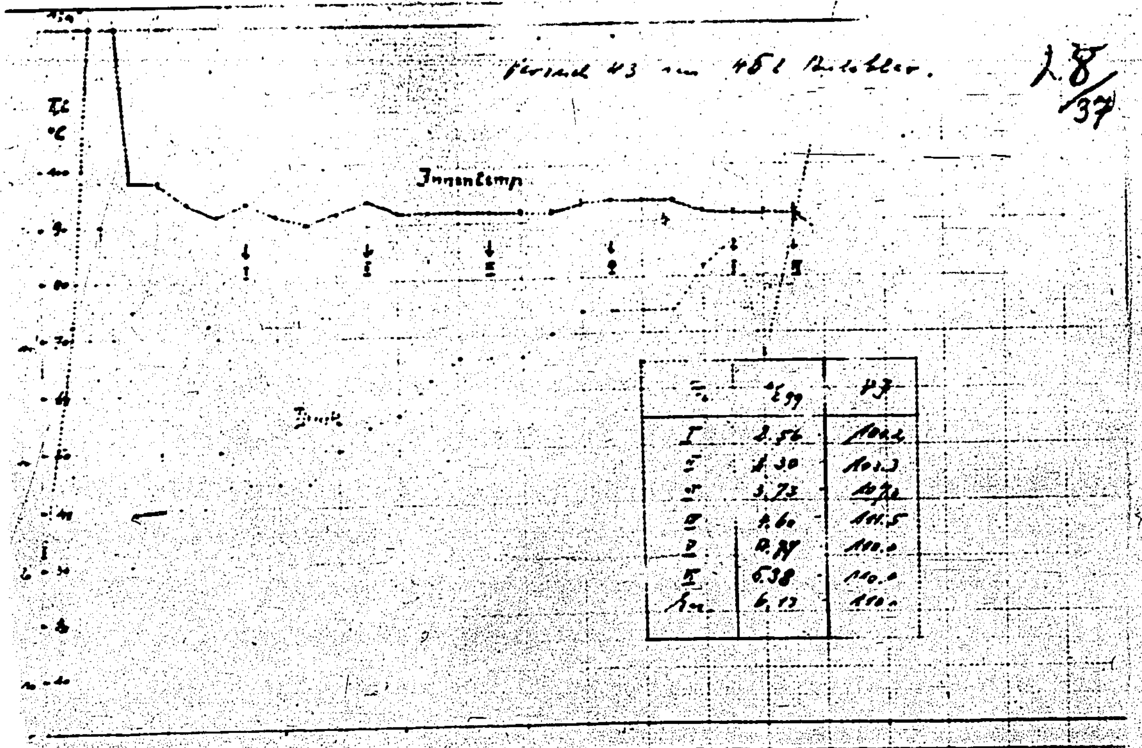
Table 27

Exp. No.	r.p.m.	Gas Supply	Light oil charge	$AlCl_3$	Duration, Hours	Yield
31	440	From the top into the vapor space	14	1400	12	23.5
32	440	From below into the liquid	14	1400	4	32.0

which shows that the ethylene must be introduced into the liquid.

Auf dem folgenden

Kurvenblatt 28



[illegible]	[illegible]	[illegible]
I	8.56	100.2
II	7.30	101.3
III	3.73	[illegible]
IV	1.60	111.5
V	0.77	110.0
VI	6.38	110.0
Am.	6.13	110.0

ist der Verlauf einer Polymerisation im 45 l V2A-Autoklaven dargestellt. Um den Prozess besser verfolgen zu können, wurde die Gasströmungsgeschwindigkeit etwas herabgesetzt, so dass eine Versuchsdauer von ca. 6 Stunden erzielt wurde. Die auf dem Kurvenblatt an der Temperaturkurve angeschriebenen römischen Ziffern sind die Nummern für die Proben, welche zu diesem Zeitpunkt vom Autoklaveninhalt entnommen wurden.

Betrachtet man die Temperatur- und Druckkurve, so sieht man, dass vor Erreichung der Maximaltemperatur von 154°C bereits der Druckabfall eintritt. Der zickzackartige weitere Verlauf der Druckkurve ist bedingt durch die unregelmäßige Äthylenzuführung und diese wiederum ist abhängig von der Forderung nach der Konstanthaltung der Temperatur.

p.37 The diagram 28 shows a polymerization in the 45 lit. V_2A autoclave. In order better to follow the process the gas velocity was reduced somewhat so that the experiment lasted about 6 hours. The roman numerals written below the curve are the experimental numbers for the samples taken from the autoclave at the corresponding time intervals.

In considering the temperature and the pressure curves it will be seen that a drop in pressure occurs even before the maximum temperature of 154°C is reached. The zig-zag course of the pressure curve is caused by the irregular supply of ethylene made necessary to maintain the temperature constant.

p.38 The experimental data on individual oil samples shown on the diagram indicate after about 4 hours the maximum V.I. has been reached. After this the polymerizate only becomes more viscous.

Particular attention was then paid to the significance of the strong rise in temperature at the beginning of the process.

In experiments up to this time the solvent was first heated to about 40° and the ethylene then forced in. In this type of operation the temperature rose to about 150-180° when the reaction started. In subsequent experiments the ethylene was not forced in with simultaneous heating, but at room temperature before heating; moreover, varying amounts of ethylene were used. In all experiments the same ethylene and the same $AlCl_3$ were used.

p.40 The experimental results of Table 29 show that with increasing ethylene pressure the maximum temperature also increases owing to the exothermic reaction forming the catalyst. A rise of the V.I. and a drop in the viscosity of the resulting end product is connected with this temperature rise. This increase in the V.I. reached its optimum for an initial pressure of 30 atm. C_2H_4 and a maximum temperature of about 200°. When still higher temperatures are reached through a further increase

Table 29

Various Operating Conditions

Manner of Operation	Exp. No. G V	Yield kg	Lube Oil $^{o}E_{99}$	V.I.	Max. Temp.
Ethylene added with simultaneous heating	208	33.3	6.18	104.5	160 - 180°
	213	33.0	5.33	104.6	
Forced in cold to 10 atm.	206	30.0	5.72	108.0	180 - 190°
	207	33.0	6.11	105.3	
	209	31.8	5.71	104.7	
" " " " 20 "	234	29.0	4.61	114.6	210 - 216°
	235	30.5	4.69	110.7	
	236	30.0	4.19	113.2	
	237	30.0	4.87	111.2	
	238	30.5	4.56	109.7	
	239	30.3	4.94	108.0	
" " " " 30 "	223	30.5	3.92	115.2	ca. 220°
	224	31.0	3.05	115.5	
	225	34.0	3.80	117.0	
	228	30.8	4.43	114.0	
	229	31.8	4.32	117.0	
	230	33.0	3.87	117.4	
	231	33.2	4.45	117.0	
	232	33.0	3.59	118.1	
" " " " 40 "	190	30.0	2.43	109.2	230 - 260°
	191	29.0	2.95	114.6	
	192	31.0	2.31	114.7	
	193	28.0	2.77	107.0	
	195	28.0	2.98	108.5	

of the ethylene pressure, the V.I. drops again. At the same time the yield in polymerizate also drops and the color of the polymerizate normally golden yellow to orange, is dark red-brown to brown black.

Table 30

Max. Temp. °C	Total crude prod. kg*	Total	Polymerizate formed				For each 100 kg. Lube Oil				
		amt. kg	Lube Oil kg	Lube Oil wt.%	Lt.Overhd.** kg	Lt.Overhd.** wt.%	Over-head kg	$AlCl_3$ kg	Solvent	Lube Oil °E_{99}	Lube Oil V.I.
152	33.0	19.7	16.5	84.0	3.2	16.0	19.5	8.5	72	7.49	104
187	32.2	18.9	14.7	77.7	4.2	22.2	28.5	9.5	81	5.40	111
205	31.1	17.8	12.9	73.0	4.9	27.0	38.0	10.9	92	4.59	112
238	30.9	17.6	11.4	64.7	6.2	35.2	54.0	12.3	104	3.56	113
253	29.5	16.2	9.6	59.0	6.6	41.0	69.0	14.6	124	2.62	114

Table 30 shows the quantitative relations of the polymerization process with respect to the maximum temperature reached. The figures are averages of five experiments made in the 45 liter autoclave with the same gas and the same $AlCl_3$. The $AlCl_3$ used contained 1.4% residue.

These data show distinctly the dependence of the quality and yield of polymerizate on the maximum temperatures reached at the beginning of the reaction. It will be seen how the amount of lube oil, i.e. the portion of the polymerizate boiling above 150° at 1 mm Hg, decreases with increasing maximum temperature, while the light overhead oil increases in quantity. The viscosity also decreases with increasing maximum temperature: although thin oils are obtained in lower yields, they possess high V.I. Should such products ever be required they can be obtained in a reproducible manner as shown in Table 31.

---

* By total product is meant the entire autoclave contents consisting of solvent, $AlCl_3$ and newly formed polymerizate.

** Operating losses are included in the amount of overhead oil.

p.41

Table 31

Experiments in 45 liter Autoclave

Solvent	15 lit. = about 12 kg overhead
$AlCl_3$	1.4 kg (with 1.3% residue)
Max. Temp.	225-235 °C
Total duration of experiment	4 hours.

Exp. No. G V	Total Crude Product kg	Pure Lube Oil Obtained	
		$^{o}E_{99}$	V. I.
441	32.2	3.98	119.5
442	32.5	3.41	119.2
443	32.7	3.79	120.2
444	32.5	3.00	120.0
445	31.6	2.69	121.9
446	31.8	3.35	118.4
447	32.5	3.03	118.1
448	32.5	3.38	118.8
449	31.7	3.36	117.8
450	31.8	3.84	118.1

The experiments in Table 31 were made with the same ethylene and an $AlCl_3$ with only 1.3% residue, at a maximum temperature of 225-235°C. The operating time was four hours in each case. An overhead distillate from previous polymerizations, 15 liters = 12 kg in each case, was used as solvent.

These data show good uniformity in the yields and quality of the products. They were confirmed by tests in a 100 liter autoclave made of N_6 material. This autoclave had a diameter of 200 mm and a length of 4 m. A Hoesch agitator was installed at the bottom.

Lubricating oils of lower viscosity may also be obtained by thermal depolymerization of highly viscous polymerizates, as shown in Table 32.

p.42

Table 32

Depolymerization

An oil of 7.23 E^o_{99} and a V.I. of 106.2 was subjected to a mild depolymerization at 330° for 15 hours. The heating was such that a temp. of 330° was reached after 5 hours.

Fraction at 1 mm		On Reaching 330°	5 Hours at 330°	10 Hours at 330°	15 Hours at 330°
to 100°		1.6	3.2	3.2	5.6
100 -125°		6.8	8.4	8.8	6.0
125 -150°		6.0	5.2	5.6	5.6
150 -155°		0.8	2.0	1.2	1.6
Total Dist. to 260°		17.2	20.0	20.8	21.2
Lube	E^o_{99}	7.23	5.52	4.44	3.64
Oil -	V.I.	107.0	107.5	107.6	107.2

For this purpose the polymerizate, from which light oil had been removed, was heated a few hours in the absence of air to 330-350°. A slight decomposition to lower boiling products took place. The viscosity drops from 7.23 E^o_{99} after 15 hours to 3.64 E^o_{99} while the V.I. value suffers no change. Table 33 shows the depolymerization of an ethylene polymerizate in comparison to that of other oils. Because the depolymerization temperature was maintained lower at 330°C, depolymerization time was accordingly very long (120 hours).

Engine tests were run in cooperation with the RLM on the oils produced in the 45 liter and the 100 liter autoclaves. In this connection the ethylene lube oils were found superior to mineral lubricating oils, previously used. The synthetic oils which received the code number SS 900 by the RLM had a considerably longer life in the one cylinder test engine, deposited less coke and had a better viscosity temperature curve so that they made possible the design of more effective aviation engines.

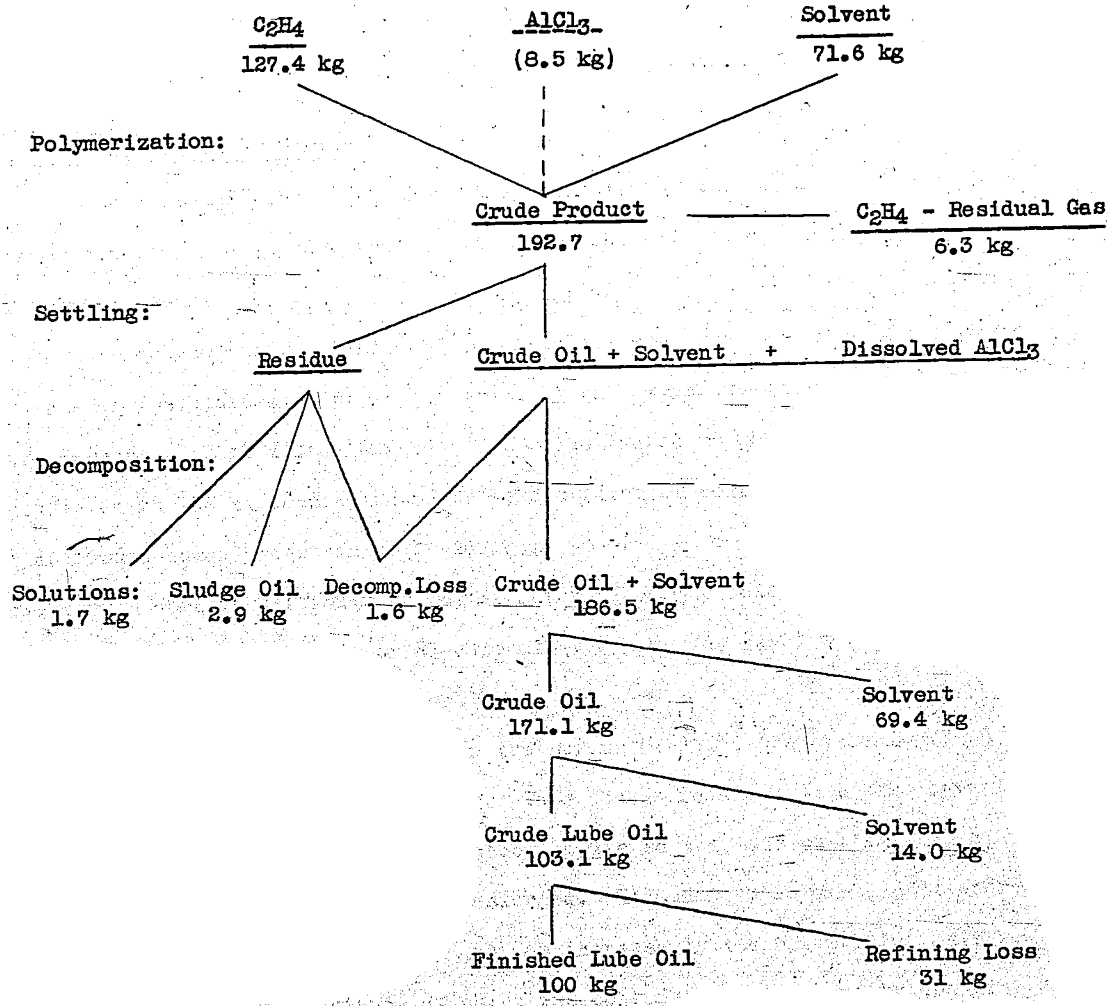
On June 10, 1936 the construction of a 700 Jato plant in Leuna was decided upon. The ethylene required was to be produced from the ethane in hydrogenation waste gases by the cracking process developed by Dr. Klein, isolated from the cracking gas in a Linde plant, and concentrated. The RLM desired above all that this plant p.44 manufacture a lubricating oil having a viscosity of 3.0 E° at 99°C. However, since the polymerization is always subject to small fluctuations in viscosity, as may be seen from Table 31, and since a flash point above 300°C was specified by RLM, (which would result in an increase in the viscosity above 3 E^{o}_{99}) this requirement could only be satisfied by subsequent depolymerization.

A balance sheet covering the quantitative polymerization of ethylene is given in Table 33. The figures are averages of numerous experiments carried out in 45 liter autoclaves. These values formed the basis for the plan of a semi-industrial 700 Jato plant in Leuna.

Table 33

C_2H_4 - Balance

45 lit. Autoclave



Obtained from 127.4 kg of ethylene:

Lubricating oil	100.0 kg	= 78.4 %
Solvent	13.5 "	= 10.6 %
Sludge oil	2.9 "	= 5.0 %
Unconverted C_2H_4	6.3 "	= 2.3 %
Decomp. and Ref'g Loss	4.7 "	= 3.7 %
	127.4 kg	= 100.0 %

PART II

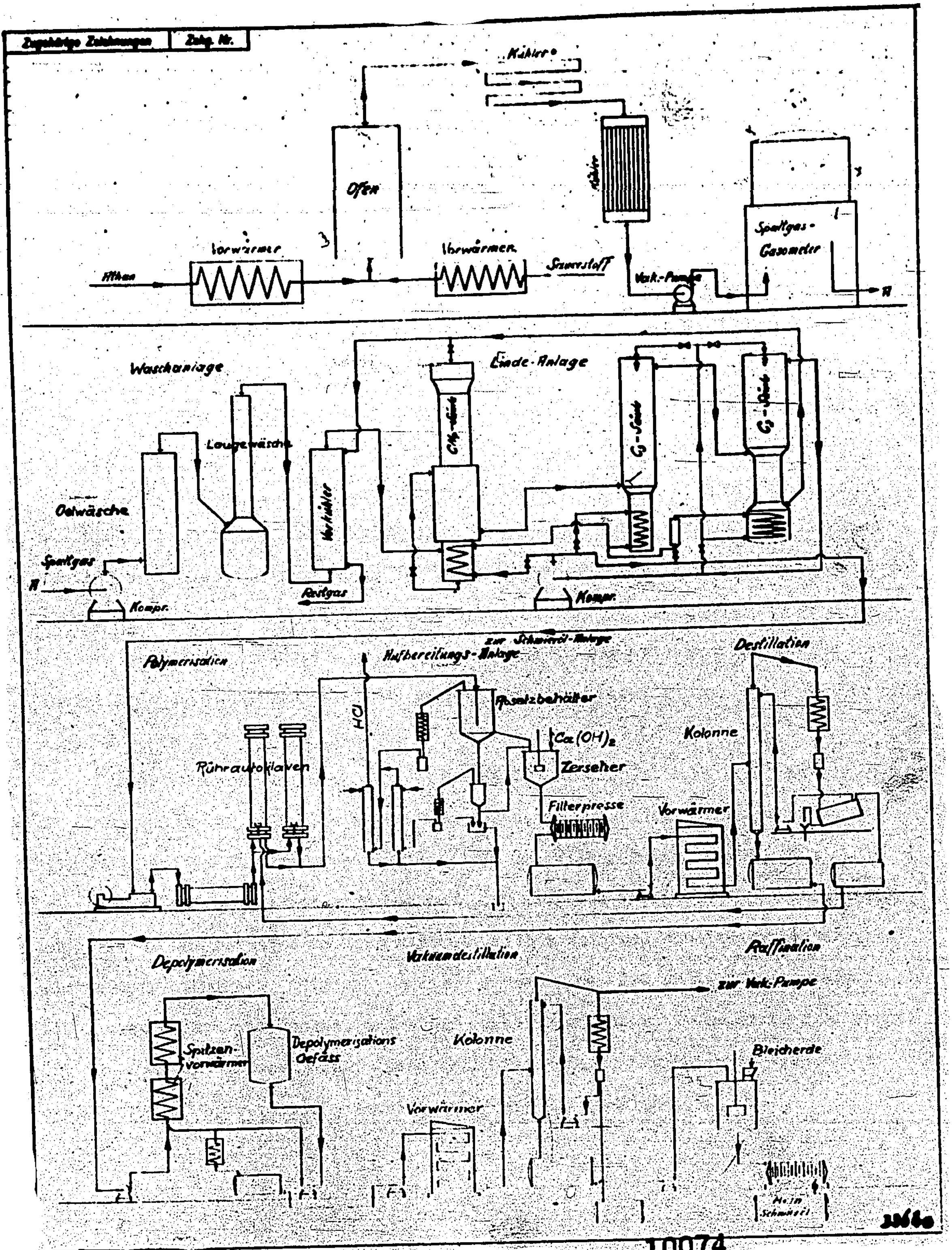
Construction of the Industrial Ethylene-Lube Oil Plants in Leuna

p.45 A. The 700 Jato SS 903 Plant.

The attached Diagram 34 shows the operation of the 700 Jato SS 903 plant whose construction was decided upon in June 1936 and the operation of which was started in August 1937.

A cracked gas containing 30% of ethylene was produced in Me 125 from the ethane in the hydrogenation waste gases, by the oxygen-vacuum process (Dr. Klein, Dr. Haubach). This dilute ethylene was concentrated to pure ethylene in a Linde plant, in Me 125 a, consisting of three distillation columns. The ethylene was then passed under pressures of 60-200 atm. to Me 126 for polymerization. After overcoming certain difficulties in the material of the hairpin-bundle type preheater--initially FF 30, later Si-chromal--the cracking plant was started in June 1937 and operated satisfactorily.

Owing to the lack of ethane in the spring of 1937, the cracking plant had to be temporarily changed to propane. This change resulted in a considerable increase of liquid products in the cracking gas so that the washing unit of the Linde plant had to be considerably enlarged. In order to remove liquid hydrocarbons entrained by the cracked gas, an increase in the oil washing unit became necessary, the efficiency of which was considerably improved by changing from B middle oil to benzene wash oil. This increase in the amount of absorption oil made oil regeneration necessary. In order to remove carbon dioxide contained in the cracking gas an "Alkazid" unit was inserted. Since this unit had a tendency to foam, a charcoal tower was added in order to remove the last traces of oil.


Zugehörige Zeichnungen
Zchg. Nr.
Kühler
Ofen
Kühler
Spaltgas-Gasometer
Äthan
Vorwärmer
Vorwärmer
Sauerstoff
Vak.-Pumpe
Waschanlage
Linde-Anlage
Laugewäsche
CH_4-Säule
G-Säule
G-Säule
Vorkühler
Ölwäsche
Spaltgas
Kompr.
Restgas
Kompr.
zur Schmieröl-Anlage
Aufbereitungs-Anlage
Polymerisation
Destillation
HCl
Absatzbehälter
$Ca(OH)_2$
Zerseher
Rührautoklaven
Kolonne
Filterpresse
Vorwärmer
Depolymerisation
Vakuumdestillation
Raffination
zur Vak.-Pumpe
Spitzenvorwärmer
Depolymerisations Gefäss
Kolonne
Bleicherde
Vorwärmer
Rein Schmieröl
23660

Betrieb

Other difficulties in the operation of the Linde plant were caused by entrainment of lubricating oil in the high pressure ethylene from the ethylene cycle compressors since the perforated trays of the last two columns clogged, resulting in poorer fractionation and finally in complete obstruction. The installation of separators eliminated this trouble to a large extent. A satisfactory operation of the Linde plant became possible after these various measures had been carried out. The plant produced on the average a 98-99% ethylene containing 0.5-1.0% acetylene and was practically free from O_2, CO and CO_2.

The polymerization plant consisted of two autoclaves of 1000 liters capacity each (500 Ø x 5000), in agreement with previous experience on the 5, 50 and 100 liter scale with N_6 material. A Hoesch agitator driven by Blauri rubber belts was used for stirring, being introduced into the autoclave from below. Discontinuous operation was adopted as on the experimental scale, the top flange being equipped for charging light overhead oil and catalyst while the bottom flange p.46 included gas inlet and crude polymerizate outlet. The autoclave was heated and cooled by a water jacket connected to a water circulation system provided with an expansion vessel.

After charging the autoclave with 150-250 liters of light overhead oil and 20-25 kg catalyst ($AlCl_3$), ethylene was forced in under high pressure, 20-45 atm. according to the final product desired, the reaction between ethylene and $AlCl_3$ started by heating the water jacket to about 120° and the internal temperature adjusted to the required maximum without further external cooling or heating, by adding more ethylene. After the maximum temperature (220 or 160°C) had been attained, the autoclave was cooled, and after reaching an internal temperature of about 120° gas was continuously introduced while maintaining the internal temperature at 110 or 120° by regulating the circulating water (50-100°).

After the autoclave was completely full, which required about 8-9 hours, the entire contents were released into settling tanks having a capacity of 10 m^3. These were insulated and provided with a conical bottom for better separation of the residue. The settling time for the filled settling tank was at least 24 hours so that of the three tanks, one was always in the process of being filled, a second was in the process of settling, and the third in operation.

After separating the catalyst sludge which consisted of an addition compound of $AlCl_3$ and oil and which at first was dumped, the supernatant oil was neutralized in batches in a decomposition tank of 2 m^3 capacity by adding powdered hydrated lime, for instance. The oil was freed from lime sludge in a filter press.

The clear crude polymerizate obtained as filtrate was fractionated in an atmospheric distillation system consisting of a heat exchanger, pipe still and bubble-cap tray colmmn into a low boiling overhead and residuum. While the overhead was returned for polymerization, the crude SS-oil obtained as bottoms was further treated. Since this oil was still too viscous, having an Engler viscosity at 99°C of 4.2-4.5, it was treated thermally, in the absence of air, in a depolymerization unit until the viscosity of the fractions boiling above 150° at 1 mm had a viacosity of only 3 E°/99.

The resulting crude product was separated in an adjoining vacuum distillation unit from lower boiling cracked products formed in the thermal treatment. The bottoms which had now correct boiling limits was refined by mixing at 80° with about 5% of bleaching earth and filter pressing.

p.47 The resulting refined SS oils were blended to the required viscosity in a mixing tank, centrifuged as a last refining step, and then filled into drums.

At the end of 1937 the first SS oil was produced. It then satisfied the equirements for SS-903 · VI. values in excess of 115 at 3E°/99.

In 1938 the first tests were made on the industrially produced oils in the Oppau laboratory and by the RLM. During the year 1938 the production was increased to about 60 Moto, reaching the full production of the plant. The yield of SS oil, on the basis of ethylene charged, was increased during the year from 56 to 70 %. By Sept. 1938 it was possible to supply the Air Forces (Luftwaffe) continuously.

Experimental work carried out in the meantime had shown that valuable aviation engines oils could be produced with practically the same excellent properties as the SS 903 oils if a highly-viscous ethylene-oil of 6 E°/99 (SS 906) were produced and then blended with a highly refined, less viscous mineral lubricating oil of about 1.8 E°/99. From then on the production of SS 903 was changed by the RLM to SS 906 and a blending ratio of synthetic oil to the mineral oil component of 1:1 specified.

By changing the production of SS 903 to the more viscous SS 906, the depolymerization step and, consequently, the vacuum distillation could be omitted. Atmospheric distillation was found sufficient to remove the overhead if about 10% of steam was injected at the bottom of the column. Distillation of the entire crude polymerizate under vacuum would have been desirable for protecting the oil in the pipe still, but was not adopted because of the high overhead (45-50 %).

Depolymerization

Experience gained in depolymerization will now be reported, although operation on a large scale was carried out only for a brief time. The depolymerization plant in Me 126b consisted of a vertical N_6 vessel of 10 m^3 capacity, insulated and with an outlet on top above a condenser. The product to be depolymerized was continuously pumped from the bottom of the N_6 vessel by means of a triple-action pump, with expansion lines for the hot oil, and recycled through an electrically heated preheater and returned at the top. The product was circulated until the desired degree of depolymerization had been obtained, determined by drawing samples at the bottom of the container. On conclusion of the process, the product was passed through a cooler to storage at about 60°C.

p.48- For a charge of 4000 lit. bottoms from the atmospheric distillation and an oil temperature of 375° the process required about 12-16 hours. It was found that after this time the desired drop in viscosity had occurred, due to cracking. The color, however, had become very dark and the <u>solidification point</u> had increased from -30 to -35° to about -16 to -22°C. This increase in solid point can be avoided if the operation is conducted at a lower temperature.

<u>Table 35</u>

<u>Depolymerization of SS oil</u>

Charge: 4000 lit. of 5.6 E°/99

Sample			SS-01	I50°	at 1 mm	
No.	after hrs.	%	°E/99	VI	Fl. pt	Solid. pt
1	0	99.0	5.6	108.8	236°	-34°
2	8 3/4	97.3	5.7	109.8	237	-35
3	10 3/4	95.1	5.1	108.9	237	-37
4	12 1/2	94.3	4.8	108.3	236	-38
5	14	92.2	4.4	109.3	235	-38
6	15 1/2	91.5	4.2	109.6	237	-38
7	17	90.2	4.0	108.4	234	-39
8	18 1/2	88.5	3.8	109.4	236	-41
9	20	86.5	3.7	105.7	238	-41
10	21 1/4	84.7	3.7	107.2	234	-40
11	22 3/4	83.2	3.6	107.0	234	-42
12	24	81.7	3.4	106.8	235	-41
13	25 1/4	80.0	3.5	106.9	233	-42
14	27	78.5	3.4	106.7	232	-42
15	28 3/4	77.0	3.4	106.8	230	-44
16	30 1/2	75.9	3.4	106.8	231	-42
17	32	74.2	3.6	107.6	230	-42
18	46	72.9	3.6	108.4	236	-40
19	47 1/4	71.7	3.5	108.2	235	-40
20	48	70.5	3.3	107.8	233	-41
21	50	68.8	3.3	108.1	231	-41

Table 35 shows the progress in the depolymerization of 4 m^3 SS oil of 5.6 E°/99.6 at 360° under carefully controlled conditions. Six hours after the heating had been started a temperature of 360° was reached and 8 3/4 hours after the start, after the first 50 liters of distillate had been recovered, sample 2 was taken; subsequent samples were drawn after each 50 lit. distillate. The process lasted 50 hours.

p.49 The table shows the amount of SS oil remaining after the given number of hours of vacuum distillation at 150° C/1mm. The other columns of the table contain the most significant analytical data of the resulting depolymerization end products.

During the first half of the distillation a drop in viscosity is noted, from 5.6 to 3.4 E°/99; in the second half the viscosity remains practically unchanged, although further cracking is recognized from the decrease of the bottoms from 80 to 68.8%. Depolymerization at 360° is therefore practically concluded in 24 hours. The advantage of this carefully controlled thermal treatment is recognized from a comparison of the flash point and solid. point of industrial samples treated under the same conditions. For the same flash point of over 230° an improvement is noticed in the solid. point from -34° to -41° during the first 17 hours, after which no change occurs up to 50th hour.

This experiment shows that the yield per unit volume and time in the depolymerization process is very poor. Since depolymerization of the SS oil no longer was necessary after changing the production to SS 906, further experiments planned to be made under pressure were not carried out.

Vacuum Distillation

Plant 2, which was originally intended for vacuum distillation, had meanwhile been rebuilt for operation at atmospheric pressure, with the provision of being immediately convertible to the original state in case of emergency.

The construction of the column head for vacuum operation is shown in the Diagram Sk 80.

Operating conditions

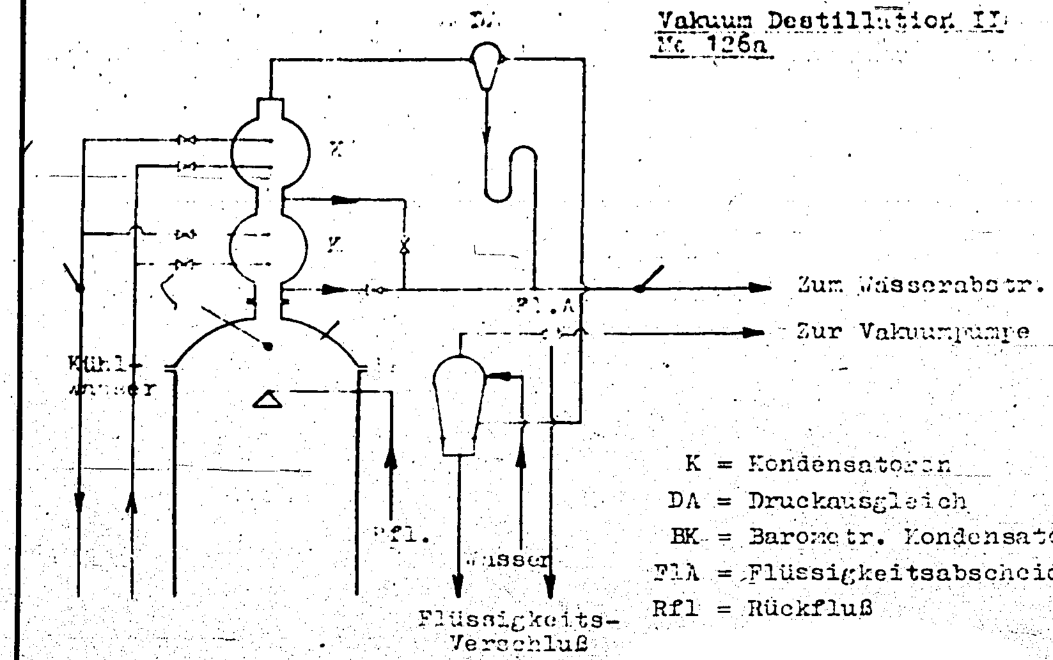
Vacuum	20 mm
Oil outlet temperature	330°C
Throughput	450-500 lit/hr
Distillate recovery	75-100 lit/hr
Reflux	200-250 lit/hr

p.50 **B. The 3000 Jato SS 906 Plant.**

After conversion of the plant to SS 906 and after reaching the intended production of 60 Moto, construction for expansion of the plant from 700 to 3000 Jato was started in the Fall of 1938. For this purpose a change was made from the 1000 lit. to the 4500 lit. autoclave (800 Ø x 9000). (See attached Drawing 35). Four 800 N6 autoclaves were built with the corresponding increases in the decomposition and distillation equipment. The operation of the first two large autoclave was started in May 1935. The change from the 1000 lit. to the 4500 lit. autoclavesproceeded without difficulty. In the Fall Furnaces 3 and 4 were started. These furnaces operated normally from the start. At the end of the year, with a 75% yield of SS oil, it was possible to increase the output of the plant to the intended 260 Moto = about 3000 Jato. By a slight increase of the decomposition unit and by improving the treatment, the potential production in 1940 was brought to 4000 Jato.

In 1940 the building construction for further expansion to a capacity of 10000 Jato was carried out. In this expansion only the number of units was increased. The erection of the additional six autoclaves (800 Ø x 9000) as well as other units was to be completed by the middle of 1941.

Vakuum Destillation II
Nr. 126a



K = Kondensatoren
DA = Druckausgleich
BK = Barometr. Kondensator
FlA = Flüssigkeitsabscheider
Rfl = Rückfluß

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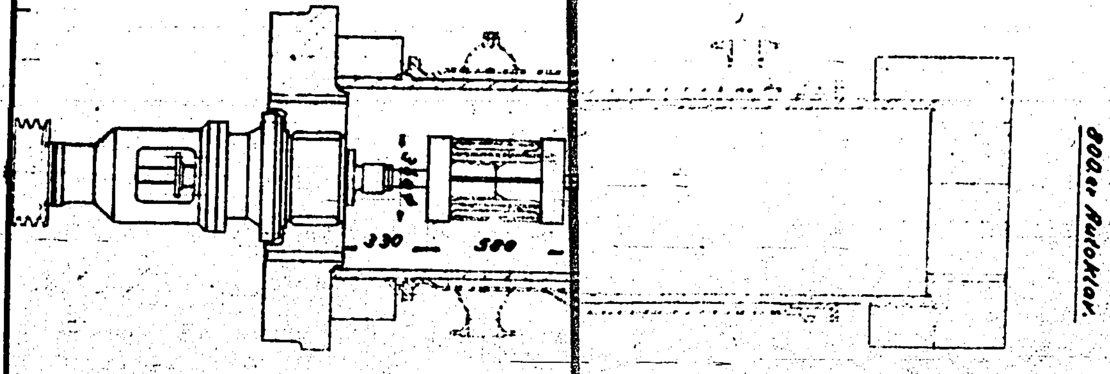
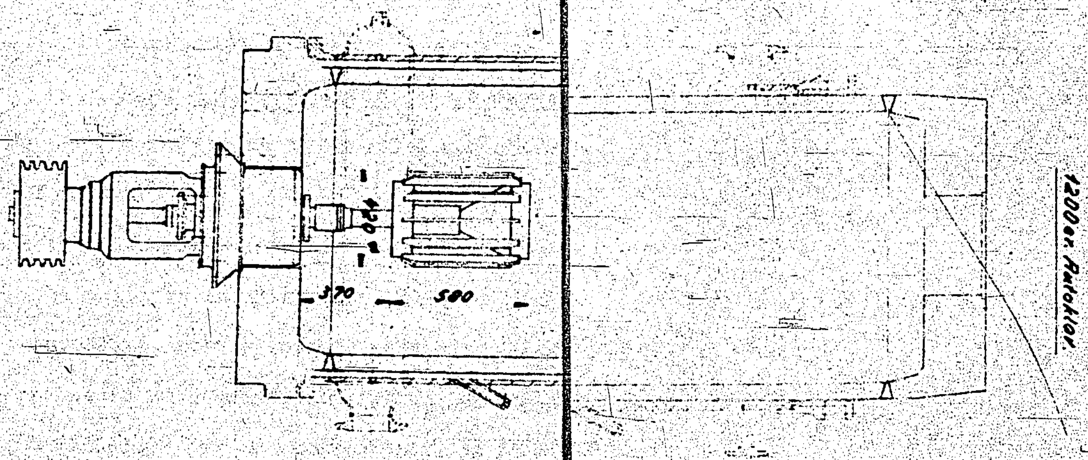
Ammoniakwerk Merseburg G.m.b.H.

Sk 80/8

DIN-Format A 4





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Leuna den 26.8.43 Leifermann

Ammoniakwerk Merseburg G.m.b.H.

e 80

M4992 —8

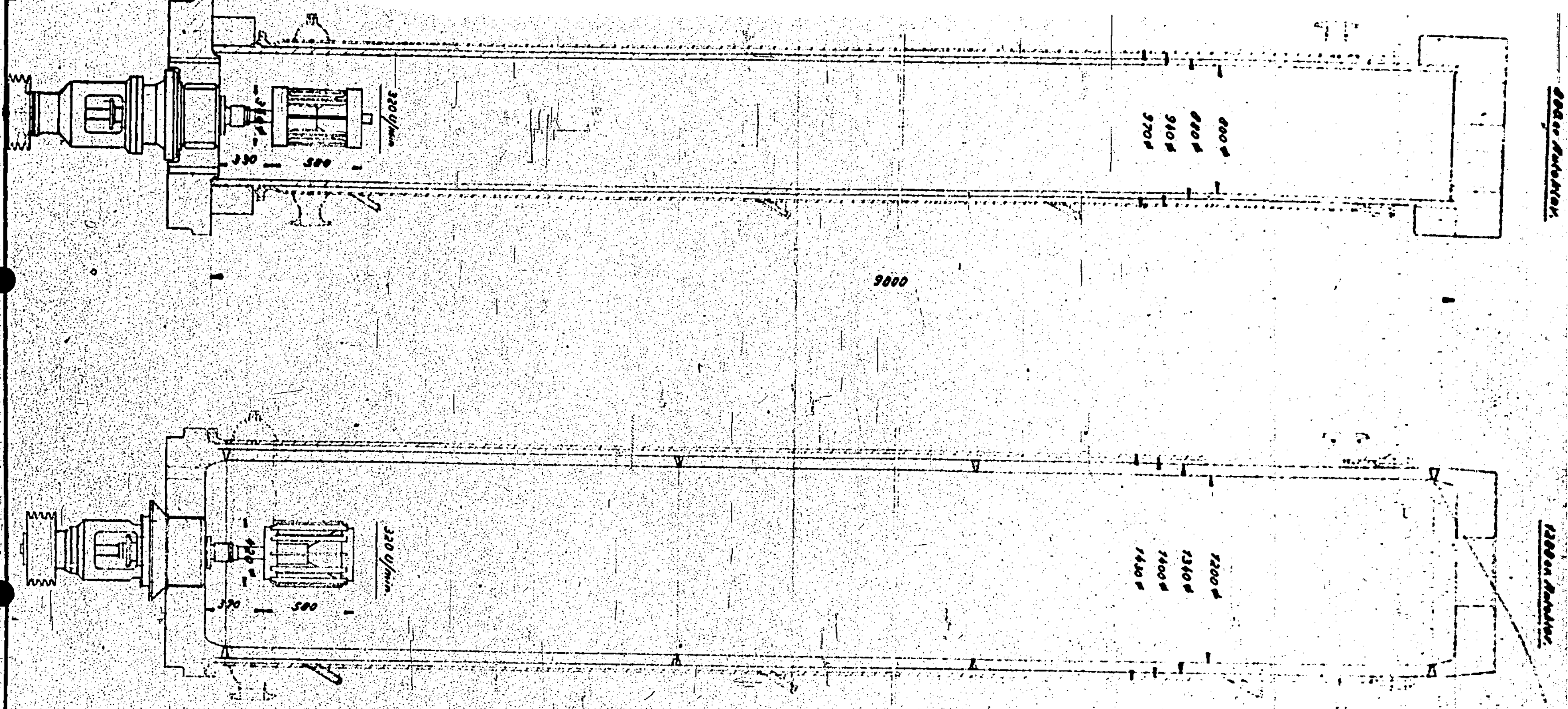
DIN A 3

Betrieb:

800er u. 1200er Auto

Fachgruppe:

Bau-Nr.



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Leuna den 26.8.43

1344/45

Technisches Büro Me 80
Tel. 9217

M4992 —8

DIN A 3

Ammoniakwerk Merseburg G.m.b.H.

Betrieb: 800er u. 1200er Autoklav mit Rührer.

Fachgruppe:

Bau-Nr.

Owing to difficulties in the supply of material from Krupp only the two first N autoclaves could be completed at the end of the year so that the plant was only increased to an output of about 500 Moto. The last four autoclaves were not supplied and put into operation until 1942. These four autoclaves could not be made of N_6 material, as previously, since Krupp no longer made this product. They were made of standard high pressure steel. At first these furnaces operated poorly but as time went on the quality of the polymerizate became better and better. The SS oil production was increased by this expansion to about 700-750 Moto in 1942.

In the new SS oil plants in Moosbierbaum, Schkopau and Heydebreck still larger polymerization furnaces of 1200 Ø (10,000 lit.) were used. The dimensions of the 800 Ø and 1000 Ø autoclaves can be seen in the attached Diagram 3 (M 4992-8).

A description now follows of the process as it is being worked at present.

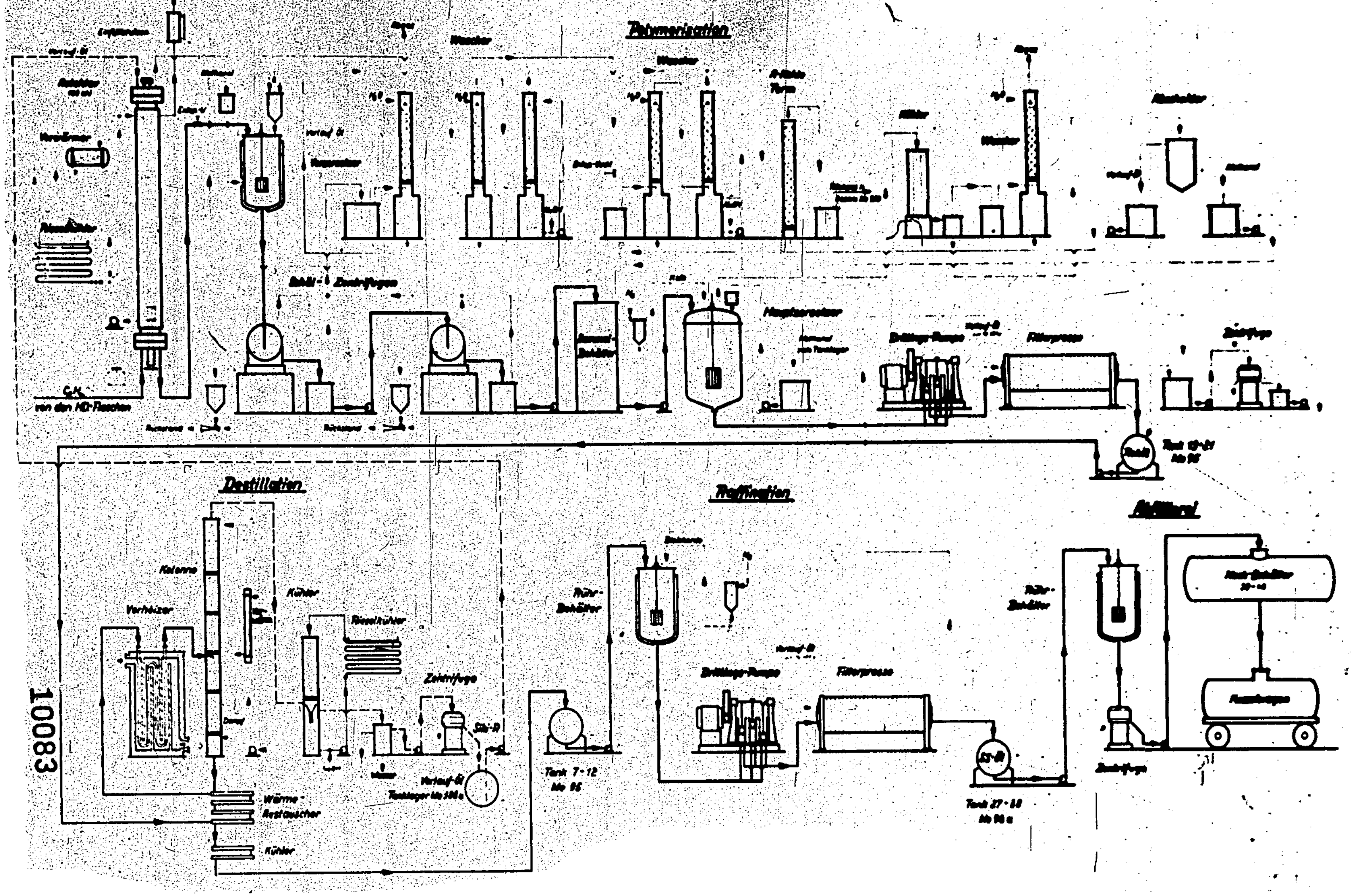
p.51 General Description of the Process (See attached Diagram 36)

The charging of an 800 Ø autoclave (4500 lit. capacity) is accomplished as follows.

1200-1500 lit. light oil distillate is introduced into the autoclave with the agitator in operation, followed by 125 kg of catalyst. After closing the autoclave, gas is introduced during 30 minutes into the cold autoclave to a pressure of about 20 atm. if SS 906 is to be produced at a maximum temperature of 150-160°, or to about 35 atm. if SS 903 is to be produced at a maximum temperature of 200-220°. Heat is now applied with the water circulation pump in operation. With about 5 atm. live steam (130-140° external temperature) the reaction starts in the course of half an hour. When the internal temperature has reached that of the heating jacket the circulation is stopped in order not

Schema 36.

Schema der SS-Öl-Herstellung.



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32074

to produce any cooling effect on the subsequent reaction. After reaching the desired maximum temperature, for which ethylene must eventually be added, the water circulation is again started for cooling and is continued without interruption to the end of the run. Introduction of gas is resumed at about 140° internal temperature. The circulating water is gradually cooled from 130° to 50-60o and 100-300 m^3/h of ethylene gradually added so that the internal temperature is kept at 110-115° for SS 906, or at 120-130° for SS 903. After gas has been introduced for about eight hours the autoclave is full, indicated by the rise of an element attached to the upper flange of the autoclave and by the rise of the autoclave pressure to 60 atm. The contents of the autoclave are now released into the pre-decomposition tanks and then passed into centrifuges while acidic methanol is continuously being supplied. The prerefined product from the second centrifuge then passes to the main decomposition unit. After the entire contents of an autoclave has reached the main decomposition unit, it is decomposed by fresh methanol at a temperature of 80°, hydrated lime being used for neutralization. The lime is separated in plate and frame filter presses. The clear filtrate then passes to the distillation equipment, the SS oil remaining at the bottom of the column being refined by treatment with 0.7% of bleaching earth at 120°. After adjusting the oil in the filling plant it passes through Alfa Laval Separators (built as a clarifying unit) and is ready for shipment.

The residual gas obtained on releasing the pressure in the autoclave and which consists chiefly of ethane and ethylene is passed through a water and a caustic wash tower for removal of hydrochloric acid. The highest boiling constituents (40-140°) are removed in a tower filled with A-carbon. The gas may then be used as recycle gas in the Linde plant or discharged into the fuel gas mains.

p.52 The residue taken from the centrifuges is carried away with water and converted to B-oil in a special plant.

Experience gained in the individual operating stages is reported as follows:

p.53 I. Polymerization

a. Agitation:

That intensive agitation is necessary in carrying out the polymerization to obtain good heat transfer has been shown in the description of experiments made on a smaller scale.

The agitation in the 1000 lit. autoclave is carried out in the same way as in the 100 lit. experimental autoclave, by means of a Hoesch agitator built into the bottom flange.

p.54 Great difficulty was encountered ~~at first~~ by severe corrosion of the shafts but this was overcome by improving the stuffing box construction so that in addition to the lubrication of the lipped packing by means of a Bosch pump through the lantern, an oil pump was installed which continuously flushed a small amount of SS oil into the autoclave, thereby effectively preventing a backflow of catalyst sludge into the stuffing box packing.

White metal, carbon, lipped leather packing and "Hecker" packing were tested as packing materials. The most reliable packing was found to be the Hecker lipped packing (asbestos, graphite, rubber).

When changing from the 1000 lit. to the 4500 lit. autoclave the construction of the stuffing box was improved in various ways, chiefly by making it in two parts so that the packing could be conveniently inserted without having to disassemble the whole agitator. ~~In addition~~, the agitator was flanged on the lower autoclave cover making insertion and removal more convenient. It was also found of advantage to apply secondary cooling to the packing through the hollow shaft in addition to the externally provided cooling. The construction of the lipped packing can be seen from the attached drawing 38.

This agitator construction was found to be extremely safe in operation during a period of four years. By careful assembly of the agitator and periodic lubrication, packing need only be renewed after several months of operation (4 hours operating time). The replacement of the entire agitator which requires about 8-10 hours, was only necessary every 8-10 months. Under favorable conditions periods between overhauls of more than a year were attained.

The following table gives the running times of the agitators in Autoclaves 1-4 in 1940.

Table 39

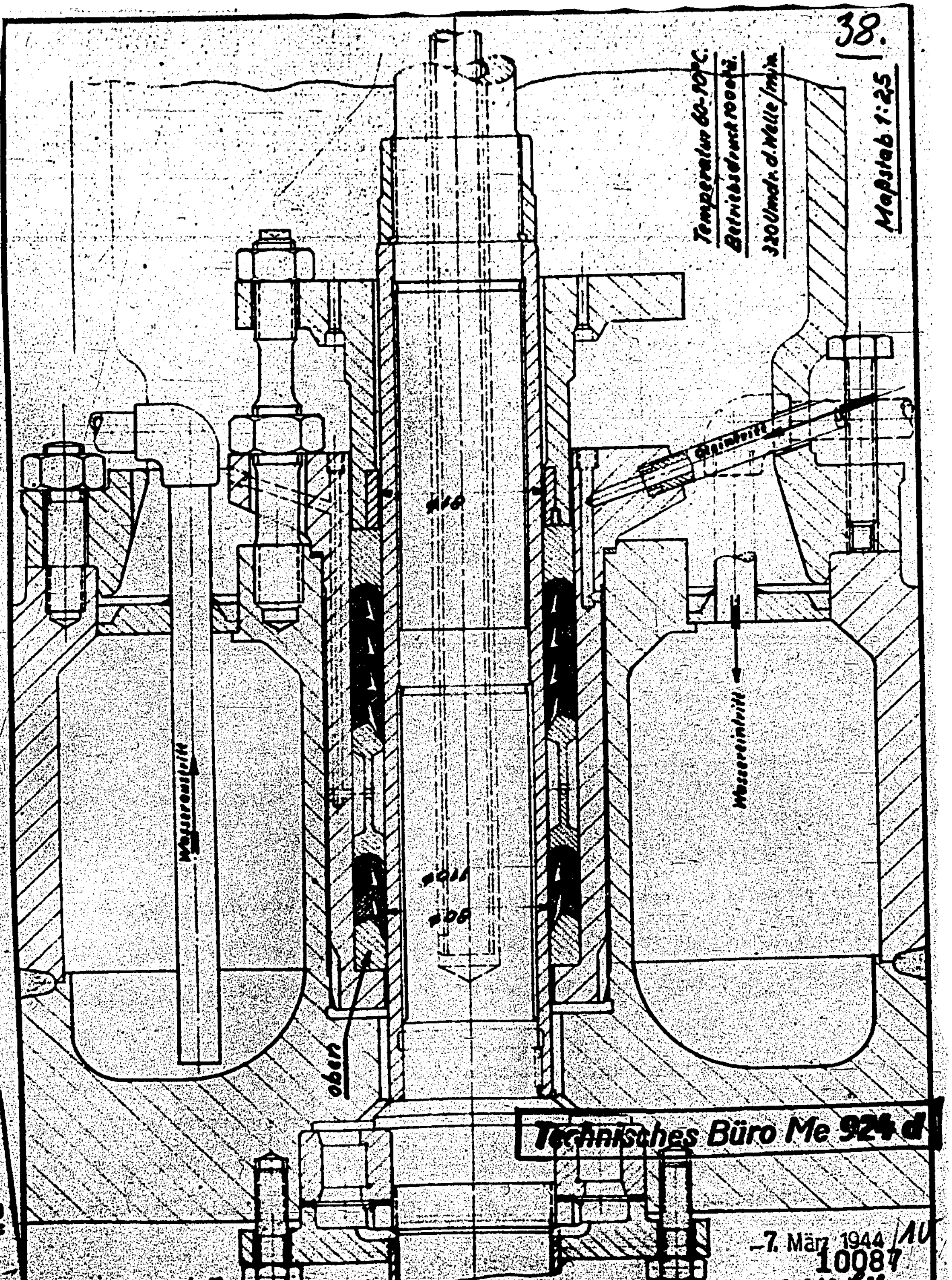
Agitator	Autoclave I	II	III	IV
Installed	2.26.1940	3.14.40	7.26.39	2.24.40
1st repacking	3.15.40	8.6.40	12.15.39	
2nd repacking	9.8.40		8.1.40	
3rd repacking	2.12.41			
Replaced	6.8.41	10.16.40	10.28.40	10.22.40
Running time in months	15	6 1/2	13	8

p.55 R oil or SS 903 oil produced in the plant was used as lubricant.

250-300 r.p.m. was found to be the optimum speed for the agitator installed in the 800 Ø autoclave. An increased speed was of no advantage and a decrease to 120 r.p.m. had a very adverse effect on the absorption, doubling the operating time.

The following operating features should be observed. When shifts are being changed the autoclave operator must assure himself of the correct adjustment of the lubricator as well as the internal and external cooling of the agitator. An excessive increase of the pressure in the line leading to the stuffing box must by

38.



Temperatur 60-70°C.
Betriebsdruck 100 atü.
320 Umdr. d. Welle/min.
Maßstab 1:25

Technisches Büro Me 924 d

-7. März 1944 /1U
10087

Geändert in ∅ am 6.2.44

6.12.43

Ammoniakwerk Merseburg G.m.b.H.	Autoklavenrührer (Stopfbüchsteil)	SK 924152 a

seen from the attached drawing 38.

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The following table gives the running times of the agitators in Autoclaves 1-4 in 1940.

Table 39

Agitator	Autoclave I	II	III	IV
Installed	2.26.1940	3.14.40	7.26.39	2.24.40
1st repacking	3.15.40	8.6.40	12.15.39	-
2nd repacking	9.8.40	— —	8.1.40	
3rd repacking	2.12.41			
Replaced	6.8.41	10.16.40	10.28.40	10.22.40
Running time in months	15	6 1/2	13	8

p.55 R oil or SS 903 oil produced in the plant was used as lubricant.

250-300 r.p.m. was found to be the optimum speed for the agitator installed in the 800 Ø autoclave. An increased speed was of no advantage and a decrease to 120 r.p.m. had a very adverse effect on the absorption, doubling the operating time.

The following operating features should be observed. When shifts are being changed the autoclave operator must assure himself of the correct adjustment of the lubricator as well as the internal and external cooling of the agitator. An excessive increase of the pressure in the line leading to the stuffing box must by all means be prevented since otherwise the packing may be crushed and the agitator run hot or even burn out entirely. It has been found of advantage to keep the agitator in constant motion in order to prolong the life of the packing, even when the autoclave itself is not in use.

I b. Wall Material

The material of the container was investigated in small scale experiments since this can be a significant factor that may largely affect the polymerization process. Therefore, the two 1000 lit. and the first six 4500 lit. autoclaves were made of N_6 material which had been found satisfactory. As might be expected, these furnaces operated satisfactorily from the first, as will be seen from Table 40.

Difficulties were first encountered when N_6 material could no longer be supplied for construction of the 800 Ø No.VII-X furnace. This will be reported more in detail under I g (Page 79).

I c. Gas:

An important factor for satisfactory ethylene polymerization was the quality of the ethylene, as was disclosed in the small scale experiments.

In operating the 1200 Ø autoclaves the same conditions applied. When in the presence of small quantities of CO or CO_2, as happened occasionally at first when the operation of the washing unit and the Linde plant was not sufficiently well in hand, the quality of the resulting oil suffered and the yield dropped, or when more than 0.1% of oxygen compounds contaminated the gas, the reaction even stopped entirely.

Acetylene contents in the ethylene which reached as high as 3% had no disturbing effect on the course of the reaction.

p.56 When the gas was free of oxygen-containing compounds and when fluctuations only occurred through the fouling of the trays in the third column of the Linde plant, through faulty heating of the still or by flooding the distillation column, (which only resulted in dilution with ethane), the polymerization process could still be carried out with an ethylene content as low as 92%.

On the basis of experience gained in the 500 Ø and 800 Ø furnaces the following requirements must be placed on the purity of the gas.

The ethylene must be as pure as possible (over 95%); an excessive content of inert gas, such as N_2, methane or ethane is undesirable. The qualtiy of the oils is not affected by these substances.

Acetylene	No effect up to 3%,
Butylene	And higher Mono-olefins, below 0.5%,
Butadiene	And higher diolefins, below 0.1%, have no effect.
Carbon Dioxide	Is very troublesome. Baryta water must not become turbid even after long exposure.
Carbon Monoside	Is still permissible in ethylene up to about 0.005%. A CO content below 0.001% is desirable. (Hemoglobin Test, 0.004 sensitivity limit, according to Linde).
Carbonoxysulfide	Notntroublesome below 5 mg/m^3.
Phosgene	Is considered harmful. The limit has not been established.
Oxygen, Molecular	Is harmful in excess of 0.01%.
Oxygen-containing organic products	Such as alcohols, aldehydes, ketones, ehters are very harmful. The limit has not been established.
Ammonia and Amines	Are undesirable. Limits not yet established.
Hydrogen Sulfide	Is troublesome. Limit not established.
Methyl Mercaptan and mercaptans	Not very troublesome. The content must not exceed 15 mg/m^3.
Chlorinated Hydrocarbons	Have no pronounced effect on the polymerization.
Phosphorus and arsenic compounds	Have not yet been sufficiently investigated as to their effect on ethylene polymerization.
Water vapor	More than 300 mg/m^3 of H_2O in C_2H_4 gives polymerizates which are not quite satisfactory. In the presence of less than 250 mg H_2O/m^3 C_2H_4 normal polymerizates are obtained.

All these data refer to percent by volume or mg/m^3 at 15°C/735 mm Hg.

p.57 Water Absorption and Dehydration of Ethylene

The water content of ethylene used for producing SS oil is important since an excessive water content may frequently disturb the polymerization. On the other hand, it has been found that ethylene has a higher water content than might be assumed on the basis of the laws applying to ideal gases. It is also known that ethylene, as well as ethane, propane and similar gases, has a tendency to form stable hydrates at these temperatures. These facts show that reciprocal effects occur between ethylene and water, particularly at higher pressures, exceeding those that might be concluded by analogy. From publications of the Linde Ice Machine Company it appears that gases with a strong association power, such as CO_2, absorb 4.5 times more vapor at 87 atm. and 50° than would be expected on the basis of the ideal gas laws.

In more recent processes for concentrating ethylene from dilute gases, e.g. the alkaline copper extraction process of Dr. Hauber, or the chemical removal of impurities from concentrated ethylene, the gas is brought in contact with aqueous solutions and becomes saturated with water. An investigation of the absorption of water by gaseous ethylene and the possibilities of removing it thus became necessary

Determination of Water

Several methods were used for determining small water concentrations, 10-50 mg H_2O/m^3, in ethylene. Direct freezing of the water from the gas at -60° is unreliable. Determination with Mg_3N_2 is rather unreliable at these low concentrations owing to the blank test that must be run, since even nitrogen which had been carefully dried over P_2O_5 or strongly cooled activated charcoal still gave a blank value of about 20 mg/m^3, which may be attributed to small amounts of NH_3 stubbornly retained in the nitride.

Since the ethylene available for the investigations was entirely free of higher olefins which might be polymerized by P_2O_5, the latter was dusted over glass wool and filled into U-tubes and used for absorbing the water from the gas. Comparative tests with magnesium perchlorate gave values which were within the usual P_2O_5 variations.

Water Absorption Power

On the basis of the vapor pressure of water at 20°, 1 m^3 of moist gas contains 17.35 g of water at that temperature. In agreement therewith, 1 N m^3* of dry ethylene may absorb 19.8 g of water at 20° and 1 atm. At higher pressures this water content should decrease inversely with the pressure in accordance with the laws for ideal gases. Since ethylene is more compressible, that is, since more N m^3 is contained per unit volume of the compressed gas than in an ideal gas, the water content per N m^3 would lie below the calculated values. The latter, together with the actually determined values for comparison, are given in Table 40a. In column 2 of this table are given the water contents assuming the validity of the ideal gas laws, in column 4 the water contents based on the compressibility of ethylene.

p.59 The water contents found varied in one series of tests within ± 5-10%. Better precision was not obtainable in spite of careful work. The procedure was as follows.

Dry ethylene from a Linde plant was introduced through a reducing valve and a regulating valve, by means of which the gas velocity was adjusted, into the apparatus which was kept in a water bath at the experimental temperature. The apparatus consisted of a pipe coil in which the ethylene was brought to the required temperature, and two containers of 450 cc capacity in series, filled with wet filter paper, It was found that the first container would have been sufficient and that the saturation for an hourly throughput of 40 liters was complete.

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* 1 N m^3 = 1 normal cubic meter (760 mm, 0°).

Table 40 a

Data in mg/N m³

	Found	H_2O content calc. from ideal gas laws.	Compressibility of ethylene	H_2O content calc. on the basis of compressibility.
20°				
1 atm.	19.8*	19.0	1.05	18.9
10 atm. (exc. press.)	1.95	1.73	1.32	1.31
25 " "	1.0	0.73	1.38	0.53
50 " "	0.6	0.372	2.01	0.185
75 " "	0.68	0.25	3.9	0.064
100 " "	0.75	0.188	3.0	0.062
125 " "	0.76	0.151	2.56	0.059
150 " "	0.73	0.126	2.27	0.056
40°				
1 atm.	71.0	63.0	1.0	63.0
10 atm. (exc. Press.)	6.55	5.7	1.1	5.2
25 " "	2.85	2.42	1.2	2.0
50 " "	1.7	1.24	1.5	0.83
75 " "	1.35	0.89	2.2	0.41
100 " "	1.45	0.62	2.4	0.26
125 " "	1.48	0.5	2.3	0.22
150 " "	1.48	0.42	2.1	0.20

* For N_2, 19.5g was found.

The pressure of the ethylene was released after it left the moistening container, and the ethylene again brought to the experimental temperature in a subsequent pipe coil. The gas then passed through the absorption vessel where the entrained water was removed and into a gas meter.

As will be seen, the water contents found are many times higher than the calculated values. They are within a range which seriously affects the use of ethylene for polymerization. Attempts were therefore made to dry the ethylene. The same apparatus was used as the one described above, being supplemented with a drying tube containing the drying material. Without enumerating the details of separate tests, the final results are given:

30 cc of Silica gel B, sufficient to dry 4 m^3 of gas to a water content of 10% = 3 g 100 atm. and 20oC., at first dried the gas from 0.75 g/m^3 to a water content of 0.3-0.4 g/m^3 but which, after passage of 2 m^3, slowly rose to above 0.5. In the regeneration, the calculated amount of water was actually found, thus confirming the low absorption by the gel.

Silica gel A was much more effective. With 30 cc of gel, water contents between 0 and 60 mg/m^3 were obtained at 180 atm. and 20° for a 40 liter gas throughput. After the passage of 4300 liters the content was still between 0-60, but from 6000 liters on it rose above 100 mg, and from 7500 liters above 200 mg.
A
After regeneration the throughput was kept at 200 liters/hr. and the same results were obtained. Only after a throughput of 6000 liters did the water content rise above 100 mg, and after 7700 liters above 200 mg. At this time about 25% was absorbed.

The recovered charge is consequently the same as in drying without pressure.
p.60 On the other hand, a calculated water content of about 0.5 mg/m^3 would be expected in the dried gas at 100 atm. The actual content, however, is about 50 mg.

Here again the high water absorption power of compressed ethylene is demonstrated.

Calcium carbide was found to be very effective; water contents between 20 and 50 mg/m^3 were obtained at 20° and 40°C for throughputs of 200 lit./hr. with a 30 cc carbide charge. After a throughput of 10 m^3 of gas only 10.9 of the original 34.5 g of carbide remained in granular form. The rest had broken down into a powder, a conversion of 23.5 g.

Drying tests with calcium chloride and caustic soda were omitted since they were unsuitable for technical reasons.

Experiments with carbide were carried out on a semi-industrial scale in order to determine the suitability of ethylene dried in this manner for polymerization. Ethylene which was first moistened to a water content of 600-800 mg/m^3 was passed at a rate of 15 N m^3/hr. at 100 atm. through 30 lit. of granulated carbide in a tower of 200 m Ø and dried to 40-60 mg.

While the moist ethylene reacted very poorly and the reaction subsided very soon; the viscosity of the resulting oil was 4-4.5° E with a V.I. between 95 and 100. On the other hand the gas after drying with carbide could be reacted normally to an SS 906 having normal properties. After complete conversion of 800 mg H_2O/m^3 the dried gas contained 0.1 vol. % of acetylene which does not hinder the polymerization. As disclosed from these experiments as well as by a large-scale test with moist gas from Schkopau produced in Me 126, a disturbance in the reaction by the possible simultaneous formation of H_2S, PH_3 etc. need not be feared. H_2S could not be qualtitatively detected in the ethylene with lead acetate, even when the uncompressed gas was charged with 20 g H_2O/m^3 and then dried with carbide.

I d. Aluminum Chloride

Another point which may largely affect the polymerization process is the condition of the aluminum chloride.

In small-scale tests the residue content of the $AlCl_3$ plays a special role. It is evident that as the amount of the charge increases, this factor will play a more and more secondary part since only the upper layer, which comes in contact with the atmosphere, forms this unsublimable residue of aluminum oxychloride, aluminum hydroxide and oxide, which is detrimental to the polymerization. Analyses of residue in an old and in a fresh shipment were as follows:

3 Months old shipment:	Sample from the upper layer:	19.9 % R
	Lower sample powder:	3.7 % R
	Lower sample granular:	0.9 % R
p.[illegible] Fresh shipment:	Original sample, top	1.8 % R
	Screened, coarse	0.7 % R
	Screened, fine	4.3 % R
	The same sample exposed 3 min. to the air.	5.9 % R

In all events, great care must be taken with the large charges (30 kg for the 1000 lit. furnace, 125 kg for the 4500 lit. furnace) to prevent unnecessary access of air or moisture. For this purpose the usual manual filling of the catalyst was replaced by a simple arrangement which has various advantages. Before charging the furnace the cover of the catalyst chamber is replaced with a special filling cover (cone with a slide valve). The exchange can be made very quickly so that harmful access of air is largely eliminated. A drum is placed in a sling, raised with a hoist, tilted and placed on the filling hopper. By opening the slide valve the catalyst is then filled into the autoclave, already containing the light oil, while the agitator is kept running.

p.62 In this manner the catalyst can be filled in quickly and easily by one man; the catalyst is not damaged and no dust or odor is formed.

In operating the two 1000 lit. autoclaves with a charge of 250-300 lit. of liquid charge and 25-30 kg of catalyst at maximum temperatures in excess of 200° with quantities, corresponding to the small-scale tests, almost the same reaction and operating time were found. Although the appearance, viscosity and viscosity index of the resulting oils were good, a much poorer solidification point was obtained with the aluminum chloride which came from a new plant in Ludwigshafen and had a low iron content. After replacing this product with one of higher iron content, the required solidification points, below -30°, were again obtained.

In the following Table 42 are given comparable data for runs with a catalyst low in iron and one high in iron.

Table 42

$AlCl_3$ low in iron (0.6% Fe)					$AlCl_3$ high in iron (2% Fe)				
No.	Max.T. °C	SS Oil 150° (Vacuum)			No.	Max.T. °C	SS Oil 150° (Vacuum)		
		$^\circ E_{99}$	V.I.	Solid.pt.			$^\circ E_{99}$	V.I.	Solid. pt.
S 139	219	4.50	121.1	- 15	S 186	204	4.34	118.4	- 33
N 142	208	4.57	118.6	- 19	N 194	210	3.39	119.2	- 33
S 140	223	4.38	120.0	- 14	S 187	208	4.37	116.6	- 35
N 143	225	3.51	120.1	- 17	N 195	230	3.81	116.8	- 32
S 141	223	3.83	121.2	- 14	S 188	201	5.00	122.0	- 34
N 144	216	4.10	122.9	- 16	N 196	206	4.51	114.9	- 32
N 145	210	4.39	119.8	- 20	S 189	213	4.03	118.5	- 35

Although these experiments were made at different temperatures ranging from 200 to 225° and at different rates, the effect of the iron content is very clear; a catalyst low in iron gives solidification points of -20 to -14°, a catalyst high in iron -32 to -35°.

After production was changed to SS 906 in 1938, which only required lowering
p.63 of the maximum temperature to 160-170°, the iron content of the aluminum chloride was no longer of importance and good solidification points were obtainable with both products.

Table 43

No.	Max. T. °C	SS Oil 150° (Vacuum)			
		°E_{99}	V.I.	Sett.pt.*	Fl.pt.
S 299	173	6.38	113.3	-37	208
N 306	170	6.58	110.1	-35	220
S 300	175	7.01	114.5	-35	212
N 307	180	6.19	113.4	-36	220
S 301	170	6.42	113.8	-37	218
N 308	170	6.23	113.7	-36	218
S 302	173	6.14	112.2	-35	216

Table 43 shows the properties of the first high viscosity oils produced in the 1000 lit. autoclave. The optimum amount of $AlCl_3$ required is the same as for the production of the previous SS 903, or 7-7.5% on the basis of finished SS 906.

At the end of 1941 we were again confronted with the problem of producing low viscosity cold-starting oils for tanks and aircraft which with viscosities of only 3 E^o/99 must have the highest possible V.I. values and the lowest possible setting points.* Since meanwhile we had changed to polymerization in 4500 liter autoclaves and now received our $AlCl_3$ from the Schkopau plant, the polymerization experiments were resumed at temperatures in excess of 200°.

The charges given in the following Table 44 were run in the N_5 autoclaves I-VI (4500 lit. content). The operation was conducted with 1200-1400 liters of light oil distillate and 125 kg of $AlCl_3$, the maximum temperature being about 220° and the operating temperature 110-120°.

p.65 It was also found that iron-free $AlCl_3$ (a) yields a product at high maximum temperatures having a very high V.I. but a very poor setting point.* With an $AlCl_3$ whose iron content exceeds 2.5% Fe(b), on the other hand, it was possible to polymerize an SS Oil at these high maximum temperatures having a setting point* of -35 to -40 for a viscosity of 3°E/99 in spite of the high flash

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* Solidification point

Table 44

Kind of $AlCl_3$	No.	$E^0/99$	V.I.	Solid.pt.	Fl.pt.
p.64 a. $AlCl_3$ I; Fe-content 0.1% Fe	III 1453	2.96	124.2	- 19	194
	IV 1397	3.67	122.7	- 22	210
b. $AlCl_3$ II; Fe-content 2.5-3.5% Fe	VI 298	2.85	107.9	- 35	192
	II 1454	2.69	114.6	- 43	202
	IV 1389	2.72	116.2	- 38	202
	II 1465	3.31	116.8	- 39	197
c. $AlCl_3$ I + II mixed in ratio 50 parts I + 50 parts II	III 1469	2.65	121.4	- 26	198
	II 1487	2.20	120.7	- 19	195
	VI 333	3.68	117.8	- 27	214
	III 1493	2.71	119.6	- 24	200
	IV 1436	2.88	123.3	- 23	204
	I 1543) V 299)	2.67	121.7	- 13	204
d. 33 parts I + 66 parts II.	I 1523	2.52	117.8	- 36	203
	IV 1431	3.49	122.3	- 15	219
	I 1542	2.61	121.2	- 21	211
	V 298	2.71	118.4	- 31	207
	II 1492) VI 338)	2.24	120.4	- 21	201

point of over 200°. The following facts, however, are important: the required iron contents must not be obtained by mixing iron-free with iron-containing $AlCl_3$ (c and d) but must be produced by sublimation as a homogeneous product (b) since otherwise wide variations result, as may be seen from the values in the experiments of series c and d of Table 44.

The disadvantage of preparing less viscous SS oils was that the filtration of the $AlCl_3$-lime sludge obtained after the main decomposition reaction presented great difficulties. The filter cloth was clogged so that the presses could not be completely filled and the cloth had to be changed frequently, resulting in much work and loss of oil and at times in complete cessation of production. The resulting crude oils could only be satisfactorily filtered and extracted by using larger amounts of lime than in the treatment of SS 906, or by the addition of filter aids, such as bleaching earth, after the lime cake of a SS 906, batch had been first deposited in the freshly cleaned press.

Not until March 1942 were large amounts (50 m^3) of SS 903 oil produced along with normal SS 906 production in this manner. The SS 903 oil had the following properties:

3.72 E°/99	117.9 V.I.	-32° set. pt.[*]	213° Fl. pt.
2.86 E°/99	113.8 V.I.	-39° set. pt.[*]	193° Fl. pt.

Since the second half of the shipment had a poorer V.I. it was distilled less extensively, a fact which explains the lower viscosity and the very good setting point.

Repeat runs under the same operating conditions (max. temp. 220°, operating temp. of 120°) in the Fall of 1942 gave products with such fluctuating properties that they could no longer be used as SS 903, as is illustrated by the following series of tests in Table 45.

[*] Solidification point.

Table 45

	No.	Dist. lit.	SS Oil 150° in vacuo °E/99	V.I.	Solid pt.	Fl. pt.
9,16,43	I 2150	1500	3.87	113.7	- 39	210
	VI 966	1200	4.27	116.0	- 36	214
9,18	IV 2047	1200	3.21	120.0	- 29	205
	III 2126	1200	3.29	120.1	- 26	212
	I 2153	1200	3.22	123.2	- 12	209
9,19	4 Furnaces	1200	2.61	125.6	- 34	194
9,21	7 Furnaces	1200	2.40	124.1	- 36	222

Above all, the decomposition of the crude oil presented great difficulties, but since the quality of the gas and of the charge of light oil was satisfactory, the variations could only have been caused by the $AlCl_3$, although its analysis disclosed no irregularities.

A check of the source of the bauxite used in the last few months at Schkopau for producing $AlCl_3$ showed that the satisfactory $AlCl_3$ shipments had been made from French bauxite but that, later, mixtures of French and Hungarian bauxite had been used.

French bauxite yields an $AlCl_3$ low in Ti with contents of less than 0.5% of $TiCl_4$. The use or admixture of Hungarian bauxite, on the other hand, gives Ti contents up to 3%. Polymerizates made with the latter $AlCl_3$ were subject to the treating difficulties described above to a high degree (according to a report from Dr. Paetsch, Schkopau, this Ti-containing $AlCl_3$ causes emulsions when used for other purposes).

An $AlCl_3$ of uniform Fe content produced from French bauxite (K-catalyst) was then supplied from Schkopau for the production of SS 903. The following tables present a series of tests carried out in the new 4500 lit. autoclaves which under identical operating conditions yield less viscous oil.

Batches with iron-free and K-catalyst were now run at varying maximum temperatures in Furnace X (V_2A) and Furnace VII (chrome-plated surface);

p.67

Table 46 a

Iron-containing $AlCl_3$ (K-catalyst), Furnace X 4500 lit. (V_2A) steel (welded)

Charge: 1200 lit. light oil, 125 Kg $AlCl_3$

Max. Temp.	No.	E°/99	V.I.	Solid.pt.	Fl.pt.
150	72	5.66	110.8	- 34	218
	73/74	5.14	113.6	- 35	209
	75	5.14	114.5	- 36	221
	76	4.24	113.0	- 36	207
	77	4.66	114.3	- 38	213
200	192	3.31	112.8	- 35	219
	194	2.24	110.3	- 38	211
	195	3.57	115.7	- 23	220
	224	3.23	116.0	- 26	210
220	196	2.86	115.5	- 20	214

Table 46 b

Iron-containing $AlCl_3$ (K-catalyst), Furnace VII, 4500 lit., chromium plated

Charge: 1200 lit. light oil, 125 lit. $AlCl_3$

Max. Temp.	No.	E°/99	V.I.	Solid.pt.	Fl.pt.
150	192	4.55	110.7	- 34	223
190	181	4.01	110.2	- 37	214
200	184	2.27	114.3	- 35	220
	191	2.96	117.5	- 37	208
	201	3.06	114.7	- 31	231
205	214	3.03	119.1*)	- 35	220
	219	3.12	109.6	- 37	235
215	226	4.04	116.9	- 21	225

* Average values of standard furnaces (I-VI) gave only V.I. values of 108 on this date.

Table 46 c

Iron-free $AlCl_3$, Furnace VII, 4500 lit., Chromium plated

Charge: 1200 lit. light oil, 125 kg $AlCl_3$

Max. Temp.	No.	E°/99	V.I.	Sett. pt.	Fl. pt.
150	190	4.77	107.8	- 38	216
	202	4.62	113.4	- 33	228
	223	5.62	108.6	- 36	228
165	230	4.34	112.3	- 37	214
160	180	3.80	118.5	- 33	216
180	182	3.63	107.0	- 41	217
200	196	3.18	121.6	- 14	198
	197	3.40	121.7	- 15	208
	198	3.27	122.2	- 17	204

p.68 It will be seen from these data that even when using furnaces made of other materials which yielded less viscous polymerizates than the corresponding N_6 furnaces, an increase of the maximum temperature to 200°C is necessary in order to maintain the required viscosity of 3-3.5 E°/99 for the SS 903 oils. While an iron-free catalyst yields products at 200° which, having a setting point* of -15 to -20°C, are no longer useful, this difficulty with K-catalyst occurs only at temperatures in excess of 210°.

Moreover in the manufacture of SS 903 in furnaces not consisting of N_6 material the purity of the gas is an additional factor of highest significance. Even in the N_6 furnace, with a gas which will just form SS 903, polymerization to SS 906 will not take place at all even at higher maximum temperatures. Still more difficulty is encountered in the 800 Furnace VII-X the operation of which, even at a lower maximum temperature, is very dependent on the quality of the gas.

The following may be said with respect to the industrial production of SS 903

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* Solidification point

crude polymerizates with K-catalyst. The previous difficulties encountered in the separation and further treatment of the catalyst residues, such as the very pronounced fouling of the centrifuges and the clogging of the sludge nozzles may be overcome if the crude product is charged into the preliminary decomposition tanks at a temperature of 125-130° and the preliminary decomposition with methanol is carried out only to acid numbers of about 9-12 mg/KOH. If an acid number half this, as in the decomposition of the SS 906 crude product, is obtained the addition compound separates in a gritty state and then gives trouble in the centrifuge bowls.

Since the addition compound of products run at high maximum temperature is more difficult to decompose than the one obtained at lower temperature, the withdrawal into the "Körting" and the treatment of the sludge in the subsequent agitator must be done at higher temperature. In this case it is also advisable not to concentrate the aluminum chloride liquor to a density of 1.3=about 40%, but to leave it at 25% in order to facilitate decomposition of the sludge.

The use of K-catalyst has also made possible the direct filtration of the lime sludge without an SS 906 lime pre-coat. When supplying the product to the filter press, a temperature of 75-80° should be maintained.

p.69 **e. Light Oil Charge**

That the amount of solvent used in the treatment of a batch has a certain influence on the viscosity of the resulting final product had already been established in the small scale experiments.

An effect of this kind was also disclosed in large scale operation. It will be seen from the following Tables 47 and 48 which give a number of successive batches in the two 100 lit. and the four 4500 lit. autoclaves with varying amounts of light oil charge.

Table 47

1000 lit. N_6 autoclave, 30 Kg $AlCl_3$
Maximum temperature 200°
Operating temperature 130°

a) 250 lit. dist.

	E°/99	V.I.	Solid.pt.	Fl.P.
N 221	4.27	110.8	-37	214
S 215	4.04	114.3	-38	195
N 222	4.35	110.6	-36	216
S 216	3.98	108.1	-36	220
N 223	4.39	110.5	-40	205
S 217	4.00	112.5	-37	198
N 224	4.38	112.3	-34	205

b) 200 lit. dist.

	E°/99	V.I.	Solid.P.	Fl.P
N 227	5.04	116.4	-30	195
S 221	5.33	109.4	-30	221
N 218	5.39	113.1	-37	200
S 222	5.00	113.8	-36	203
N 229	5.26	113.8	-33	226
S 223	5.31	109,4	-34	211
N 230	5.87	110.0	-34	220

Table 48

4500 lit. N_6 AutoclavesI-IV; 125 kg $AlCl_3$
Maximum temperature 160°
Operating temperature 120°

a) 1200 lit. dist.

10, 13, 40.		E°/99	V.I.	Solid.P.	Fl.P.
13.40	IV 711	5.58	110.7	-34°	198
15.00	II 768	6.06	109.3		215
17.00	I 808	6.57	110.6		220
19.10	III 760	5.80	113.1		199
23.10	IV 712	6.21	112.6		205

b) 800 lit. dist.

10,14,40		E°/99	V.I.	Solid.P.	Fl.P.
23.30	IV 714	7.82	112.9	-35°	226
3.40	II 771	7.98	114.1		220
8.30	I 811	7.20	116.6		222
12.15	III 763	7.89	114.8		215
16.00	II 772	7.75	113.4		226

p.70 As will be seen, a reduction of 20% of the light oil in the two 1000 lit. furnaces at maximum temperatures of over 200° causes an increase in the viscosity at 99°C from 3.8-4.40 to 5.0-5.9. In the 4500 lit. furnaces, which were run on SS 906, the effect is much less. In this case a reduction in the light oil charge of 33% causes an increase in the viscosity from less than 7 to over 7E°/99.

f. Polymerization

The following three experimental records in Table 49 of batches in 4500 lit. N_6

furnaces give a picture of the course of the polymerization process.

A: Good reaction with normal starting velocity

B: Good reaction with too high a starting velocity

C: Poor reaction

p.72 The charging and starting of the furnaces were done as described on page 53.

The optimum gas feed rate established for this type of furnace is 250-350 m^3/h; For higher rates up to 500 m^3/h a poorer quality product was usually obtained. Moreover, it was found that the quality of the oil improves if the process is operated with a slowly increasing amount of gas.

Table 49 contains data on pressure, temperature and time. Here T2 is the most important temperature in the lower part of the furnace, T_1 the head temperature which applies only after charging the furnace (A and B), and T_3 the temperature of the autoclave jacket, which is low for an active, highly exothermic reaction, (A and B), but which must be kept high for a declining or hindered reaction in order to maintain the temperature at the desired height in the crude liquid polymerizate (C)

"A" represents a normal reaction with a maximum temperature of 150° and an operating temperature of 110°. The entire process from the first introduction of the 20 atm. C_2H_4 to the cessation of the gas supply is completed in 7 hours in this case. After 6 1/2 hours it can be seen that the furnace is full of liquid reaction products by the rise of T_1 and the sudden rise of the internal pressure from 28 to 60 atm. In the last quarter hour the external temperature T3 must be raised in order to maintain T_2, since no more gas can be introduced because of the rise in pressure.

While in example A the operation was conducted with a quantity of gas ultimatel 350 m^3/h, polymerization B was started with 350 m^3/h, gradually increased to 480 m^3. For a cooling water temperature of 50° the operating temperature was 120-130°. The

Table 49

Autoclave No.	II/1910	VI/541	VI/403
Light oil charge	1400	1200	1200
$AlCl_3$ kg	120	120	120
Gas introduced	13.20 h 20 atm.	4.30 h 20 atm.	18.15 h 20 atm.
Heated	13.50	5.0	18.45
Max. press.	14.15 19 atm.	5.15 32 atm.	19.00 30 atm.
Max. temp.	14.25 150°	5.20 160°	19.15 180°

Time	Temp. °C 1	2	3	p atm.	C_2H_4 m^3/h
14.30	98	139	77	12	
45	80	120	61	10	
15.00	74	112	53	10	230
15	72	111	53	10	
30	71	111	52	10	
45	70	110	52	12	
16.00	75	110	52	15	300
15	87	112	52	16	
30	88	112	52	16	
45	85	111	52	17	
17.00	83	110	54	17	320
15	85	110	65	18	
30	90	115	60	19	
45	87	112	58	20	
18.00	87	110	62	21	350
15	88	110	64	21	
30	90	110	66	22	
45	95	110	68	24	
19.00	98	112	68	26	340
15	99	110	68	26	
30	100	110	67	26	
45	110	110	65	28	
20.00	110	110	62	60	350
15	110	110	110	60	

Time	Temp. °C 1	2	3	p atm.	C_2H_4 m^3/h
5.45	78	140	70	13	
6.00	72	139	52	12	350
15	72	123	60	13	
30	78	121	52	17	
45	80	125	53	20	
7.00	80	128	52	20	350
15	82	122	51	22	
30	82	125	51	23	
45	82	125	51	26	
8.00	85	128	51	27	430
15	85	127	51	28	
30	85	122	50	29	
45	87	122	50	30	
9.00	92	123	50	33	480
15	102	128	50	36	
30	123	127	70	39	
45	135	135	100	60	
10.00	130	130	115	60	430

Time	Temp. °C 1	2	3	p atm.	C_2H_4 m^3/h
19.30	85	140	70	12	
45	15	115	75	20	
20.00	75	115	60	28	250
15	75	115	60	28	
30	80	120	60	33	
45	80	118	60	36	
21.00	75	115	60	38	260
15	75	110	60	40	
30	80	115	70	41	
45	80	112	60	42	
22.00	80	110	60	44	235
15	80	110	65	50	
30	80	110	60	52	
45	80	110	60	54	
23.00	80	110	60	58	265
15	85	110	65	60	
30	80	110	80	60	
45	90	110	90	60	
24.00	90	115	90	56	200
15	90	115	80	60	
30	95	115	80	60	
45	92	110	90	60	
1.00	92	110	90	60	200
15	95	110	95	52	
30	100	115	110	52	
45	100	115	110	52	
2.00	100	112	80	58	-
15	100	110	100	60	
30	100	110	100	60	
45	100	110	105	60	
3.00	100	120	110	60	100
15	100	118	100	60	
30	100	110	100	50	
45	100	110	100	60	
4.00	100	110	100	60	-

Analysis of SS oil boiling at 150°C in vacuo

	A II/1910	B VI/541	C VI/403
E°/99	5.93	5.60	4.64
V.I.	112.4	107.4	106.9
Solid. pt.	-39°	-39°	-39°
Fl. pt.	205°	223°	206°

operating time in this case was only 5 1/2 hours, the V.I. of the oil dropping to about 107.

Example C demonstrates a hindered reaction which may occur when the gas is slightly contaminated. While the pressure in autoclave A and B only rises to 60 atm. in the last half hour, in spite of the strong influx of gas, this occurs in C in the middle of the process and the desired internal temperature must consequently be maintained by external heating because of the weak supply of gas. That the autoclave in example C is not entirely full is evidenced from the fact that T_2 and T_1 do not become equal. In order to investigate the progress of the polymerization, samples were taken from a 4500 lit. furnace, first at short intervals, then every thirty minutes after the maximum temperature had been reached.

p.73 IV 870 (Chart 50 a) was run with a hydrogenated, high boiling (250-340°), I 998 (Chart 50 b) with hydrogenated low-boiling (130-250°) overhead. In addition to the indications furnished by the internal temperature of the light oil charge and the pressure in the autoclave from the first hour on, the synthesis of oil is apparent from the gradual increase in viscosity and the amount of fractions boiling above 150° in vacuo. The high boiling oil described gives the most viscous end product.

Table 51 gives data on the progressive polymerization of charge T 998. (See p. 79).

p.74 **Working Knowledge Pertaining to the Polymerization.**

A summary now follows of technical details and knowledge important for carrying out the polymerization:

Before loosening the cover from the catalyst inlets for filling the autoclave, all gas must be removed from the autoclave as follows:

1)- After the crude product has been blown out, most of the residual gas is allowed to escape by carefully opening the high pressure valve (next to the alkali

Betriebserfahrungen bei der Polymerisation:

Es folgt nun eine Zusammenstellung von technischen Einzelheiten und Erfahrungen, die sich als wichtig für den Betrieb der Polymerisation herausgestellt haben:

Bevor zum Füllen des Autoklaven der Deckel vom Kontakteinfüllstutzen gelöst wird, muss alles Gas aus dem Autoklaven entfernt sein, was folgendermaßen geschieht:

1.) Nachdem das Rohöl fertig entspannt worden ist, wird die Hauptmenge Rückgas durch vorsichtiges Öffnen des Hochdruckventils (neben Laugewaschturm im Erdgeschoss) entspannt. Hierbei ist darauf zu achten, dass die danebenstehende Rückgaswaage nicht durch zu schnelles Entspannen durchschlägt.

2.) Der noch im Autoklav verbleibende Gasrest wird über Dach entspannt, auf keinen Fall in den Füllraum (Explosionsgefahr).

3.) Nun werden von den 12 Schrauben des Blindflansches vom Einfüllstutzen 10 Schrauben entfernt, die beiden letzten werden nur gelockert. Der Blinddeckel wird jetzt gelüftet. Sollte noch ein erheblicher Gasdruck bemerkbar sein, wird der Deckel nochmals angezogen, bis sich auch der letzte Druck über Dach entspannt hat. Erst jetzt dürfen auch die beiden letzten Schrauben entfernt werden. Diese Maßnahme ist unbedingt zu beachten, da es vorgekommen ist, daß beim unvorschriftsmäßigen Öffnen der Deckel mit großer Gewalt hochgeschleudert worden ist, evtl. sogar unter explosionsartigen Erscheinungen und unter Flammenbildung.

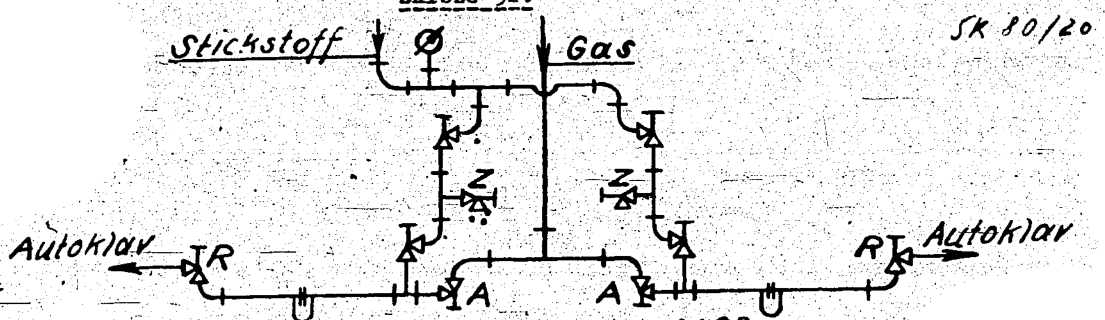
Bricht am Autoklavenkopf ein Brand aus, so ist folgendermaßen zu verfahren: Entsteht ein Feuer beim Öffnen des zuvor entleerten Autoklaven, so ist das Feuer mit dem Handlöscher zu bekämpfen.

Steht beim Ausbruch eines Feuers der Autoklav noch unter Druck, ist der Druck durch die "Schnellentspannung" im Erdgeschoss oder der "Über-Dach-Entspannung" im Füllraum abzulassen. Darauf muss in den Autoklav Stickstoff gefahren werden.

Folgendermaßen geschieht das Umschalten von Gas auf Stickstoff:

Skizze 52.

SK 80/20



26/V

10108

wash tower on the ground floor). Care must be taken to prevent residual gas from breaking the adjacent gas meter by too rapid release of pressure.

2.) The gas still remaining in the autoclave is allowed to escape up the vent, but under no conditions inside of the room (danger of explosion).

3.) Of the twelve bolts on the blind flange of the inlet, ten are removed but the last two only loosened. The blind flange is now raised. Should the gas pressure still be high, the cover is lifted until the pressure has been completely released up the vent. Only then should the two last bolts be removed. This precaution must always be observed because if these instructions are not followed the latter may be thrown high with great force, even explosively, with ignition of the gas.

If fire should start at the top of the autoclave the following steps should be taken. Fires occurring on opening the empty autoclave should be put out with hand extinguishers.

If a fire starts when the autoclave is still under pressure, the pressure should be released through the "quick release" valve on the ground floor or through the "outside vent" valve in the room. Nitrogen must then be introduced into the autoclave.

A change from gas to nitrogen is accomplished in the manner shown on Diagram 52.

p.75 1- The gas is shut-off, the regulating valve R and, particularly, the shut off valve A are closed.

2- The gas meter is disconnected.

3- The intermediate release valve Z is closed and the nitrogen gage checked at 200 atm.

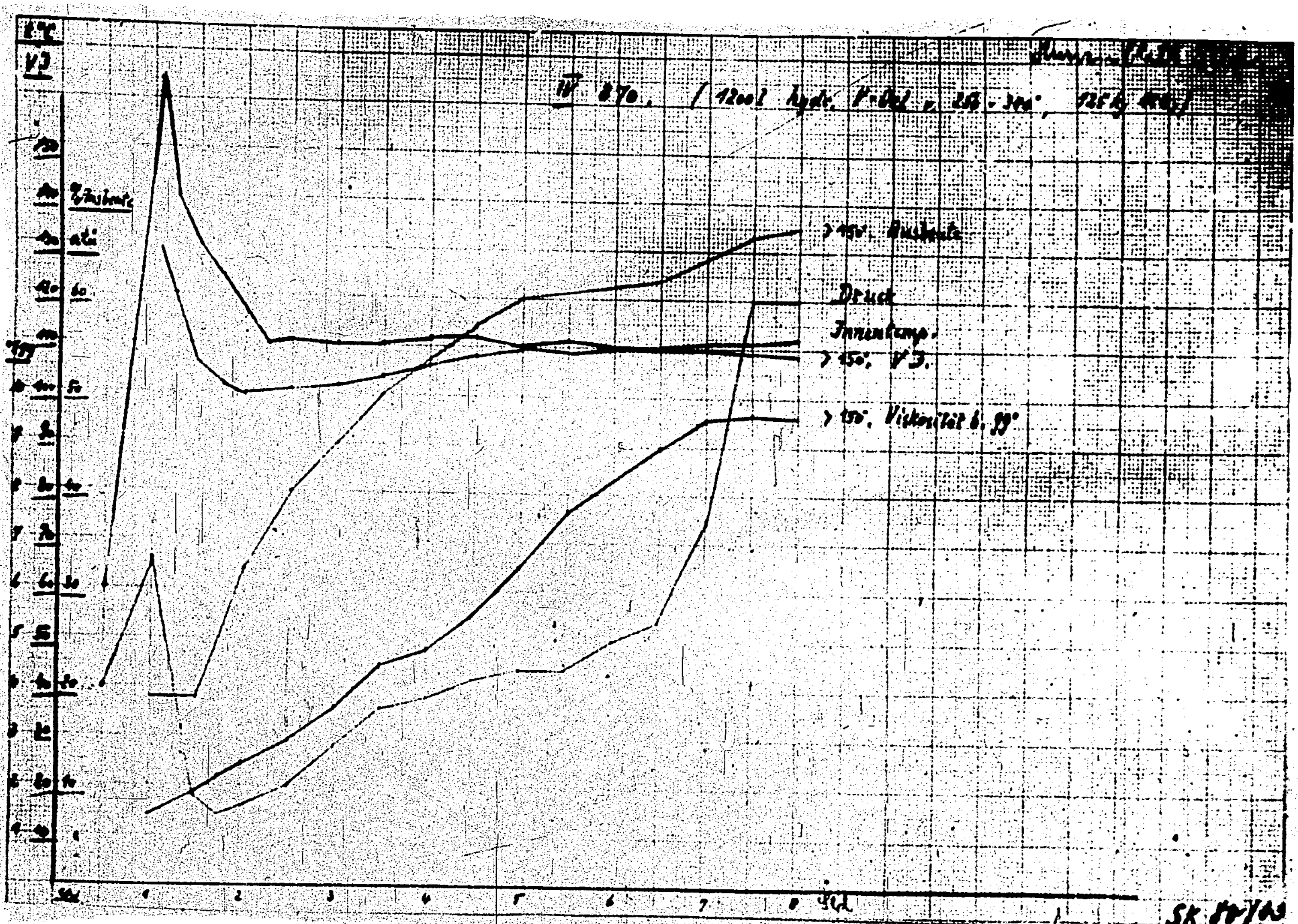
4- Both nitrogen valves are opened.

5- Nitrogen is introduced through the regulating valve R.

The operators of the autoclaves should always remember that the intermediate release valve between the gas line and the nitrogen line should always remain open (no gas in the nitrogen line, and vice versa).

In charging the catalyst, the cover of the catalyst drum resting against the conical hopper should be removed quickly (to prevent access of air): the catalyst should be introduced only after the light oil has been charged, and then only when the agitator is running (to prevent the granular catalyst from sticking to the bottom). when charging the powdered catalyst the latter should not be blown from the open autoclave with air, but wiped off.

Before closing the cover: the groove and spring shall be well cleaned and a new packing inserted if necessary. When the inlets are cleaned waste should not be used. Before the "filler" tells the operator that the autoclave is "ready" he must make certain that all the valves on top are closed and that the water circulation tank is filled, i.e. the level must show in the lower gage glass of the expansion chamber. The operator must make sure of the correct setting of all valves at the bottom of the autoclave before introducing the gas. In operating the autoclave it should be noted that on cooling down after the maximum temperature has been reached, the difference between the internal and external temperatures should not exceed 100° for reasons of safety (cracks in the high pressure jacket). If a maximum temperature in excess of 200° occurs, care must be taken, on cooling from the maximum temperature and during the introduction of gas, that the internal temperature does not drop below 120° which would affect the reaction). The pressure in the autoclave should not exceed 60 atm. Should the internal temperature drop in a completed autoclave run and have to be raised before releasing the pressure, this pressure must be noted, because if the autoclave be strongly heated at 60 atm., the pressure might quickly rise to excessive values. In this case the pressure must be released to about 40 atm. before heating. Every time the pressure rises above 60 atm. the gas must be shut off, the heating discontinued and the quick release opened if necessary.


IV 870. (1200 l hydr. V-Öl v. 250-300°, 125 kg
V.Z.
% Ausbeute
atü
> 450°, Ausbeute
Druck
Innentemp.
> 450°, V.Z.
> 450°, Viskosität b. 99°
Std.
1
2
3
4
5
6
7
8
Std.
SK 10/43

Kurvenblatt 50B

T 998. (120 l hydr. Voröl n. 130 - 237°, 12,5 kg AlCl3)

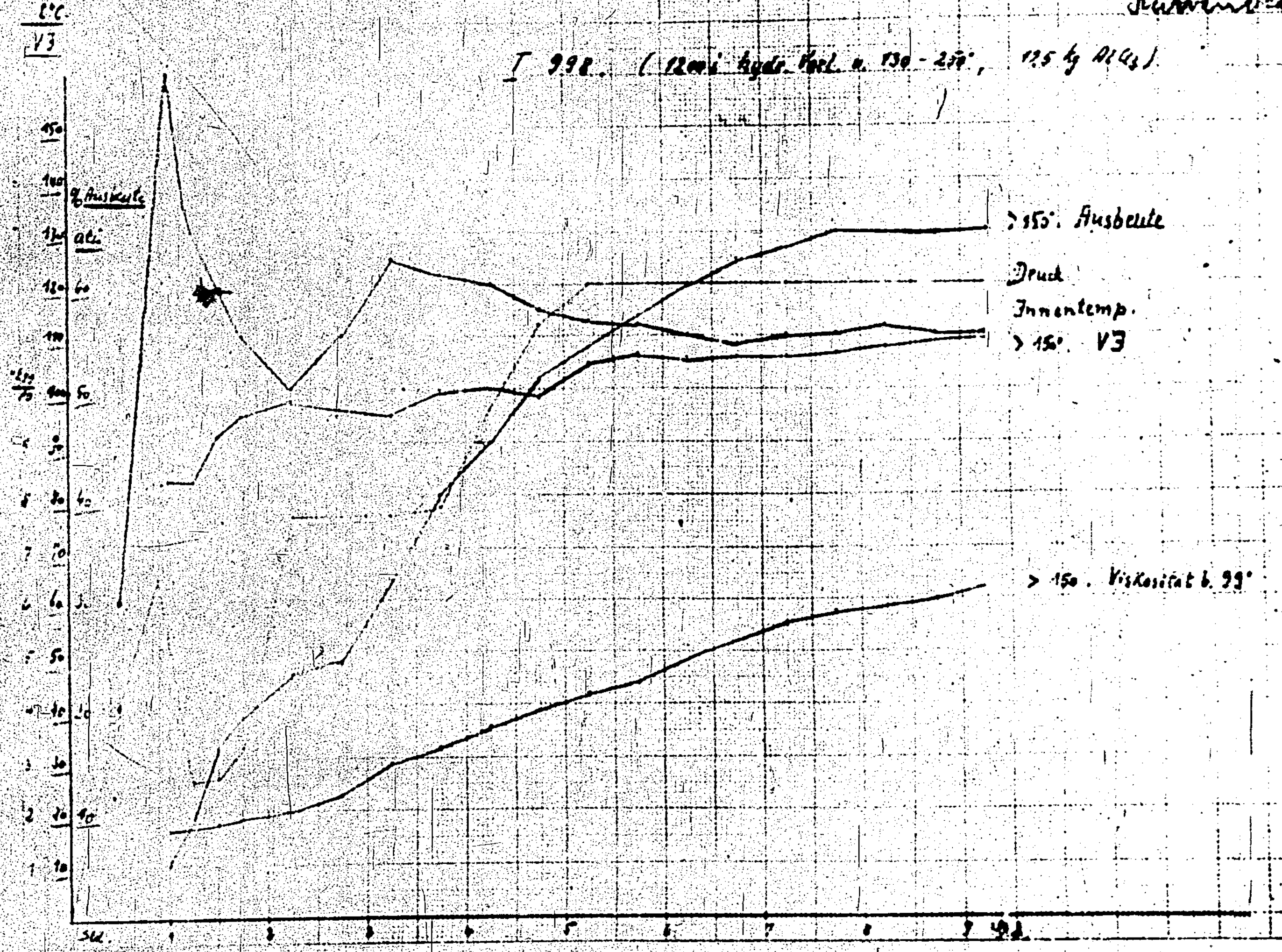


Table 51

p.73

Exp.	Time	Press.	Temp.		SS Oil		150° in vacuo 0.4 mm			I-no (Hanus)		
No.	min.	atm.	int.	ext.	% wt.	E°99	V.I.	Solid.pt.	Fl.pt.	crd.prod.	Overhd.	Residue
1	60	25	160	120	4.5	1.6	86.1	-73		0.0	-	-
2	5		145		5.0	1.6	86.0			0.0	-	-
3	5		135		8.3	1.6	86.0			0.0	-	-
4	5	13	130	70	8.8	1.6	86.0		198	0.0	-	-
5	15	13	123	60	15.8	1.7	91.0	-47	188	0.0	-	-
6	15	16	110	60	19.1	1.9	94.7	-46	187	0.0	-	-
7	30	35	100	65	23.6	2.0	98.0	-45	200	0.0	-	-
8	30	36	110	60	24.2	2.2	96.0	-41	204	0.0	-	-
9	30	37	125	70	32.5	2.9	94.8	-37	219	0.0	-	-
10	30	39	122	65	40.8	3.2	100.2	-38	213	0.0	-	-
11	30	48	120	70	45.0	3.6	100.1	-36	217	0.0	-	-
12	30	56	115	72	52.4	3.7	98.3	-37	208	4.2	0.0	8.9
13	30	60	120	65	54.0	3.9	105.9	-36	213	-	-	-
14	30	60	112	80	57.4	4.1	107.3	-36	208	4.8	1.6	6.8
15	30	60	110	90	60.0	5.1	102.5	-35	227	4.2	2.0	6.4
16	30	60	108	82	63.0	5.1	106.4	-35	223	5.7	2.3	6.7
17	30	60	110	83	63.0	5.6	105.9	-31	226	10.0	7.5	10.7
18	30	60	110	92	65.0	5.8	106.3	-32	223	10.1	8.5	11.8
19	30	60	112	100	65.0	5.8	107.1	-32	224	8.5	4.6	9.2
20	30	60	110	100	65.0	5.9	107.5	-31	230	9.8	6.7	9.8
21	30	60	110	100	65.0	6.3	109.0	-32	226	7.3	4.5	8.8
22	30	60	110	100	65.6	6.3	108.6	-32	230	5.7	1.6	7.3

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I g: Effect of the Wall Material of the Autoclave on the Polymerization Reaction.

With the two furnaces of 400 mm Ø first installed at Leuna and the subsequent 800 mm Ø furnaces (No. I-IV), all made of N_6 material, oils were obtained immediately after starting up which satisfied the analytical data required. 6°E/99 and a V.I. above 108.

The next two furnaces of N_6 material (No. V and VI) operated in the same manner.

The Autoclaves VII and VIII could no longer be built of N_6 due to shortages in the supply. For this reason S_2 steel, provided with an inner N_6 lining was used. However, it was found after finishing the autoclaves that the N_6 lining exhibited hair cracks extending into the base material, and the lining was therefore machined off. For this reason the inner surface of Autoclaves VII and VIII consisted chiefly of machined S_2 material.

Although small scale tests had shown the harmful effect of ferrous wall materials, Furnaces VII and VIII were installed in the condition described inasmuch as it had been found that in larger reaction chambers the effect of the wall is largely repressed. This observation was made during polymerizations in a N_6 agitator autoclave of 4500 liters capacity (No. IV). In these tests the autoclave was provided to a height of about 5^{m} with iron inserts of M-1 material which had only the normally rolled surface. The polymerization results obtained in this autoclave are summarized in Table 1. This table shows that the iron surface can no longer be considered to have any damaging effect on the oil. These results justify the decision to use normal steel in changing from 800 mm Ø to 1200 mm Ø furnaces, since the furnaces of the SP plants could no longer be supplied with high grade Cr steel owing to difficulties of supply.

The effect of the ferrous surfaces in Autoclaves VII and VIII is shown in Table 2. The viscosities and V.I. of the resulting oils were far below the specifications. It seemed probable that the lower quality was due to the freshly machined surface while, on the other hand, the Fe inserts in Furnace IV which were not harmful, had been annealed.

Tests were then made in 50 lit. N_6 furnaces with different pretreated Fe inserts.

1. Fe feed pipe. The results (Table 3) are better than in the iron Furnace VII (Table 2) and similar to those with the Fe liner in the N_6 furnace (Table 1).

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Table 1

Fe feed pipe in 800 mm Ø N_6 Furnace IV

No.	Tl	E 99	V.I.	Fl. pt.	Solid.pt.
IV/208	160	5.16	110.4	203	- 31
209/10	160	5.33	112.8	198	- 30
211/12	160	5.54	111.2	205	- 27
213/15	160	5.65	110.3	220	- 32
216/17	160	5.40	112.2	213	- 34
218	220	4.04	118.9	208	- 30
228	220	2.89	123.2	200	- 26
225	220	3.08	121.7	210	- 19
229	220	3.44	123.3	224	- 25

Table 2

800 mm Ø Fe Furnace VII untreated

No.	E 99	V.I.	Fl. pt.	Solid. pt.
1	4.75	107.1	223	- 35
2	4.05	108.9	227	- 39
3	3.67	109.5	207	- 41
4	3.51	104.3	213	- 39
5	3.66	108.3	218	- 39
6	3.57	110.8	215	- 44
7	3.86	110.9	199	- 39

Table 3

Fe feed pipe in 50 lit. N_6 experimental furnace

Date	No.	T 1	E 99	V.I.	Fl. pt.	Solid.pt.
3,30,42	N 685	200	4.02	108.3	201	- 36
3,31,42	686	157	4.83	106.3	210	32
4,1,42	687	158	5.94	108.0	220	29
4,2,42	688	160	5.65	110.2	219	33
4,3,42	689	181	4.49	112.3	212	34
4,4,42	690	147	5.45	106.8	213	35
4,5,42	691	166	5.15	108.0	208	35

78-2. - Fe pipe. The results (Table 4) are poorer than required.

Table 4

Fe pipe, in 50 lit. N_6 furnace

Date	No.	T 1	E 99	V.I.	Fl.pt.	Solid.pt.
4,10,42	693	205	4.17	115.4	198	- 37
4,10.42	694	230	3.25	124.6	200	-
4,11,42	695	160	6.03	110.0	208	28
4,12,42	696	160	4.39	112.2	-	29
4,13,42	697	160	6.07	110.0	209	31
4,15,42	698	173	4.54	109.6	206	36
4,16,42	699	160	3.94	110.7	198	33
4,17,42	700	160	4.39	107.1	192	35
4,18,42	701	155	4.65	105.7	207	38
4,19,42	702	190	3.68	107.5	199	38

3. - Fe feed pipe annealed. The results (Table 5) are similar to those in Table 3.

Table 5

Fe pipe, annealed for N_2 furnaces

Date	No.	T 1	E 99	V.I.	Fl.pt.	Solid. pt.
4,24,42	N 705	150	3.37	98.2	-	-
4,25,42	706	148	4.07	106.4	194	- 33
4,26,42	707	142	5.40	105.7	211	32
4,27,42	708	153	4.15	109.3	178	38
4,28,42	709	170	5.18	105.8	208	36
4,30,42	710	180	5.06	108.6	207	33
5,3,42	711	180	4.75	107.0	198	35
5,3,42	712	171	5.10	103.6	203	37
5,4,42	713	180	5.63	112.7	208	37
5,6,42	714	180	5.77	110.6	215	30
5,6,42	715	175	5.73	110.1	206	32

4. - Fe pipe annealed and turned (Table 6). Half of the tests had to be terminated prematurely, the rest gives no clear picture.

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Table 6

Fe pipe, machined for N_2 furnaces

Date	No.	T1	E 99	V.I.	Fl. pt.	Solid.pt.
5,16,42	716)					
5,16,42	717)	discontinued				
5,17,42	718)					
5,17,42	719)					
5,18,42	720	172	6.10	101.2	224	- 30
5,19,42	721	159	5.72	106.8	213	36
5,20,42	722	162	7.11	110.5	220	31
5,21,42	723	182	2.40	80.2	178	41
5,22,42	724	180	3.52	95.4	193	35
5,22,42	725)					
5,25,42	726)	discontinued				
5,26,42	727)					
5,27,42	728	180	2.87	93.4	209	37
6,1,42	729)	discontinued				
	- 732					

These tests were then transferred to the 800 mm Ø Furnace VII.

1. - Fe feed pipe, severely scaled (Table 7); no effect in comparison to the plain furnace.

Table 7

Fe plate, annealed, severely scaled in 800 mm Ø Fe Furnace VII

No.	E 99	V.I.	Fl.pt.	Solid. pt.
24	3.77	111.9	199	- 36
25	2.94	114.1	210	27
26	2.53	113.1	207	30
27	2.77	108.0	187	41
28	2.34	101.3	190	42
29	2.96	102.8	207	38
30	2.68	112.5	199	39
31	4.93 ?	109.1	215	34
32	2.80	101.4	215	43

p.80 2. - Fe feed pipe, machined (Table 8). Results are distinctly better (particularly V.I.) than in the plain furnace, but not yet satisfactory.

Table 8

Iron plate, machined, 800 mm Ø Fe Furnace VII

No.	E 99	V.I.	Fl.pt.	Solid. pt.
76	5.51	110.6	227	- 37
77	3.74	108.4	196	36
78	4.37	110.9	212	37
79	4.15	100.5	218	35
80	3.94	110.4	216	37
81	4.61	113.3	218	38
82	6.55	110.0	246	32
83	5.23	113.2	223	35
84	5.39	114.2	213	36
85	5.05	111.8	212	37
86	5.40	112.7	214	38
87	5.01	112.4	206	36

3. - Fe feed pipe, treated with copper sulphate (Table 9), results more or less the same as in the plain furnace.

Table 9

Iron plate, treated with copper sulphate, 800 mm Ø Fe Furnace VII

No.	E 99	V.I.	Fl. pt.	Solid. pt.
89	2.53	112.7	204	- 39
90	3.25	103.0	201	31
92	2.14	118.4	199	39
93	2.69	100.8	203	37
94	3.53	104.6	219	35
95	4.93	103.7	240	35
96	3.67	109.2	213	37
97	4.06	105.2	215	37
98	3.15	197.2	207	38
99	3.79	109.5	219	41
100	3.81	111.6	210	37
101	3.16	112.6	205	44
102	4.86	112.0	223	33
103	4.13	105.3	225	38

p.81 4. - Fe feed pipe, treated with aqueous chromic acid (Table 10) Results better than in the plain furnace, but not satisfactory.

Table 10

Fe inserts treated with Cr_2O_3, 800 mm Ø Fe Furnace VII

No.	E 99	V.I.	Fl.pt.	Solid. pt.
126	3.77	108.5	212	- 38
127	3.26	107.0	217	31
128	4.42	107.7	225	37
129	4.17	112.6	213	39
130	3.90	110.9	203	35
131	4.42	112.1	216	40
132	4.81	111.9	196	36
133	3.89	113.4	209	37
134	3.88	112.8	233	38
135	4.86	110.1	217	38
136	3.90	106.4	207	36
137	3.18	103.8	210	40
138	4.52	110.9	208	38
139	4.37	110.1	206	35
140	4.24	107.8	208	37
142	4.65	112.8	200	36
143	4.07	108.2	199	33

5. - Fe feed pipe, ground and electrolytically chrome plated; the Cr plating was soon eroded. (Table 11). Results as before.

Table 11

Fe insert, electrolytically Cr plated, 800 mm Ø Fe Furnace

No.	E 99	V.I.	Fl.pt.	Solid. pt.
178	3.61	110.7	210	- 41
179	4.19	113.4	226	36
180	3.80	116.5	216	33
181	4.01	110.2	214	37
182	3.63	107.0	217	41
183	4.11	101.9	223	39
184	2.27	114.9	220	35
185	4.63	117.2	215	39
186	4.96	113.1	218	42
187	4.91	111.1	208	41
188	4.66	108.2	214	35
189	4.77	107.8	216	38
191	1.96	117.5	208	27
192	4.55	104.7	223	34

p.82 6. - V_2A feed pipe in 800 mm Ø Fe Furnace VIII (Table 12). The viscosity and particularly the V.I. are the best of all tests.

Table 12

Furnace VIII with V_2A pipe, 800 mm Ø as Fe Furnace VII

No.	E 99	V.I.	Fl.pt.	Solid.pt.
281	3.06	122.7	206	- 19
282	3.27	107.1	207	38
283	4.52	114.3	220	35
284	3.41	117.4	225	31
285	3.97	113.8	215	40
286	4.18	116.3	215	38
287	5.14	109.2	208	32
288	2.00	112.8	204	39
289	3.66	116.4	228	31
290	3.16	119.7	215	21
291	3.66	112.2	213	38
292	4.67	115.4	229	36
293	4.49	110.8	228	36
215) 296)	5.81	109.6	230	32
297	4.30	112.0	214	34
298	5.03	111.3	208	33

7. - Cu pipe was totally destroyed after a few experiments (no exact data).

8. - An Al liner was destroyed after the first test.

Meanwhile it was decided that V_2A liners would be installed in the large 1200 mm Ø Fe furnaces if their oils proved to be of as poor quality as those from the 800 mm Ø Fe furnaces. The correctness of this decision was confirmed when Furnace X(800 mm Ø Fe lined with V_2A) gave results identical to those under 6 (Table 13)

Table 13

p.83

Furnace X, 800 mm Ø lined with V_2A

No.	E 99	V.I.	Fl. pt.	Solid. pt.
1	3.86	105.1	206	- 35
2	3.22	104.7	202	45
3	2.85	105.3	206	44
4	3.54	112.7	200	35
5	4.46	108.7	199	35
6	2.20	104.2	188	40
7	2.37	102.3	202	38
8	2.79	105.0	204	37
9	3.61	107.9	193	41
10	4.10	108.8	203	40
11	3.06	104.7	200	40
12	3.80	104.5	215	36
13	4.09	107.6	218	35
14	5.16	111.2	210	35
15	5.13	111.3	213	38
16	5.10	109.8	215	38
17	4.63	112.3	218	37
18	4.28	110.3	226	38
20	3.92	109.9	211	38
21	4.71	107.6	216	39
22	4.62	109.3	213	38
23	4.33	108.8	206	38
24	4.43	111.2	206	38
25	4.70	110.0	203	36
26	3.93	107.7	210	36
27	4.22	107.2	209	38
28	2.87	108.7	205	41
29	4.45	113.2	196	37
30	4.34	108.9	212	36
31	3.55	112.3	217	38
32	4.98	109.3	216	36
33	5.37	109.3	223	36
34	3.64	101.3	211	40

Since in the meantime another 800 mm Ø furnace of N_6 gave results (Table 14) which did not correspond to those of the old 1-4 furnaces of N_6, although the analysis of the liner material had the normal composition of N_6 steel (6% Cr, 0.3% Mo and 0.15% V), it was concluded because of the difference in the irons that the variations in the properties of the oil did not depend on the materials of the furnace wall.

Table 14

Furnace IX, 800 mm Ø, N_6

No.	E 99	V.I.	Fl. pt.	Solid. pt.
1	2.89	104.1	285	- 42
2	2.89	106.5	194	41
3	3.92	108.6	207	44
4	3.80	106.5	203	41
5	3.39	114.5	202	44
6	3.15	105.8	202	43
9	4.05	107.2	195	36
10	3.79	105.5	203	35
11	4.19	109.2	207	37
12	3.34	102.3	196	39
13	4.69	109,0	199	34
14	3.85	104.6	208	35
15	3.71	108.8	210	42
16	4.18	110.0	208	38

When the large 1200 mm Ø Fe furnace arrived (Furnace III) it gave correct data (Table 15) agreeing with that obtained in the small N_6 furnaces as well as in the second furnace (Furnace III) which was obtained from another concern (Table 16).

Table 15

Furnace III, 1200 mm Ø, Iron

No.	E 99	V.I.	Fl. pt.	Solid. pt.
1	4.17	96.4	208	- 37
2	5.55	110.7	231	34
4	5.78	107.0	228	34
5	6.66	107.0	224	35
6	6.15	108.0	220	34
7	6.55	107.7	225	33
8	5.37	107	228	32
9	4.12	95	215	33
10	5.50	111	230	35
11	5.19	108.9	223	35
12	5.35	108.7	230	35
13	5.42	105.8	231	36
14	5.89	109.8	228	37
15	4.55	108.8	218	36

p.85

Table 16

Furnace II, 1200 mm ∅, Iron

No.	E 99	V.I.	Fl. pt.	Solid. pt.
1	5.18	111.8	214	- 33
2	5.70	110.8	218	34
3	6.18	113.2	233	34
4	6.16	108.9	228	33
5	6.58	111.3	225	33
7	7.59	109.3	247	34
8	6.00	107.8	221	38
9	6.48	112.2	258	35
10	5.65	108.3	215	41
11	6.63	112.2	220	33
12	6.20	107.7	223	32
13	6.11	108.3	227	30
14	6.06	109.7	220	36
15	6.37	104.0	229	37
16	6.21	107.8	230	36
17	6.25	108.0	234	35
19	7.72	111.0	234	33
20	6.48	112.3	234	35
21	5.69	107.3	231	35
22	4.42	100.3	227	37
23	5.90	104.0	226	31
24	5.57	111.1	224	34
25	6.23	106.0	236	36

The large furnaces consequently produced oils with the correct properties without any surface treatment (activation or passivity) or installation of liners. The small Fe furnaces which were supposed to operate satisfactorily only after a more or less extensive preliminary period of operation improved very slowly (after 300 charges) but still failed to fulfill the requirements. Since the large Fe furnaces immediately gave correct data regardless of the make or the quality of the gas on which they operated (the four furnaces in Schkopau give the same results) it is assumed that the difference in results obtained with the two smaller Fe furnaces are not caused by incidental differences in the metallic composition of the respective furnaces (when the furnaces in Heydebreck and Moosbierbaum start operating, furnaces from 4 different concerns can be compared). The true reason for the abnormal behavior of the two 800 mm Ø iron Furnaces VII and VIII is rather to be sought in the fact that failures during factory tests caused the manufacturer to make changes which introduced unrecognized and uncontrollable factors.

The furnaces which gave the poorer oils do not furnish very good arguments for the experimental conditions. The expectation of more reliable manufacture of SS oils in the small iron furnaces proved to be groundless since no better results were obtained than in the other furnaces. Moreover, the color of the abnormal oils (SS 906 and SS 903) were very dark (opaque blue green to dark brown) with a slightly increased Conradson test.

II. Treatment of the Crude Polymerizate

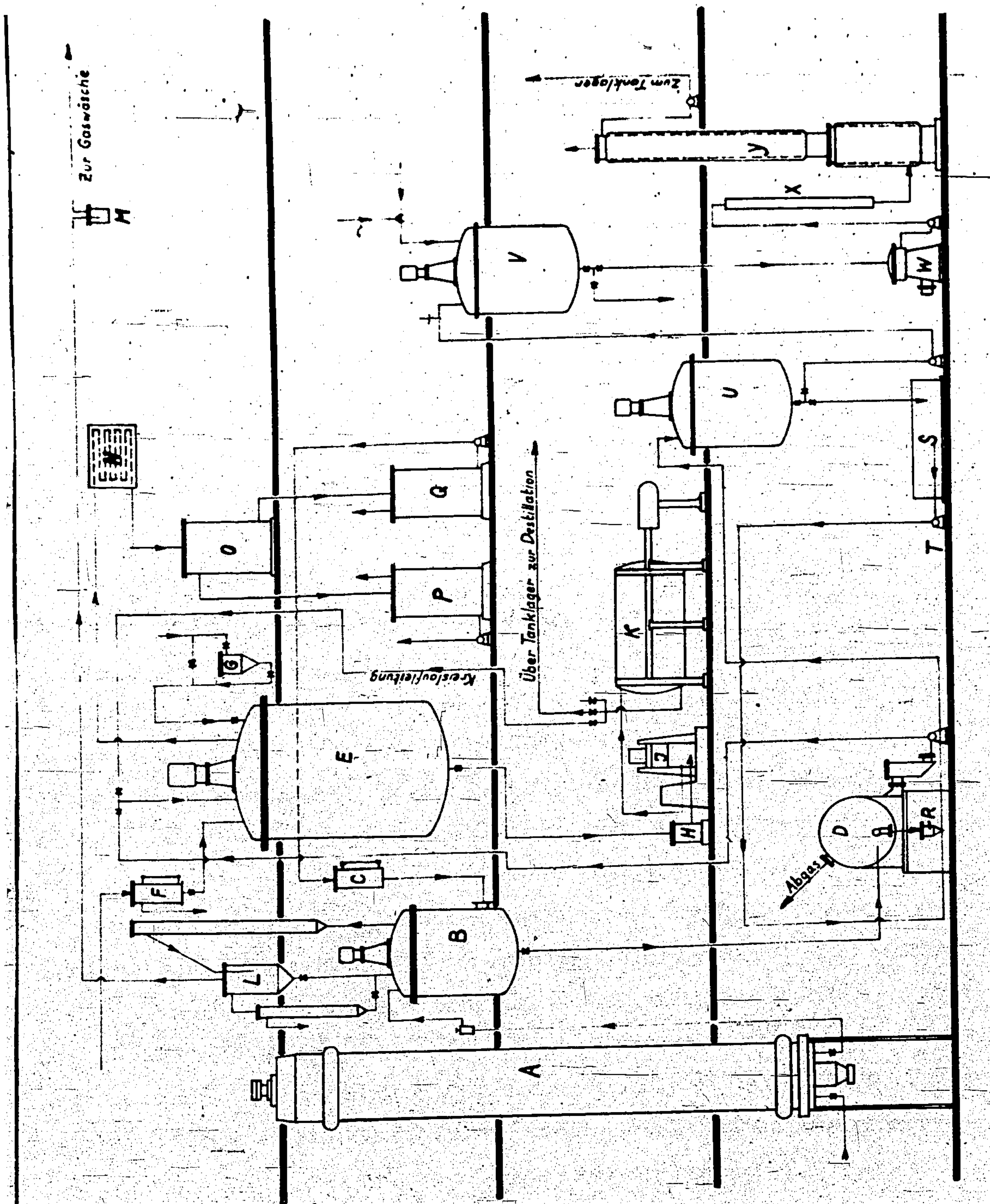
a. Old Method of Treatment:

In the older method of treatment described on page , which consisted in allowing the insoluble addition compound to settle hot and withdrawing the heavy sludge, the following difficulties were encountered.

Much settling capacity was required and the sludge outlets were easily clogged. The problem of introducing lime into the decomposition tank for removal of the addition compound still remaining in solution had not yet been technically solved. By introducing the material into an open tank, much trouble was caused by vapors from the solvent or HCl fumes; the filling equipment with its screw conveyor failed because the powdered lime caked when exposed to the vapors from the tank. Moreover, the lime sludge was difficult to filter and the oil losses were high because of the high oil content of the filter residues.

In order to overcome the trouble experienced in settling the catalyst sludge, a closed, gas-tight disk-type centrifuge with large outlets was developed in cooperation with Alfa-Laval, designed to allow a continuous separation of the hot, liquid catalyst sludge immediately after polymerization. In continuous operation, however, this method of sludge removal did not prove satisfactory because of the low throughput (owing to frequent repairs) and the insufficient purification of the product. The insertion of a Haubold centrifuge for preliminary separation of the sludge allowed a more uniform operation of the Laval centrifuge but, nevertheless, it did not provide a satisfactory solution since the cleaning and maintenance of the Laval centrifuge was time consuming and costly.

Experiments were therefore continuously conducted to develop a better method of treating the crude oil. Attempts to decompose the oil by washing with water, alkali or salt solutions always resulted in emulsions that were very difficult to filter or centrifuge because of precipitated aluminum hydroxide. This type of wet treatment was therefore finally abandoned.


Zur Gaswäsche
M
W
O
Q
P
G
E
F
C
B
L
A
Kreislaufleitung
Über Tanklager zur Destillation
K
J
H
D
Abgas
R
T
S
U
V
W
X
Y
Zum Tanklager

6.6.44.

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Treatment with alkaline methanol solutions and with gaseous ammonia was then tried, both in the laboratory and on an industrial scale. Precipitation of NaCl or sublimation of NH_4Cl frequently gave trouble due to clogging of the lines, or caused filtration difficulties; moreover, the solubility of ammonium chloride in the oil gave much trouble in the subsequent distillation.

During these experiments it has been observed that the addition product which remained dissolved in the oil could be precipitated by small quantities of methanol
p.87 without causing aluminum hydroxide to be formed by hydrolysis and without allowing undesirable constituents of the oil contained in the sludge to enter the SS oil, as happens when even small quantities of water are used.

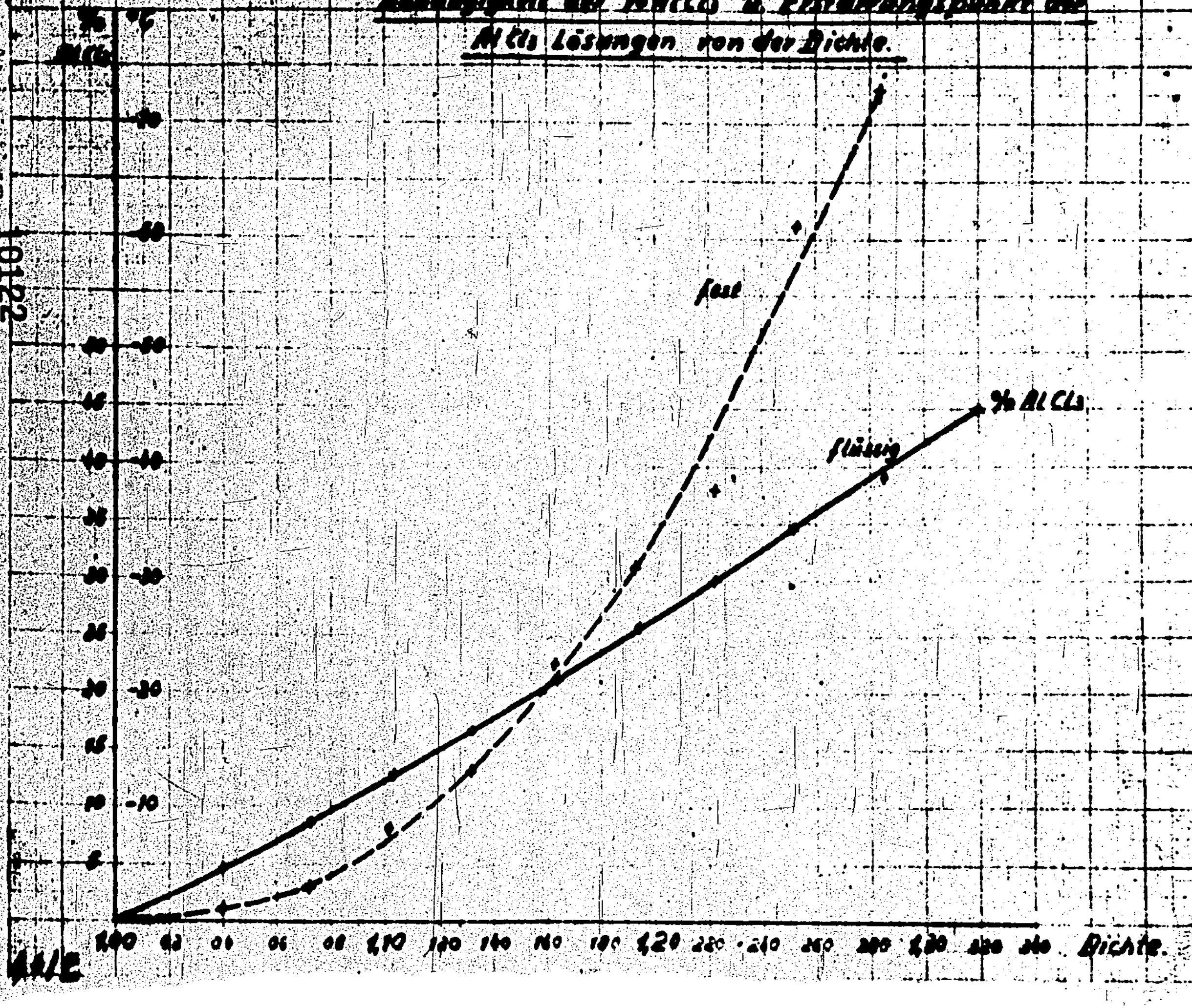
Since this precipitation can also be accomplished in the presence of undissolved sludge constituents, the following procedure was adopted. (O.Z. 13190)

b. The Present Method of Operation is Illustrated in the Attached Diagram 53

The crude polymerizate from the autoclave A is continuously discharged into an agitator B, the so-called preliminary decomposition vessel, into which methanol is simultaneously introduced from C. The HCl-containing methanol originating in the main decomposition process is used in this step. The quantity of methanol must be adjusted so that the resulting sludge can be introduced as a hot liquid into the subsequent centrifuges D. Excessive amounts of methanol produce granular precipitates which may give trouble in the centrifuge, while an insufficient addition of methanol causes some residue to remain in the oil which, in the subsequent treatment of the oil in the main decomposition step, produces lime sludges that are difficult to filter. In the centrifugal separation of sludge it has been found to be inadvisable to operate in batches, as is customary, but to run the unit as an overflow centrifuge. As a safety factor a second centrifugal separator is provided. The supply from the preliminary decomposition tank B to the centrifuge D is interrupted every 20 minutes, the supernatant oil in the drum withdrawn and the residue

Tabelle 53a

Abhängigkeit der % AlCl3 u. Erstarrungspunkt der AlCl3 Lösungen von der Dichte.



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peeled off. The amount of residue from the charge of an 800-autoclave is about 350 kg. It consists of equal parts by weight of $AlCl_3$ and hydrocarbon oil. This double compound decomposes at first very slowly with cold water. After some time, however, the reaction becomes very violent so that the water may reach the boiling point.

This decomposition is carried out in a Körting sprayer with a spray nozzle of cast iron, not with pure water but with an aluminum chloride liquor from a previous treatment.

The oil-$AlCl_3$ sludge accumulating in the centrifuge D is carried away from the sludge container R by means of a sprayer fed with aqueous $AlCl_3$ liquor. This AlCl3 solution is supplied from the liquor through S by means of a ferro-silicon pump T to the Körting sprayer located below the container R. The sprayer forces the resulting mixture of $AlCl_3$-oil sludge and $AlCl_3$ liquor into the sludge decomposition tank U. In this tank the $AlCl_3$-oil sludge is completely decomposed by stirring it for 10-15 minutes. After stopping the agitator, the oil and $AlCl_3$ liquor separate in 10-15 minutes in two layers: oil at the top and liquor at the bottom. p.87a.

The oil is conducted to the agitator V and washed with hot water to remove the remaining $AlCl_3$. The bulk of the water is then decanted and the remaining water removed in a Laval centrifuge W. The resulting oil still has a water content of 1 to 1.5% and an acid number of 1-5. It is now passed through the preheater X to the alkali wash tower Y for neutralization. This tower is operated with a 50% caustic soda solution. The caustic liquor is renewed when the NaOH content has dropped to 5%. During this neutralization step aluminum hydroxide is formed depositing for the most part on the wall of the tower from which it can be flushed off. The remainder passes, together with the neutralized oil which still contains 0.5% of water, to the storage tanks. Here water and $Al(OH)_3$ settle and are withdrawn from time to time. The oil must therefore be withdrawn for further treatment (see Section V) at some distance from the bottom of the tank.

The separated $AlCl_3$ liquor is again passed to the sprayer. This cycle is continued until the density of the liquor has reached 1.25-1.30. At higher concentrations the decomposition of the oil-$AlCl_3$ sludge is incomplete. Table 53 a shows the relation between specific gravity and solidification point of the $AlCl_3$ solution, and its $AlCl_3$ content.

Table 53 b

Corrosion of Iron -M_1- by $AlCl_3$-water mixtures at 20°C

Mixture H_2O	9	8	7	6	5	4	3	2	1	Al
Al Soln. 40%	1	2	3	4	5	6	7	8	9	Soln.
Wt. % Loss of M_1 After 785 hrs.	0.69	1.50	1.52	1.0	0.91	0.76	0.41	0.2	0.1	0.05
Wt.% Loss of M_1 After 1459 hrs.	1.45	2.78	3.28	2.18	2.12	1.67	0.98	0.49	0.62	0.42

p.87b. Table 53 b shows the corrosive action of the $AlCl_3$ liquor. It will be seen that the corrosion of iron is the most severe in 8-12% solutions. Solutions of higher concentration are less corrosive. The above liquor which has a specific gravity of 1.25-1.30 is, generally speaking, very stable. Only after long storage, about 3 months or more, does hydrolysis result in a white precipitate of oxychlorides and hydrates. Of the $AlCl_3$ used in the polymerization, about half is recovered in the manner described above. The $AlCl_3$ liquor is utilized in the tanneries at Ludwigshafen.

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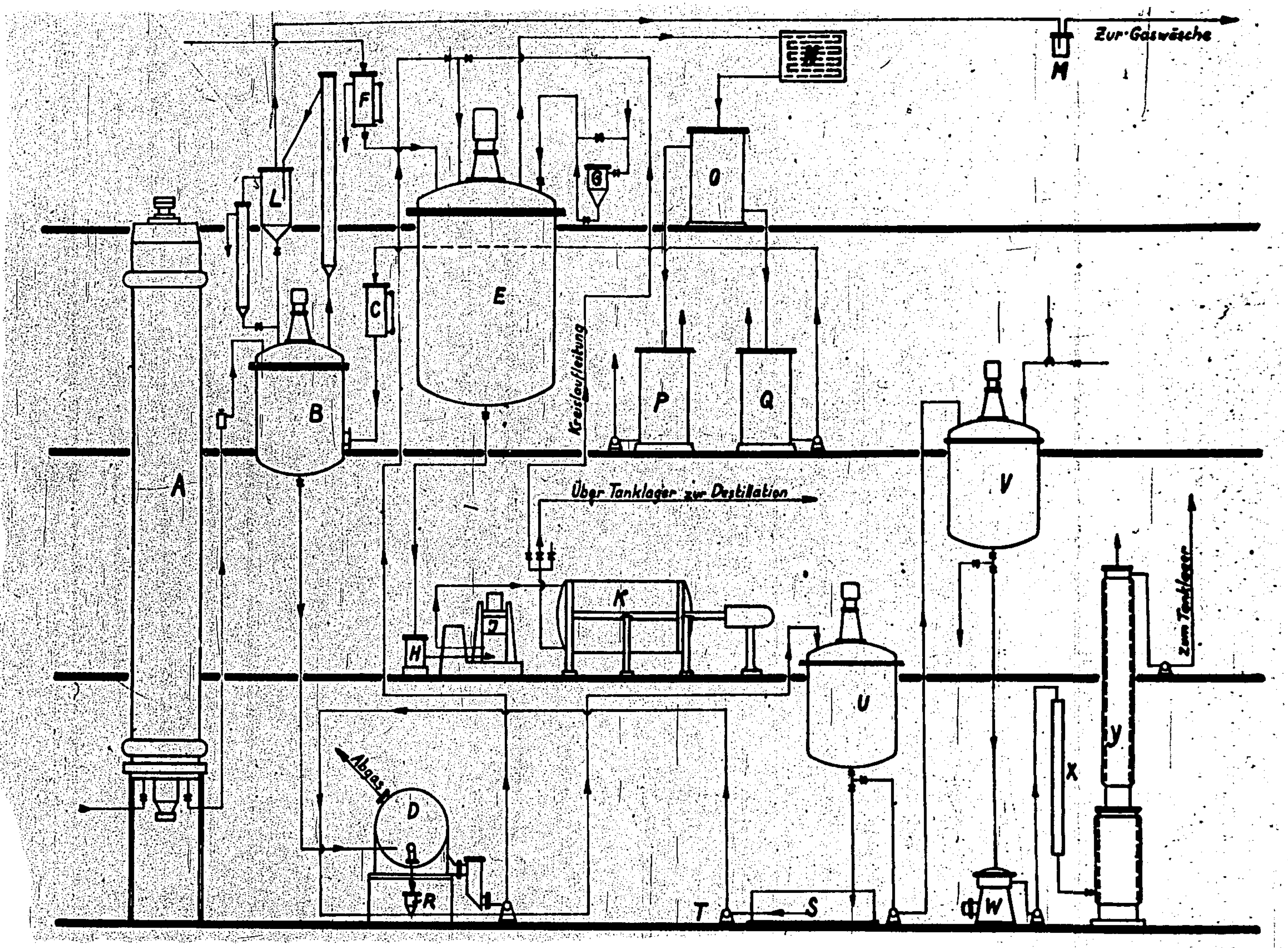

6.6.44.

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SK 80/2.

p.88 The preferred nozzle construction of this jet apparatus is illustrated in Diagram 53 a.

By operating with a pair of centrifuges, the treatment of an autoclave charge (about 4.0 m^3) lasts about 1 1/2 hours.

The centrifuged crude oil is now pumped directly to the main decomposition unit E (no longer through the collective container shown in the diagram of page). The oil (acid number 2-3 mg KOH due to hydrochloric acid) is now mixed with small quantities of fresh methanol from the measuring tank F until all HCl has distilled off with the methanol. The last traces are neutralized with lime which also takes up the small amounts of $Al(OH)_3$ remaining and thus facilitates filtration. A pneumatic transfer of the powdered hydrated lime from an iron hopper C_2 by means of nitrogen has been found very practical. (see Diagram 54 on page).

The oil-lime sludge is then led through the rock settler H to the triple action pump I which forces it into the filter press K. As long as oil leaves the filter press in a turbid state, the cloudy filtrate must be returned through the recycle line to the main decomposition tank E: only when the oil is completely clear is it switched to storage tanks from where it goes to the distillation units.

Gases liberated by releasing the pressure on the crude polymerizate in the preliminary decomposition tank B are passed through the receiver L and the oil seal M to the gas washing plant (see Diagram 53).

Vapors forming in the main decomposition step are condensed in the "Igelit" condenser N. Light oil and methanol separate in the separator O. Light oil returns to the process through the receiving tank P; the acid methanol is returned from the receiving tank Q to the preliminary decomposition step through the measuring tank C.

The filter press cake still contains about 50% oil. By extraction with light overhead oil, which is then returned together with the crude oil to the distillation step, followed by blowing of the hot cake with nitrogen, a dry, easily removable cake is obtainable. Although it appears to be free of oil, nevertheless, it still contains considerable amounts as can be shown by the following methods.

Test 1: 40% of ether-soluble constituents can be extracted with ether.

Test 2: By heating in vacuo, 21.5% oil distils over: by low cooling, 15.5% of water and 10.0% of light oil can be obtained.

Test 3: After dissolving the lime in dilute HCl, 27% oil remains floating on the $CaCl_2$ solution.

p.89 In carrying out the tests of the last type it was noticed that when the filter residue was placed in water at 90°C, a reaction took place, with foaming, in which the water goes into the lime displacing the oil. The pure, oil-free lime settles in the water on which the oil floats (O.Z. 14328). A completely dry, non-crumbled sample of lime gives 20% oil which on distillation gives 62.5% of dist. bottoms having the following properties:

Viscosity	38°C	68.5 E°
"	99°C	5.01 E°
V. I.		112.2
Solid. pt.		- 35.5
Flash pt.		223
Conradson test		0.063

The oil remaining in the lime consequently has the same composition as the crude SS product and, after distillation, the same properties as the SS oil, although the color is often somewhat darker than that of the SS oil. The boiling point analysis of the oil derived from the lime is surprising inasmuch as it was found in another test that the light overhead oil used for flushing contained little oil (after the customary flushing time of the filter press with light overhead):

Time of Flushing	% Light Overhead in the Flushed Filtrate
15 Min.	64 %
20 "	77 "
30 "	83.3 "
40 "	95.5 "
50 "	94.4 "
60 "	97.2 "

Nevertheless, the lime contains more viscous oil and less light overhead than the outflowing light flushing oil.

In practice the lime is introduced in triple the amount of water at 90°C in a tank in which an anchor-type agitator with a small clearance between the bottom and wall rotates slowly (20 r.p.m.). In this manner the lime which becomes lard-like due to the reaction, is slowly cut without being stirred up, thus allowing segregation to take place. After settling for one half to one hour water is introduced into the water zone through an annular horizontal pipe causing the oil level to rise. The oil is run out by addition of water through a nozzle located at the upper most point of the conical cover until water overflows. After starting the anchor agitator the lime sludge is pumped into the sludge line from the lower outlet at the bottom of the tank by a centrifugal pump, and dumped.

Thus, besides recovering oil, the lime sludge is disposed of in a cleaner and more convenient manner than by dumping it by hand, as was done previously.

The reactivity of the lime sludge with hot water is highest immediately after its removal from the press. When the lime sludge is left a few days, its reactivity disappears, presumably because of water absorption, through which the last traces of unslaked CaO are removed (which is probably necessary for the reaction to be successful).

This lime treatment is particularly profitable when there is trouble with the filter presses (for instance in the production of SS 903) since in that case the filter residues are particularly rich in oil. The oil obtainable in this manner amounts on the average, to 25% of the resulting lime filter cake. With a consumption of 30 Moto dry $Ca(OH)_2$, corresponding to a capacity of 10,000 Jato SS 906, this would represent about 10 Moto of oil. From 9/11/1943 to 10/13/1943 (33 days), 25,740 m^3 of oil was obtained in Me (Merseburg) 126, representing about 20 tons per month with a daily output of 0.2-1.5 m^3 (0.78 m^3 on the average). These quantities were added to the SS filtrate since repeated tests showed identical composition and properties.

c. Operating Experience.

The following points must be particularly stressed in the treatment of the crude oil:

Since in the preliminary decomposition the acid methanol is simply added to the agitator by means of a measuring tank and look box, and the measurement of hot, sludge-containing crude polymerizate under various pressures between 60 and 0 atm. has not yet been solved, experience and a reliable procedure are particularly necessary in this step.

In supplying the centrifugal separator, the feed must be as uniform as possible. This applies particularly to the ammeter control in the first of the two separators; the proper amperage must not be exceeded if overloading of the motor is to be prevented. A uniform supply to the separator also results in a more uniform discharge of the crude polymerizate into the preliminary decomposition tank so that the operator of this tank needs only to maintain a constant level in his tank.

During the run, the oil level in the look box of the collecting tanks of both separators must be continually observed. Should the pressure in the look box rise suddenly, indicating that the product pump is not working, the separator motor must be immediately shut down, after which the supply valve from the preliminary decomposition tank is closed. In this manner it is possible to prevent the oil, suddenly rising in the drum space, from acting as a liquid brake on the separator drum and burning out the overloaded motor.

Während des Fahrens ist bei beiden Schälern der Ölstand im Schauglas der Anfallbehälter dauernd zu beobachten. Sollte der Stand im Schauglas plötzlich ansteigen, ein Zeichen dafür, dass die Produktpumpe nicht arbeitet, ist als erstes sofort der Schälermotor auszuschalten, dann erst das Zulaufventil vom Vorzersetzer zu schliessen. Hierdurch kann vermieden werden, dass das plötzlich im Trommelraum angestiegene Öl auf die Schälertrommel als Flüssigkeitsbremse wirkt und der Schälermotor durch Überlastung durchbrennt.

Obwohl zur Vermeidung des Durchbrennes des Motors in die Produktvorlage eine Stickstofftauchung eingebaut wurde, in der bei Anstieg von Flüssigkeit der Druck ansteigt und den Schälermotor ausschalten soll, sind die Schälerfahrer über die Wichtigkeit dieser dauernden Kontrolle des Standglases zu unterrichten.

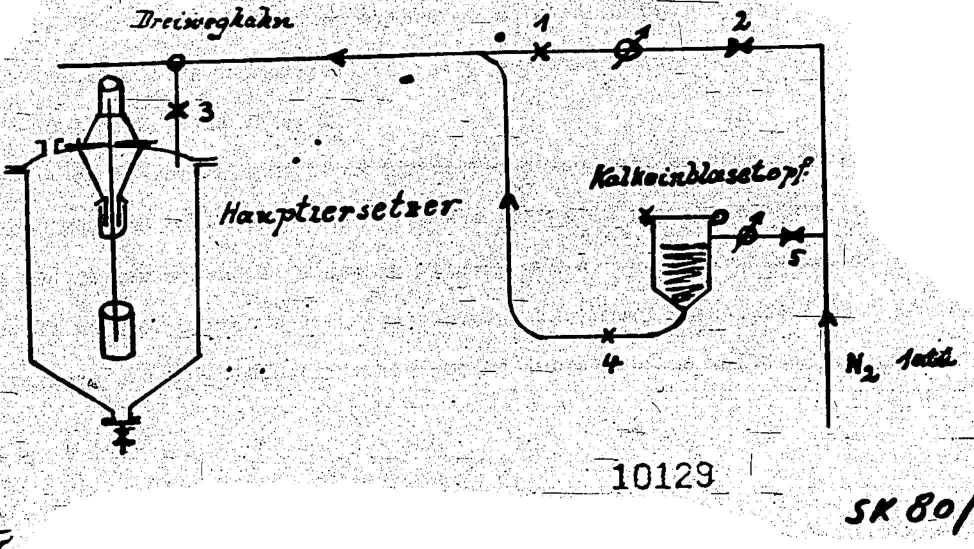
Das Schnüffeln hat langsam zu erfolgen, um eine saubere Trennung von Öl und Schlamm zu ermöglichen, ebenfalls danach das Schälen, um dabei zu hohe Stromaufnahme zu vermeiden. Auf keinen Fall darf ohne Anweisung die Feineinstellung an der Hydraulik von Schnüffelrohr und Schälermesser verstellt werden.

Zur Schmierung des Schälers ist zu beachten, daß im Ölkasten der Ölstand ausreicht, das Druckmanometer anzeigt, aber nicht über 0,1 atü steht und das Kühlwasser läuft.

Um ein einwandfreies Arbeiten der pneumatischen Kalkförderung bei der Hauptzersetzung zu gewährleisten, hat das Einblasen des Kalkhydratpulvers in folgender Weise zu erfolgen:

Zeichnung 54

Pneumatische Kalkförderung.



Although a nitrogen seal (in which the pressure increases when the liquid rises) is installed in the receiver to prevent the separator from burning out by shutting it off, the centrifuge operator should be advised of the importance of continuously controlling the gage glass.

The discharge must be slow in order to afford a clean separation of oil and sludge, likewise the subsequent centrifugal treatment in order to prevent excessive consumption of current. Under no circumstances should the adjustment of the hydraulic discharge pipe and the centrifuge meter be changed without instructions.

In lubricating the centrifuge it should be made certain that the oil level in the oil container is high enough, that the pressure manometer registers (but not above 0.1 atm) and that the cooling water is running.

To insure satisfactory operation of the pneumatic lime supply in the main decomposition step, the powdered hydrated lime must be blown over in the following manner:

p.92 1. The lime hopper is filled.

2. The valve 1 is opened, and valve 2 slowly until an excess pressure of 0.1 atm. is indicated in the line.

3. Valve 3 is opened. Nitrogen flows slowly into the main decomposition tank and thus prevents penetration of hydrocarbon vapors into the line.

4. Valve 4 is opened and a pressure of 1 atm. is kept on the hopper by means of valve 5 until the gas flows unhindered. 5 and 4 are then closed.

5. Valve 3 is closed, than valve 2.

The filter presses should be controlled continuously so that a pressure of 250 atm. is not exceeded on closing them with the hydraulic pump. In order to prevent straining the filter cloth the pressure release valves on the triple-action pumps should be set to blow off at 8 atm. In cleaning the press care should be taken to see that the packing faces (particularly the lower) are clean and rubbed with an oil-graphit composition before assembling. The original packing consisted of an 8 mm thick leather cord, but later 3 mm thick pasteboard was used which lasted a year. However, since this packing is now very defective and of poor quality, packing cords 8 mm thick of PC fabric or Perbunan are to be used in the future.

Double Igelit cloth is used as filter material in the decomposition presses. A fine, very closely woven PC cloth is first placed on the perforated plate and a coarse PC cloth on top thereof, strong enough not to tear when the cake is scraped off.

When the filtration slackens or when a cloudy filtrate is produced the cloths are removed and washed with hydrochloric acid and Tetra (CCl_4). Before using the cloths again, they are tested for thin spots or tears which are repaired. In this manner the cloths will stand as many as 30-50 washings.

The following procedure was found satisfactory for cleaning the PC cloths. The fouled cloths coming from the press are softened in water at 60°C over night. The cloths are then scraped on a table and brushed off with water. Finally the cloths are soaked 1/2 day in 3% hydrochloric acid, thus dissolving the lime in the pores of the fabric, and are then rinsed with water and allowed to drain. Oil still adhering to the cloths is washed off in Tetra, (CCl_4) whereupon the cloths are hung up to dry. Before reinstalling, the condition of the cloths is checked on a plate of glass illuminated from below: damaged spots are mended with an acetone solution of PC.

p.93 d. Protection Against Corrosion.

Initially, the corrosion in the decomposition units caused by hydrochloric acid vapors was very high, particularly in the condensation zones, such as the covers of the preliminary and main decomposition units and their exhaust gas lines. The usual protective measures against hydrochloric acid failed under the prevailing conditions; HCl-containing methanol, temperatures of 90-120° and the presence of low boiling aliphatic hydrocarbons

The following linings were tested in practice in 2 m^3 agitators:

1. A coating of the cover with "Asplit" and a top coating of "Höchst" cement SW 20 was not satisfactory, since the unit is run alternately cold and hot and the coating cracked, particularly along welded seams and at the edges.
2. The application of an elastic intermediate layer of Oppanol B 200 between the cover and the Asplit - Höchst cement caused the protective coating to rupture even after a few charges because of swelling of the Oppanol.
3. A hard rubber top coating of Para Hard 28 (natural rubber) peeled off from the cover in one day. After 8 days operation the rubber coating was entirely destroyed.
4. A 5 mm thick SPML hard rubber coat (natural rubber + 50% graphite) applied to the cover was found satisfactory for a 12 months' operating period. The rubber coating retained its full strength during this period of operation and suffered no substantial external damage from the hydrochloric acid-hydrocarbon vapors. Exposed pipe lines were also satisfactorily protected in this manner. The same rubber, although not completely vulcanized, was also used as packing material.
5. Since the above natural rubber could no longer be supplied, available Buna-type rubbers were used for the expansion of the decomposition plant. This material, however, was found to be entirely unsuitable, since it cracked and peeled off.

The following protective measures against corrosion are now in use:

A lining of acid-proof tile has been found satisfactory for many years as a lining in the liquid zone of the 5 and 10 m^3 agitators. The tongue and groove tiles are placed in two layers with alternating joints in a support of rubber and sealed with Höchst cement SWD 20.

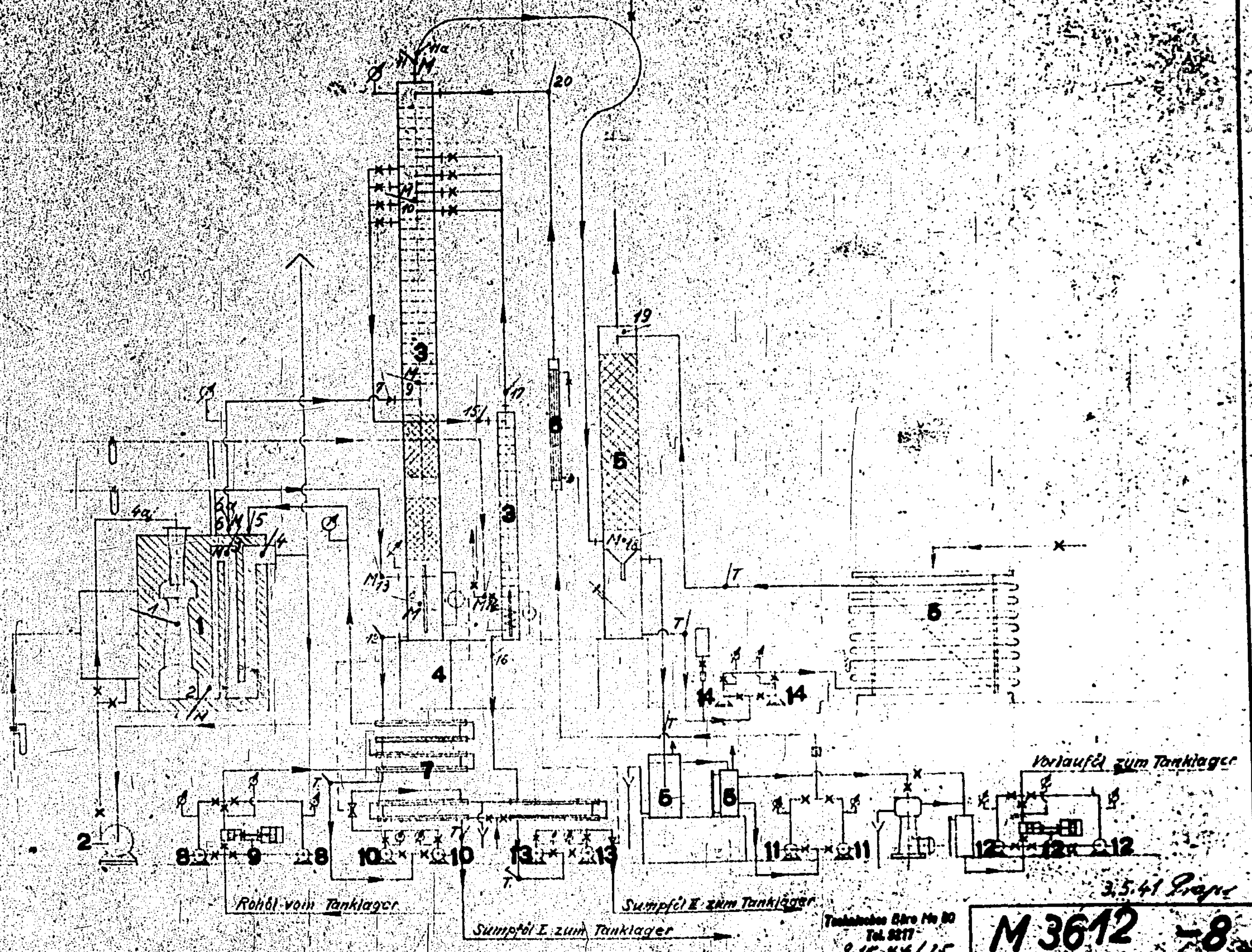
p.94 The cover and agitator are protected as follows:

Preliminary decomposition unit:	Cover:	"Neoresit" baked enamel and external insulation
	Shaft:	Baked enamel
Main decomposition unit:	Cover:	Brick-lined
	Cone:	Enamel or "Asplit"
	Shaft:	Unprotected
Immersion basket:		Rubber Coated
Cooler on main decomposition unit:		Igelit (Construction by Dr. Henning and Dipl. Eng. Gebauer, Leuna)
Gas washing towers:		Brick-lined

Igelit is the best material for all exposed lines and armatures at temperatures below 80°, and Igelit linings for cold vessels such as separating units, immersion equipment etc.

The following types of pumps are used:

For acid methanol	Porcelain pumps
For acid light overhead oil	Stoneware pumps, which are now being replaced by resistant ferro-silicon (Fesi) pumps.



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Technisches Büro Me 80
Tel. 3217
9.11.44/25

M 3612 -8

5. Mai 1941

Übetrieb Me 126a / Schema zur Destillation IV

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III Distillation

The attached drawing 55 (M 3612-8) and photograph 56 illustrate the Distillation Plant IV in Me 126a.

The crude oil pumped from the storage tanks by pumps 8 or 9 passes through the heat exchanger 7 and pipe still 1 to column 3. The furnace is built as a plain convection furnace with horizontally arranged tubes and is heated by an automatic burner. High local overheating of the tubes is prevented by rotary gas blowers 2. The column, 1,000 mm in diameter is equipped above the point of injection of the feed with 25 bubble cap trays and below this point with Raschig rings to facilitate cleaning.

p.96 The oil having the correct flash point is pumped from the bottom through heat exchanger 7, pump 10 and a cooler to a storage tank. From a tray of average height a higher boiling overhead fraction can be withdrawn and fed to a stripper 3 a, a secondary column of 500 mm diameter with 2 bell cap trays where it is blown with steam. The stripper is periodically connected in when this intermediate fraction, designated as V oil, has reached about 20-30% of the total light overhead used in the polymerization.

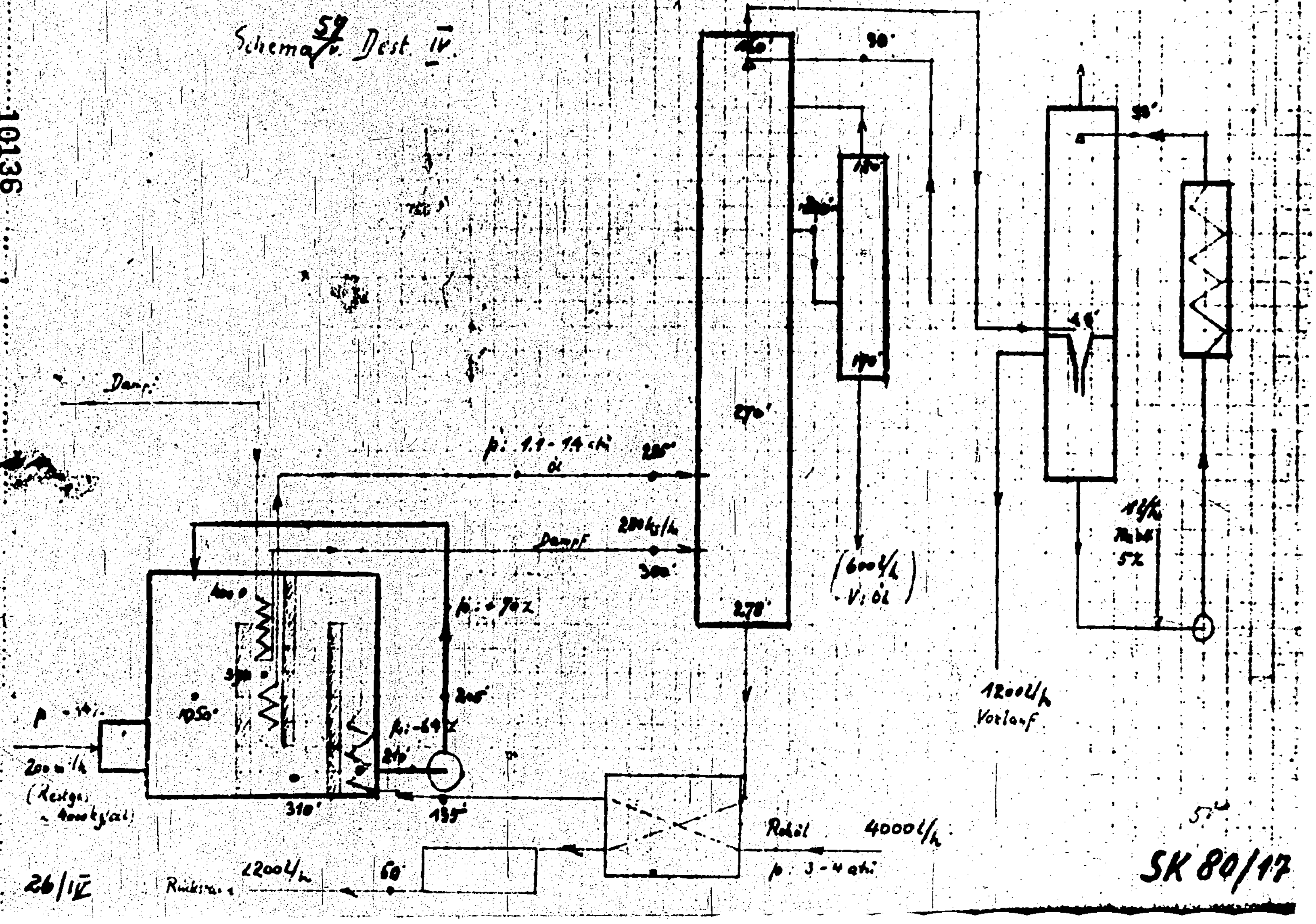
In this plant the SS oil, boiling above 330° or 300°, and having a viscosity of 6 E°/99 or 5 E°/99, respectively, is drawn-off from the crude polymerizate as a residual oil at the bottom of the column. The yield of bottoms is about 50-55%. In order to retain the desired flash point of above 225°, about 10% (referred to the crude product) of superheated steam is blown in at the bottom of the column. The remaining 45-50% of crude polymerizate is obtained as overhead. The small quantity of hydrochloric acid, produced from chlorine compounds still remaining in the filtered crude polymerizate and liberated during the steam distillation, causes heavy corrosion in the condensation zones.

Ammonia blown into the head of the column eliminated this corrosion but clogged the subsequent coolers due to precipitation of ammonium chloride, the elimination of which gave rise to new difficulties.

The condensation was therefore carried out in spray jet condenser 5 provided with weakly alkaline cooling water in the circulation system. The only thing to be considered is that the head of the column and the vapor line to the condenser must be exceptionally well insulated so that no condensation can take place in them. Condensation takes place first in the brick-lined jet condenser. Since this condenser normally operates in a slightly alkaline state, but may be slightly on the acid side through faulty operation, the bricks must be cemented with Asplit which is resistant under both conditions.

Condenser 5 operates as follows: The mixture of light overhead, oil vapor and steam flows into the injection cooler from the bottom up, being condensed by the cool circulating water flowing down in condenser 5a. The major portion of the upper part of the cooling tower is filled with Raschig rings, the lower portion is embodied as a separating unit. This lower portion of the tower, or the outflow line for the circulating water installed at the bottom, contains the electrode by means of which the pH can be controlled from the instrument panel. The alkalinity of the water is regulated by dropwise addition of the weakest possible NaOH solution, preferably not stronger than 5%, at the suction side of the water circulating p.97 pump 14. Through this line water alone is pumped from the lower portion of the separating unit of the cooling tower and returned through the condenser 5a to the head of the Raschig ring section. The total distillate from the column, including condensate from the injected steam, is fed to a separating unit 5b through a higher line running from the bottom of the cooling tower. In this unit the water is separated from the total distillate. In the subsequent equalizing unit 5c the lower efflux establishes a constant supply of reflux to the column which is supplied through the pump 11 and the preheater 6 to the head of the column. The overhead

Schema 57 v. Dest. IV.



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goes to the storage tanks through the upper outflow line through a closed Laval centrifuge 13 and is then returned to the polymerization units. Careful dehydration is absolutely necessary to render the overhead suitable for polymerization.

Diagram 57 gives operating data of the plant for a charge of 4,000 lit./hr.

With respect to the operation and construction of the Laval centrifuges, the following should be noted: (See Diagram 57a)

The drum is used for both methods of oil purification,

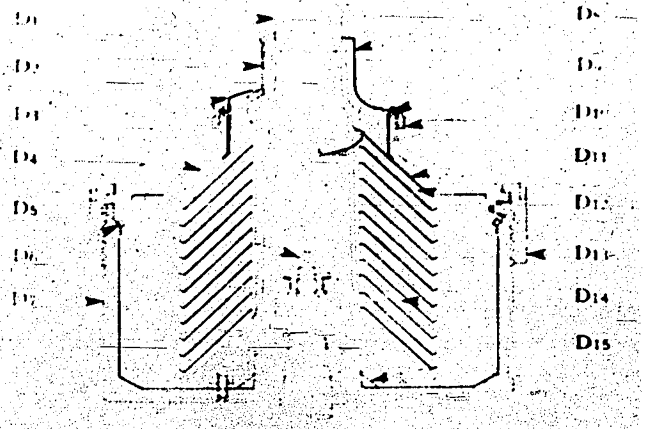
as purifier, for separating two liquids of different specific gravities (R-Oil and distillate).

as clarifier, for liquid refining, that is, for separating solid matter such as dirt and decolorizing clay and /or small amounts of liquid when this amount is not larger than can be accumulated in the sludge space of the drum.

The assembly of the drum when used for the two methods of separation is carried out as follows:

	Purifier	Clarifier
Upper plate	with neck	without neck
Regulating disc	without neck a)	with neck
Lower plate	with inlet ports	without inlet ports
water seal	yes b)	no

p.98 a) The purifier drum is adjusted for the separation of mixtures of different specific gravities by changing the diameter of the outlet for the heavier liquid. Regulating discs having internal diameters of varying sizes serve this purpose. The opening should decrease in proportion to the viscosity and density of the light liquid component, or an increase in feed rate.



für Purifikation angeordnet. für Klarifikation angeordnet.

Abb. 4.
Die Separatortrommel.

D1	Verteiler
D2	Oberteller mit Hals (nur für Purifikation)
D3	Regulierscheibe ohne Hals (nur für Purifikation)
D4	Trommeldeckel
D5	Kapselmutter
D6	Großer Gummiring
D7	Trommelkörper
D8	Regulierscheibe mit Hals (nur für Klarifikation)
D9	Kleiner Gummiring
D10	Kleiner Verschlußring
D11	Oberer Zwischenteller (nur für Klarifikation)
D12	Ergänzungsteller (nur für Klarifikation)
D13	Großer Verschlußring
D14	Zwischenteller
D15	Siebring

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b) In starting the machine the drum must be filled with the heavier liquid (usually water). The liquid is introduced into the separator (in the closed type after removal of the threaded bolt closing the filling opening) until it flows by the look box. In this manner a liquid seal is formed in the drum which prevents the lighter components from escaping with the heavier component through the water outlet.

In assembling the centrifuge care should te taken that the plates are assembled in the correct order (No. 1 below) and that the closing rings which are provided with left hand threads are set so that the markings register.

Crude Product	Initial b. p.	100°
	to 330° about	45%
	d_{20}:	0.820
	Mol. wt.	400

	Overhead Distillate	V 120	SS oil as residue
Boiling range	130 - 250°	250 - 330°	330°
d_{20}	0.778	0.815	0.850-55
Mol. wt.	155	238	800

The most important temperature to be observed in the SS oil distillation is the fuel gas temperature ahead of the oil tubes, which must not substantially exceed 400°, in order to prevent damage to the oil.

The following operating notes are worthy of mention.

When a cold furnace is to be heated the temperature must of course be raised very slowly (1-2 days) to prevent cracks in the furnace masonry.

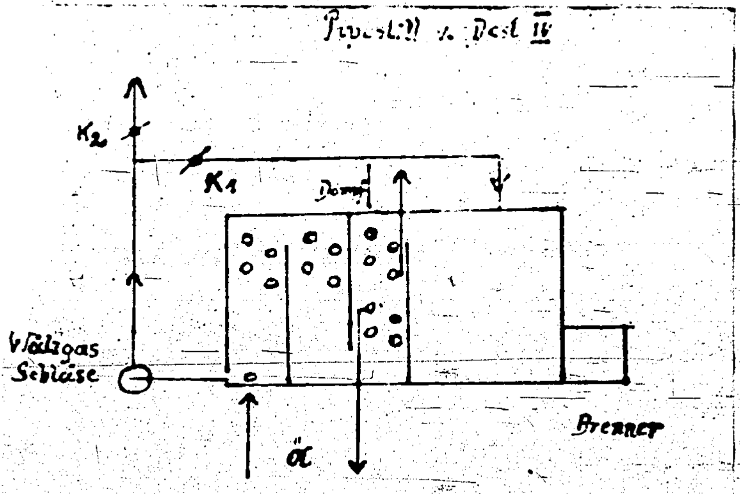
Lighting of the Furnace:

Only in the presence of the foreman. Before lighting, the furnace should be flushed with air for 15 minutes. With a rotary gas-blower the operation is as follows:

Soll der kalte Ofen angeheizt werden, hat die Temperaturerhöhung selbstverständlich sehr langsam zu erfolgen (1-2 Tage), um Rißbildung im Ofenmauerwerk zu vermeiden.

Zünden des Ofens: nur in Gegenwart des Meisters. Vor jedem Zünden ist der Ofen 15 Min. mit Luft zu spülen. Bei Vorhandensein eines Wälzgasgebläses geschieht das folgendermaßen:

Skizze 58



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1.) Wälzgasgebläse einschalten
2.) Umgangsklappe K_1 schliessen.

Nach dem Spülen wird K_1 geöffnet und K_2 so stark gedrosselt, dass am Brennermanometer ein Unterdruck von höchstens 40 m/m herrscht. Jetzt erst wird die Lunte eingeführt und langsam das Gasventil geöffnet. Hat der Brenner gezündet, werden K_1 und K_2 auf die ermittelte Normalstellung gebracht.

Plötzliches Abstellen der Anlage:

1.)
Gas so weit als möglich zurückfahren (Ölausgang bis 150°) oder ganz schließen.
2.)
Rückstand auf Kreislauf stellen
3.)
Falls Stand in Kolonne verschwindet, mit Durchsatzpumpe Rohprodukt nachfahren bis Sumpf wieder erscheint.

After flushing, K_1 is opened and K_2 throttled down so that a vacuum of 40 mm, at the most, registers on the burner manometer. The torch is then introduced and the gas valve slowly opened. When the burner is lighted, K_1 and K_2 are brought to their normal positions.

Quick Shutdown of the Plant

1. Shut off the gas as much as possible (oil outlet at 150°) or close entirely.
2. Recycle residue.
3. Should the level drop in the column, crude product is to be added by the feed pump until the sump (bottoms) appears again.

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Shutdown of Electric Current

1. Shut off gas
2. Connect duplex pump to residue
3. Recycle residue
4. Connect duplex pump to distillate
5. Shut off all valves of disconnected pumps, centrifuges and blower.

A sudden rise in pressure ahead of the furnace may be caused by water or methanol in the crude product evaporating suddenly in the pipe coil, as may happen when switching to a fresh tank. Switch over to the next tank and run off the bottoms.

The differential pressure recorder shows a sudden rise in pressure: should the temperature of the individual plates drop successively from the bottom up, this is a sign that the column fills too slowly.

Possible Causes:
1. Failure of the residue pump.
2. The GST bottoms level regulator does not open.
3. The residue cooler operates too cold.
4. The bottoms inlet of the heat exchanger may be clogged.

The pressure rise of the recorder may also be caused by clogging or freezing of one of the lines to the recorder.

Electrode: The dropwise addition of caustic to the suction line to the water circulating pump must be regulated so that the MV-recorder does not drop below $P_H 7$ (27 V), as this would cause the circulating cooling water to become acid and corrosive. Operation above 30 MV should also be avoided since with very alkaline water the separating unit fails because of emulsification difficulties. It is advisable not to use alkali of more than 5% concentration.

Hydrocarbon vapor blow off at the head of the jet condenser: the water circulation pump does not operate or the water circulation is only partial. Add condenser water.

By the correct selection of distillation conditions it is to some extent possible to compensate, within certain limits, for viscosity fluctuations in the SS oil resulting from variations or irregularities in gas, catalyst and operating conditions.

p.101 In order to determine the effect of distillation on V.I., solidification point and flash point, polymerized SS oils were distilled to a variable extent and the data on the resulting residual oils obtained. The first two Tables include low polymer oils used principally as cold-starting oils of low viscosity. (See Table 59).

IV. Refining

p.102 The SS-oils were originally refined with "Tonsil AC" from the Bavarian Bleaching Clay Plant and then with "A-Special" from Moosbierbaum. The bleaching takes place at temperatures above 90°. When very viscous oils are treated, such as SS 906, a temperature in excess of 120° must be used to speed up the filtration. The darker SS 903 requires about 3-5% bleaching clay, for SS 906 0.7-1.0% is sufficient. An addition of 10% hydrated lime is used to neutralize the slightly acid clay.

The bleaching material is charged pneumatically by means of nitrogen from a hopper having a conical bottom; the special precautions required for blowing hydrated lime into the main decomposition unit are not necessary in this case since the refining agitators operate at atmospheric pressure and no vapors of lower boiling hydrocarbons are evolved. In order to minimize dust, the very finely powdered bleaching clay is not blown in until the agitator has been completely filled with oil; the inlet pipe is kept submerged in oil.

Refining is complete after 30 minutes agitation. The bleaching clay is filtered in frame extraction presses. Since there are no low boiling products to vaporize, presses with open outlets at each filter unit have been found of advantage. In this manner the slightest leak is immediately discovered through the black color of the filtrate; thus defective units are at once detected, which is often very difficult and time-consuming when working with the closed presses used in the decomposition treatment. Another advantage of the open-type press is that the filtration process need not be stopped before all the units are full when a cloudy filtrate is obtained through some slight damage to the filter cloth. By switching the cloudy filtrate from the respective unit to the agitator, the remaining units may be kept in operation until they are full, which is necessary for the subsequent extraction.

PC-fabric can not be used as filter cloth because of the high temperatures that are required; moreover this is not necessary since the oil is neutral. All kinds of fabrics of cotton, cotton-cellulose wool mixture and 100% cellulose wool that are not too thin have been found satisfactory. The strength of the cloth is sufficient even at the high filtration temperature of 120° required for SS 906. A set of filter cloths for a 1000 0 press with 24 units (= about 50 m filter cloth) is good for a throughput of 1000 m^3 oil.

p.103 When the press shows 8 atm. gage pressure, the units are normally filled and the cross-flushing of the cakes with light distillate oil and the blowing with nitrogen can begin. In this washing process it has been found of advantage to limit the permissible moisture content of the bleaching clay to about 8%. Access of moisture during the storage of the bleaching clay is particularly to be avoided.

Table 59

Dist. in Vacuo to 150°		Wt. %	$^{\circ}E_{99}$	V.I.	Flash pt.	Solid. pt.
$2.4^{\circ}E_{99}$	110°	65.8	1.77	132.0	148	-53
	120°	64.8	1.84	130.8	158	-51
	130°	62.0	1.94	126.8	169	-48
	140°	59.0	2.08	123.7	176	-45
	150°	54.5	2.41	119.4	184	-41
$4.4^{\circ}E_{99}$	110°	77.0	2.42	128.5	160	-50
	120°	70.0	3.12	120.5	173	-48
	130°	67.4	3.52	117.8	190	-46
	140°	66.0	3.57	116.8	195	-45
	150°	62.0	4.43	114.6	210	-40
$5.8^{\circ}E_{99}$	110°	74.5	2.21	124.0	154	-56
	120°	71.2	2.39	118.2	170	-52
	130°	62.2	4.04	108.8	190	-41
	140°	56.6	4.75	107.5	208	-36
	150°	54.4	5.66	106.2	214	-34
$6.5^{\circ}E_{99}$	110°	73.2	3.97	115.0	195	-39
	120°	69.3	4.53	113.0	205	-35
	130°	66.2	5.31	110.0	213	-31
	140°	64.5	5.75	109.0	233	-32
	150°	62.8	6.52	108.0	247	-23
	160°	61.2	7.17	108.0	246	-27
	170°	59.7	7.49	108.0	254	-28

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V. Processing of Residual Oil

In the section relating to the treatment of the crude polymerizate the processing of the oily $AlCl_3$ sludge was described (on page ___ .) The resulting crude residual oil has the following properties:

d_{20}	0.8510
Vis. at 38°	125.3 E°
99°	5.39
V. I.	80.2
Flash point	185
Solid. point	- 23
Coke test	0.63
Acid No.	0.1
Sap. No.	0.17
Iodine No. (Hanus)	122
Aniline point	82

Owing to its high iodine number it was first attempted to hydrogenate the R-oil over the solid catalyst 3076 at 10-18 MV. It was found that the catalyst was very quickly exhausted. An increase in the hydrogenation temperature did not prolong the life of the catalyst. The used catalyst was partly crumbled and partly coated with coke.

The refining of this residual oil by hydrogenation was therefore given up and a treatment with aluminum chloride was adopted. (Application O. Z. 13,649). For this purpose the anhydrous neutral R-oil is heated with 5-7.5% aluminum chloride, with agitation, for about 3 hrs. at 120-150°. The aluminum chloride goes into solution again forming an $AlCl_3$-hydrocarbon complex, which is separated, after agitation is complete, by settling and decantation. The oil which is still acid is neutralized with lime and methanol, filtered and then distilled to the desired flash point.

If the purified oil, freed from aluminum chloride sludge, is neutralized with lime alone instead of with lime and methanol, its properties are better, as is shown in Table 60 on the following page.

p.105

Table 60

Neutralization with and without Methanol

Date	Exp. No.		Conradson Test	Iodine No.
6- -42	52	I	0.188	16.5
		II	0.216	17.1
		IV	0.237	17.4
8-11-42	53	I	0.157	16.6
		II	0.200	27.5
		IV	0.234	24.2
8-12-42	54	I	0.242	27.3
		II	0.285	30.0
		III	0.218	26.4
8- -42	55	I	0.169	15.3
		II	0.204	15.7
		III	0.180	15.2
8-18-42	56	I	0.180	15.3
		II	0.215	16.2
		III	0.175	15.6

I. Plant sample of acid oil, in lab. + lime.

II. Plant sample of acid oil, in lab. + methanol + lime.

III. Plant sample of acid oil, in plant + lime

IV. Plant sample of acid oil, in plant + methanol + lime.

On distillation of the treated R-oil an overhead is obtained in which, as shown in Table 61, the unsaturation increases with increasing boiling point of the individual fractions.

Table 61

Iodine Number of R-oil Overhead

Fraction to	160	2.28
	180	4.80
(at 0.1 mm)	190	5.25
	200	5.98
	210	7.32
	220	9.70
	240	12.55
	250	15.05
Average of Sample		6.53

This overhead can be used, in combination with normal overhead from the SS-oil polymerization, in the polymerization process.

From 100 parts crude R-oil there is obtained 60 parts refined R-oil and about 27 parts R-oil overhead. In addition there is obtained 5 parts of a so-called R^R-oil from the $AlCl_3$ sludge resulting from the R-oil treatment, by decomposition with hot water.

The refined R-oil has the following properties:

d_{20}		0.8457
Vis.	38°	60.4
	99°	4.33
V.I.		106.3
Flash point		194°
Solid. point		-39°
Coke Test		0.12
Acid. No.		0
Sap. No.		0.18
Iodine No.		32
Aniline point		157

This oil is used for manufacturing a cold-resistant car journal oil for the German Railroads.

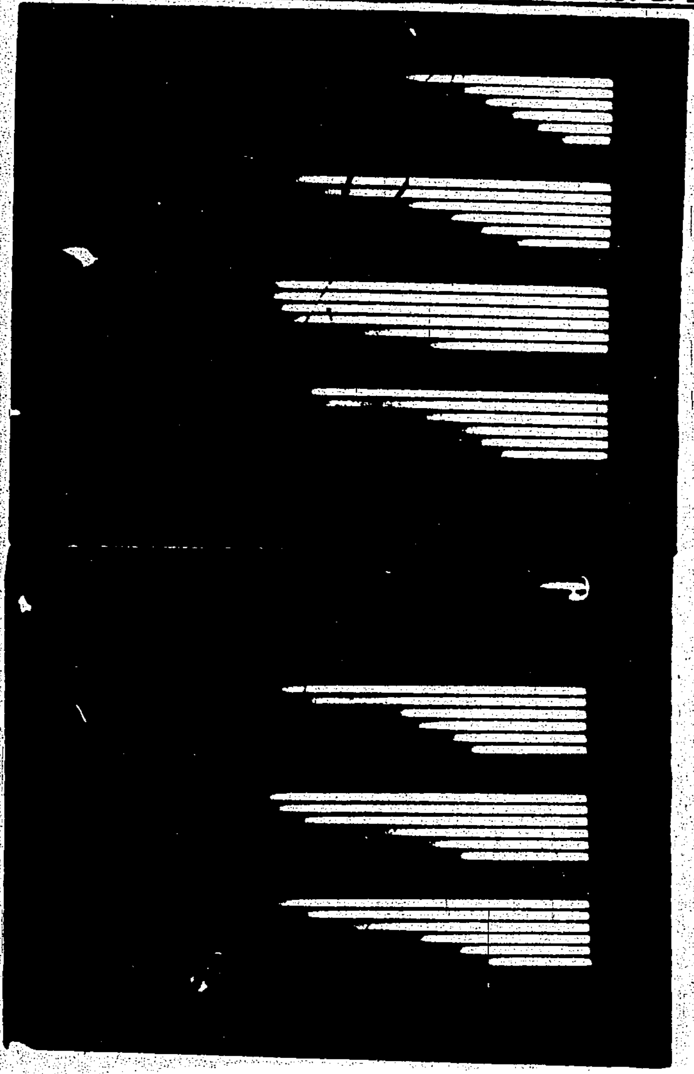
The oily aluminum chloride sludge resulting from the $AlCl_3$ treatment of the R-oil consists of 65 parts oil and 35 parts $AlCl_3$. This sludge does not react with cold water but is violently decomposed by hot water. In this manner a black very viscous oil is obtained having the following properties.

d_{20}		0.960
Vis.	80°	2622.0 E°
	99°	26.4 E°
V.I.		67
Flash point		1.88
Solid. point		-10
Coke test		5.68
Acid No.		3.58
Sap. No.		8.06
Iodine (Hanus)		137
Aniline point		60 - 63

p.107 This oil can be hydrogenated with the catalyst 3390 at 17 MV. There is some cracking and a water-white oil of faint blue fluorescence is obtained in a yield

Tabelle 62

ektralanalytische Untersuchung der Öle auf Gehalt an Aromaten und durch Ultraviolett-Absorption.



	% Lichtdurchlässigkeit zwischen 2.500 u. 2.800
R-Öl roh	5,8
R-Öl hydriert mit 3096 im Ölbetrieb Me 126a	27,5
R-Öl hydriert mit 5390 bei Dr. Becker (Hydrierung)	68,0
R-Öl mit $AlCl_3$ gereinigt im Ölbetrieb Me 126	29,7
RR-Öl roh	5,0
RR-Öl hydriert mit 5390 bei Dr. Wiedemann	40,5
SS-Öl (Ofen VIII/41)	38,0
SS-Öl (Ofen VIII/42)	47,5

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of 68%, having the following properties.

d_{20}	0.881
Vis. at 38°C	15.58
99°C	1.816
V.I.	51
Flash point	163
Solid. point	-35
Coke test	4.55
Acid No.	0
Sap. No.	0
Iodine No.	137
Aniline point	143

In comparison with the raw material it will be seen that the viscosity has dropped considerably, that the V.I. is still poorer, the coke test very high while the Iodine number (Hanus) remains practically constant. It should be noted that the solidification point has dropped from -1 to -35°. The most important fact is that the coke-forming constituents of the RR-oil are not removed by hydrogenation. The attached Table 62 shows that the RR-oil, in comparison with the R-oil, is characterized by a high content of aromatic hydrocarbons. The latter are responsible for the high coke value.

The high iodine number of the RR-oil prompted us to have this product tested in our Lacquer Laboratory by Dr. Heidinger as a drying oil. With his assistance it was possible to prepare lacquers which, depending upon the solvent, gave glossy, dust-dry coatings in one half to 12 hours (O.Z. 13,650) from which it may be concluded that the RR-oil might find application as a drying oil. However, the observation that drying is not markedly affected by driers, and the fact that the dry lacquer is soluble in the same solvents in which it was originally dissolved makes it appear that in this case the drying process is not the same as that with vegetable drying oils, i. e. absorption of oxygen with resulting increase in molecular weight and setting to a film, but is due to a bituminous product contained in the RR-oil. For example, if 2% cobalt-lead and manganese Soligen drier is added to the

RR-oil and the latter blown with air for 2 days at 20°, not even a trace of oxygen is absorbed, as is shown by the following elementary analysis:

p.108

	RR-oil Untreated	RR-oil blown with air for 48 hours
Carbon	87.60	87.10
Hydrogen	10.89	10.72
Oxygen	1.25	1.23

The bituminous character of the RR-oil is also brought out by the fact that it may be boiled with Vinoflex to very glossy, dense lacquers, an effect which is characteristic of normal bitumens.

The RR-oil was registered and accepted by the Lacquer Commission under the name "Karboresin R". It serves as a priming-coat for wood and masonry.

The RR-oil is also usable as a plasticizer in Buna processing, as was found by tests in the Rubber Laboratory of the Schkopau Works. The RR-oil can also be processed with mineral fillers, such as ground shale, to a mass which, when applied to rough cement floors, produces a surface resembling linoleum. This coating is in itself not sufficiently resistant to pressure but becomes very hard when coated with a hard emulsion-type lacquer.

p.109

VI. Experiments Relating to the Treatment of Finished SS-oils.

a.) Effect of Hydrogenation on the Properties of the Oils

We wished to establish whether a favorable change in the stability of the oil or in its cold test might be obtained by subsequent hydrogenation of the finished SS-oil. From the large number of experiments which were conducted at various temperatures and different charges over catalyst 3390 3076 (Dr. Wiedemann Me 13a), only a characteristic series of tests is reported, as follows:

Hydrogenated with Cat. 3090 at 150 atm. H_2 and MV.	not hydrogenated.	5 MV	6 MV	7 MV	8 MV	9 MV	10 MV
Density at 20°	0.848	0.848	0.846	0.846	0.847	0.847	0.847
Vis. at + 99° C	2.95	2.92	2.94	2.96	2.96	2.95	2.99
+ 50° "	14.6	14.3	14.3	14.4	14.5	14.4	14.5
+ 38° C	26.2	25.3	25.3	25.7	25.8	25.8	26.0
+ 20 "	77.3	73.5	74.1	74.5	77.3	75.0	75.5
0 "	354	377		359			362
-10 "	841	1448		1344			1495
-15 "	1476	3375		2930			3430
-20 "	2690	12580		10690			10600
-25 "	5180	not measurable		20490			not measurable
V. I.	121.7	122.6	122.6	122.8	122.5	122.1	123.3
Solid. point	-39°	-16°	-17°	-19°	-15°	-17	-16°
Flash point	169°	174°	178°	190°	185°	184°	188°
Iodine No.	5.21	1.77	1.40	1.04	0.74	0.39	0.0
Conradson test	0.114	0.038	0.034	0.036	0.030	0.028	0.024

The hydrogenation conducted at 5 and 6 MV still gave products that were slightly yellow; the oils were colorless starting at 7 MV. Complete saturation was obtained under the above operating conditions at 10 MV. The cold test of the hydrogenated oil, however, is of interest. In continuous operation the solidification point decreases markedly at 8 MV, but in the above operation in autoclaves it decreases from -39° to -16° at 5 MV while the viscosity at -20° increases, for example from 2700 E° to 11000-12000 E°

p.110 The very pronounced deterioration of the cold test of the SS-oils caused us to give up further experiments in this direction.

In this connection the possible improvement of the solidification point and th cold resistance by an addition of Paraflow should be mentioned.

1.)
By adding Paraflow to the product hydrogenated at 10 MV shown in the last Table the viscosity at low temperatures may be improved as follows:

SS 903 of 2.99 E°/99 hydrogenated at 10 MV

°C	Without Paraflow	+ 0.05% Paraflow
0°	362	340
- 10°	1435	952
- 15°	3430	1163
- 20°	10600	3190
- 25°	not measurable	6960
- 30°		16800

2.)

SS 903 hydrogenated without addition of Paraflow	Solid. pt.	-20°
+ 0.02 % Paraflow	" "	-27°
+ 0.04 % "	" "	-30°
+ 0.06 % "	" "	-35°
+ 0.08 % "	" "	-35°
+ 0.10 % "	" "	-34°

3.)

Effect of the Pour Point Depressant Paraflow on Synthetic Oil SS 902 (F 25)

Paraflow added % wt.	Solid. pt. °C	Vis. E°/-30°.
0	- 39°	10950
0.01	- 40°	9749
0.02	- 45°	6296
0.05	- 47°	4912
0.075	- 47°	4702
0.10	- 47°	4250

p.111 4.)

Effect of Oppanol and Paraflow on Synthetic Oil SS 902

Oppanol added % wt.	Paraflow added % wt.	Solid. pt.	Viscosity in E° + 99°	Viscosity in E° -30°
0	0	- 39	2.18	4940
0.5	0	- 49°	2.42	6160
0.5	0.05	- 51°	2.42	4560

b. Modification of the Oils by Subsequent Polymerization

In order to improve the properties of SS-oils, in particular to increase their thermal resistance and limit their thickening, the resulting crude polymerizates should be subjected before their release from the autoclaves to subsequent heating in the presence of the still reactive addition compound.

The first experiments of this nature were conducted in a 1000 liter autoclave in February, 1938. After completing the normal polymerization at 110°, the entire contents of the autoclave were stirred for a few hours at 130 or 140° under the remaining pressure, without addition of more gas. The $AlCl_3$-addition compound (about 14% referred to the finished oil) contained in the crude polymerizate should then act as a condensation agent. A few of the experiments are shown in the following Table. Inasmuch as no changes could be detected analytically in the oils, the products were not subjected to engine tests.

p.112 Table 63

No.	Additional heating		E°/99	V.I.	Solid. pt.	Flash pt.	
	Hrs.	°C					
N 254	0	-	4.14	116.1	- 36	201	without additional heating
	1	130°	4.05	116.6	- 36	195	
	2	130°	4.15	115.8	- 36	201	
N 257	0	-	4.23	118.1	- 37	207	without additional heating
	2	120	4.52	118.4	- 37	197	
	3	120	4.27	116.1	- 36	201	
	4	120	4.70	117.1	- 34	205	
S 254	0	140°	4.54	114.7	- 33	207	
	3	140°	4.29	113.3	- 36	212	
	4	140°	4.07	113.4	- 35	210	

An after-polymerization was conducted later in the same manner in a 4500 liter N_6 autoclave at a higher operating temperature and with longer agitation. The SS-oils thus obtained were tested for stability to oxidation. The oxidation conditions were as follows: 255 g SS-oil were treated at 170° for 200 hours with 10 liters of air per hour. (I/1271).

Table 64

After-polymerization	Oxidation	$E^o/99$	SS-oil Analyses					
			V.I.	Solid. pt.	Flash pt.	Acid. No.	Sap. No.	Carbon
Sample after completed polymerization without additional heating	Untreated	4.55	108.6	-34	218°	0.0	0.0	0.026
	Oxidized 200 hrs.	8.37	103.2	-27	213	7.73	20.61	0.832
4 hrs. additional heating at 155o	Untreated	5.52	108.3	-33	221	0.0	0.0	0.030
	Oxidized 200 hrs.	10.15	101.0	-25	198	7.06	19.38	0.817
10 hrs. additional heating at 155°	Untreated	4.49	108.5	-35	214	0.0	0.0	0.022
	Oxidized 200 hrs.	8.92	96.3	-24	208	7.06	22.18	0.677

p.113 Although the after-polymerization was extended beyond ten hours, no favorable effect on the thickening was noted. A slight improvement in the coke test after oxidation was observed as the additional heating was prolonged. The experiments are to be continued at a still higher after-polymerization temperature and the resulting products will eventually be subjected to engine tests for stability.

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VII. Summary of Production in Leuna 1938-1943

The following table gives a summary of the oil yields from 100 parts of ethylene by weight, in the various autoclaves.

Table 65

	45 lit.		1000 lit.		4500 lit.	
SS Oil	78.4%		77.2%		76.0%	
Light Distillate	10.3%	93.7%	8.6%	91.4%	7.7%	91.0%
Residual Oil	5.0%		5.6%		7.3%	
Unconverted Gas	2.3%		3.2%		2.7%	
Operating Loss	3.7%		5.4%		6.3%	

The figures for the 45 liter autoclave are taken from an experiment made in 1936 in Op 140. The figures for the 1000 liter autoclave are taken from a number of completed batches, the balance for the 4500 liter autoclave representing monthly averages.

Table 66 gives a summary of the improvements in yield and consumption of material and power attained in the years 1938 to 1942. The decrease of the total yield to 83% in 1942 must be attributed in the first place to a temporary switch to the production of SS 903 in that year and the resulting working difficulties, and in the second place to fluctuations in the quality of the supplied gas.

With respect to the power consumption figures per ton of SS 906 oil it should be noted that the data also cover experimental work in the Technical Division Me 96.

Tables 67a, b, and c give a true picture of the treatment of the polymerizate from the 1000 liter and 4500 liter autoclaves.

Tables 68a and b show the quantity and quality of oils supplied to "Wifo". It will be seen that up to 1942 no tank car was shipped with a V.I. below 107.

In 1942 for the first time 2.6% had to be shipped with a V.I. of 106 (according to RLM specifications 107 is the minimum required). In the first half of 1943 it became necessary to release two tank cars (=0.7%) with a V.I. of 106. The bulk of shipments during all three years had a V.I. of 108-110, but values in excess of p. 115 110 were also attained. The goal for further research ~~work~~ must be to bring the bulk of production to an average V.I. of 112, or higher. This goal can be reached, in the first place by perfecting the gas purification and, in the second place by improving the aluminum chloride catalyst.

VIII. Summary of Specifications for the Various Products of the SS Oil Manufacture.

1. The main product was SS 906 oil. The technical specifications of the RLM are as follows:

Appearance	The lubricating oil must be clear, free from undissolved water and mineral acids and should contain no foreign solid matter.
Density at 20°C	below 0.862
Visc. at + 50°	334-350 cst. = 44-46 E°
+ 100°	at least 42.3 cst. = 5.63 E°
Viscosity Index	above 107
Bearing Constant "m"	below 3.05
Pole height Vp	below 1.73
Solidification point	below -25°C
Flash point	above 225°
Fire point	above 263°
Neutralization number (mg KOH/g)	below 0.06
Saponification number (mg KOH/g)	below 0.30
Vaporization test, Noack's method at 250° % by wt.	below 8
Conradson test "	below 0.2
Ash Content "	0
Hard Asphalt "	0
Water Content "	0

For use in aircraft engines SS 906 oil is blended with an equal weight of a mineral oil component which should have the following properties:

Density at 20°	below 0.897
Viscosity at +50o	51-60 cst. = 6.8-7.9 E°
" " +100°	at least 9.35 cst = 1.77 E°
p. 116 Viscosity index	at least 88
Bearing constant "m"	max. 3.66
Pole height	" 2.08
Solidification point	" -15°
Flash point	min. + 225°
Fire point	" + 258°
Neutralization number, (mg KOH/g)	max. 0.06
Saponification number, (mg KOH/g)	" 0.17
Vaporization test, Noack	at 250°C % by wt. max. 14
Conradson test, % by wt.	max. 0.25
Ash content	0
Hard Asphalt	0
Water	0

The finished blend (about 50 parts by wt. of 906 + about 50 parts by wt. of mineral oil + 0.2 % by wt. of inhibitor) should satisfy the following requirements;

Density at + 20°	max. 0.895
Viscosity + 50°	125-143 cst.
" + 100°	min. 19.0 cst. = 2.75 E°
" Index	" 98
Bearing constant	max. 3.35
Pole height	" 1.85
Solidification point	" -20°
Flash point	min. + 225°
Fire point	" + 225°
Neutralization No., mg KOH/g	max. 0.06
Saponification No., mg KOH/g	" 0.2
Vaporization test, Noack	at 250° C, % by wt.
Conradson test	max. 0.25
Ash content	c 0
Asphalt content	0
Water content	0

2. In addition to the oil of 6 E°/100, an SS 903 oil of 3 E°/100 was manufactured.

This oil should satisfy the following requirements:

p. 117

Density at + 20°	below 0.860
Viscosity at + 50°	106-114 cst. = 14-15 E°
" " + 100°	max. 21 cst. = 3 E°
" Index	min. 115
Bearing constant	max. 3.20
Pole height	" 1.60
Solidification point	" -35°
Flash point	min. 200°
Conradson test	0.20

This SS 903 oil is not directly used as a lubricant but is first blended with esters in order to produce the following oils:

Air Torpedo Oil:	LTK 12
Lubricant for LT Equipment	VS 1
Breaking-in and cold-starting oil	SS 1600

The compositions and specifications for these oils are:

a) For LTK 12: Composition:	40 parts SS 903
	57 " Ester 515
	3 " KSE

Density at + 20°	below 0.910
Viscosity at + 20°	87-95 cst. = 11.5-12.5 E°
" " + 100°	min. 6.25 cst. = 1.50 E°
Solidification point	below -50°
Flash point	above + 180°
Neutralization No., mg KOH/g	below 0.20

b) For VS 1: Composition:	25 parts SS 903
	72 " Ester 515
	3 " KSE

Density at + 20°	below 0.910
Visc. at + 50°	16.7-18.5 cst. = 2.5-2.7 E°
" " + 100°	min. 5.1 cst. = 1.4 E°
Solidification point	" -60°
Flash point	above + 180°
Neutralization No., mg KOH/g	below 0.20

p.118 c) SS 1600: Composition: 45 parts 903
55 " Ester 515

Mesulfol and KSE are added to 100 parts of this blend, but the quantities have not yet been established.

Density at + 20°	below 0.900
Visc. at + 50°	23.8 - 27 cst. = 3.3-3.7 E°
" " + 100°	min. 6.25 cst. = 1.50 E°
" " -30°	not above 7600 cst. = 1000 E°
Solidification point	below -55°
Flash point	above 200°
Neutralization No., mg KOH/g	below 0.20

For the further development of the three types of oil listed under 2a, b, and c the goal set for SS 903 polymerization should be: to increase the V.I. above 120, with a solidification point below -35° and a flash point above + 200°. The viscosity at 99° should be between 2.5 and 3.0 E°.

3. The higher boiling constituents are distilled from the total overhead distillate of the crude SS polymerizate. These constituents have a very good cold test and are still liquid below - 70°. They are disignated as V-oils followed by an index denoting flash point. These V-oils are used as blending components for the manufacture of the following oils:

a) Liquid Hydraulic Oil (Fl.-Drückol) Do 2000
b) Ordnance Oil, Blue 44
c) Ice Machine Oils SV-Oils

The composition and specifications for these oils are.

a) Do 2000: Composition
73 parts V 120
25 parts Ester 455
2 " KSE
0.006 " Fluorol 5 G
and 10 g phenolphthalein
per ton of Do 2000

p.119	Density at + 20°	below 0.850
	Visc. at + 20°	above 9.1 cst. = 1.75 E°
	" " - 60°	below 4940 cst. = 650 E°
	Solidification point	" -70°
	Flash point	above + 120°
	Vaporization test, Noack	at 20°, below 12% by wt.
	Swelling with liq. material	5383.7) ± 0 to 2 vol. % after 24 hrs. at + 80° C
	" " " "	5344.7)
	Neutralization No., mgKOH/g	below 0.2
	Saponification No., "	above 30

To satisfy these requirements V 120 must have the following properties:

Density at + 20°	0.816
Visc. at -60°	330 E°
" " + 20°	1.71 E°
Solidification point	below -70°
Flash point	above 120°

b) Ordnance Oil, Blue 44: Composition:

	45 parts	SV 20
	45 "	455 Ester
3 pts. S =	10 "	Mesulfol II
	0.05 "	Sudan blue

SV 20 and VK 20 are blends of V 120 with SS 906. Tables 69a, b, and c show the properties of blends of SS 906 with V 120, and V 140, respectively.

Density at + 20°C	below 0.895
Vis. at + 00°C	not below 10.8 cst. = 1.9 E°
" " -60° C	not above 7600 cst. = 1000 E°
Flash point	above 125°
Vaporization test, Noack	at 120°, max. 7.5%
Sulfur Content	min. 3% by wt.
Neutralization No. mgKOH/g	below 0.3

Firing Rate with MG 17:	at least 1150/min. for 2 m belt
" " " " 81:	" " 1500/min. " 4 m "

Table 69a

Blends of SS 906 + V 120

p. 119 a

Blend		Viscosity					Fl.pt.	Solid.pt.
SS 906	V 120	20°	38°	50°	99°	V.I.		
100 g	-	332.9	91.3	45.1	6.01	110.8	235°	- 34°
97.5	2.5	266.8	75.8	37.5	5.28	110.8	194	- 32
95.0	5.0	219.5	63.8	32.3	4.81	112.7	177	- 34
92.5	7.5	181.6	93.5	28.1	4.42	113.1	168	- 37
90.0	10.0	149.7	45.6	24.00	3.97	115.6	164	- 40
87.5	12.5	123.1	38.7	20.63	3.62	117.2	154	- 41
85.0	15.0	102.1	33.2	17.40	3.37	119.7	150	- 43
82.5	17.5	85.3	28.4	15.47	3.06	120.1	145	- 45
80.0	20.0	70.8	24.25	13.51	2.82	121.5	138	- 47
77.5	22.5	59.7	20.93	11.85	2.62	122.9	137	- 47
75.0	25.0	50.0	17.90	10.32	2.45	125.4	133	- 51
72.5	27.5	42.2	15.53	9.07	2.31	127.8	129	- 52
70.0	30.0	35.9	13.51	8.02	2.20	129.0	128	- 53
67.5	32.5	31.4	11.93	7.11	2.06	130.2	126	-56
65.0	35.0	26.4	10.54	6.57	1.969	132.4	125	- 57
62.5	37.5	22.64	9.12	5.75	1.874	134.7	124	- 59
60.0	40.0	19.5	7.86	4.92	1.778	136.1	125	- 60
57.5	42.5	16.33	6.88	4.41	1.705	139.5	124	-61
55.0	45.0	14.03	6.06	3.92	1.643	142.2	125	- 62
52.5	47.5	12.18	5.42	3.59	1.588	144.0	119	- 64
50.0	50.0	10.51	4.78	3.24	1.536	146.8	117	- 64

Table 69b

Blends of SS 906 + V 120

p. 119 b

Blend		Viscosity					Fl.pt.	Solid.pt.
SS 906	V 120	20°	38°	50°	99°	V.I.		
47.5 g	59.5 g	9.62	4.48	3.06	1.511	149.9	119°	- 67°
45.0	55.0	8.15	3.89	2.75	1.456	152.5	117	- 69
42.5	57.5	7.13	3.50	2.53	1.420	156.1	117	- 69
40.0	60.0	6.12	3.10	2.31	1.372	157.7	117	- 72.5
37.5	62.5	5.28	2.77	2.08	1.329	157.2	116	below - 73
35.0	65.0	4.60	2.51	1.972	1.305	167.3	117	"
32.5	67.5	4.02	2.32	1.873	1.279	171.8	116	"
30.0	70.0	3.58	2.17	1.780	1.256	175.2	117	"
27.5	72.5	3.16	2.02	1.695	1.237	185.7	114	"
25.0	75.0	2.83	1.881	1.612	1.210	187.6	114	"
22.5	77.5	2.55	1.783	1.559	1.191	192.4	117	"
20.0	80.0	2.35	1.700	1.527	1.171	188.2	118	"
17.5	82.5	2.17	1.616	1.443	1.154	-	116	"
15.0	85.0	2.02	1.556	1.402	1.140	-	115	"
12.5	87.5	1.892	1.498	1.360	1.123	-	116	"
10.0	90.0	1.784	1.446	1.329	1.111	-	113	"
7.5	92.5	1.697	1.403	1.296	1.099	-	115	"
5.0	95.0	1.615	1.358	1.263	1.086	-	115	"
2.5	97.5	1.546	1.324	1.239	1.078	-	114	"
V 120	100	1.502	1.302	1.221	1.068	-	115	below - 73°

Table 69c

p.119 c.

Blends of SS 906 + V 120

Blend							Fl.pt.	Solid.pt.
SS 906	V 140	20°	38°	50°	99°	V.I.		
100 g	-	359.2	96.6	47.7	6.03	108.3	235°	- 33°
90	10	179.8	53.2	27.04	4.22	111.4	108	- 46
80	20	94.3	30.6	16.09	3.04	114.4	165	- 50
70	30	52.9	18.53	10.49	2.43	121.5	161	- 52
60	40	29.5	11.14	6.60	1.950	125.5	155	- 53
50	50	16.32	6.71	4.22	1.665	138.7	153	- 55
40	60	10.31	4.62	3.05	1.502	142.0	150	- 66
30	70	6.33	3.10	2.29	1.375	159.0	146	- 71
20	80	3.97	2.27	1.816	1.253	150.3	143	- 73
10	90	2.77	1.83	1.565	1.183	147.4	141	below -73
-	100	2.08	1.55	1.389	1.123	-	139	" -73

p.120 As has been described, the so-called R-oil is obtained from the $AlCl_3$ sludge. This oil serves to prepare Y-Journal Oil-Red for the Railroads of the Reich. The R-oil should have the following properties:

Density at + 20°	below 0.85
Vis. at + 50°	42.0 cst. = 5.6 E°
Solidification pt.	at least -50°
Flash pt.	above + 140°
Conradson test	below 0.3

Y-Journal-Oil:	Composition:	60 parts R-oil
		20 " V 160
		20 " Ester 504
		0.02 " Sudan Red

Vis. at + 50°	above 3.4 E°
" " - 30°	below 900 E°
" " - 40°	below 3300 E°
Solidification pt.	below - 60°
Flash pt.	above 140°

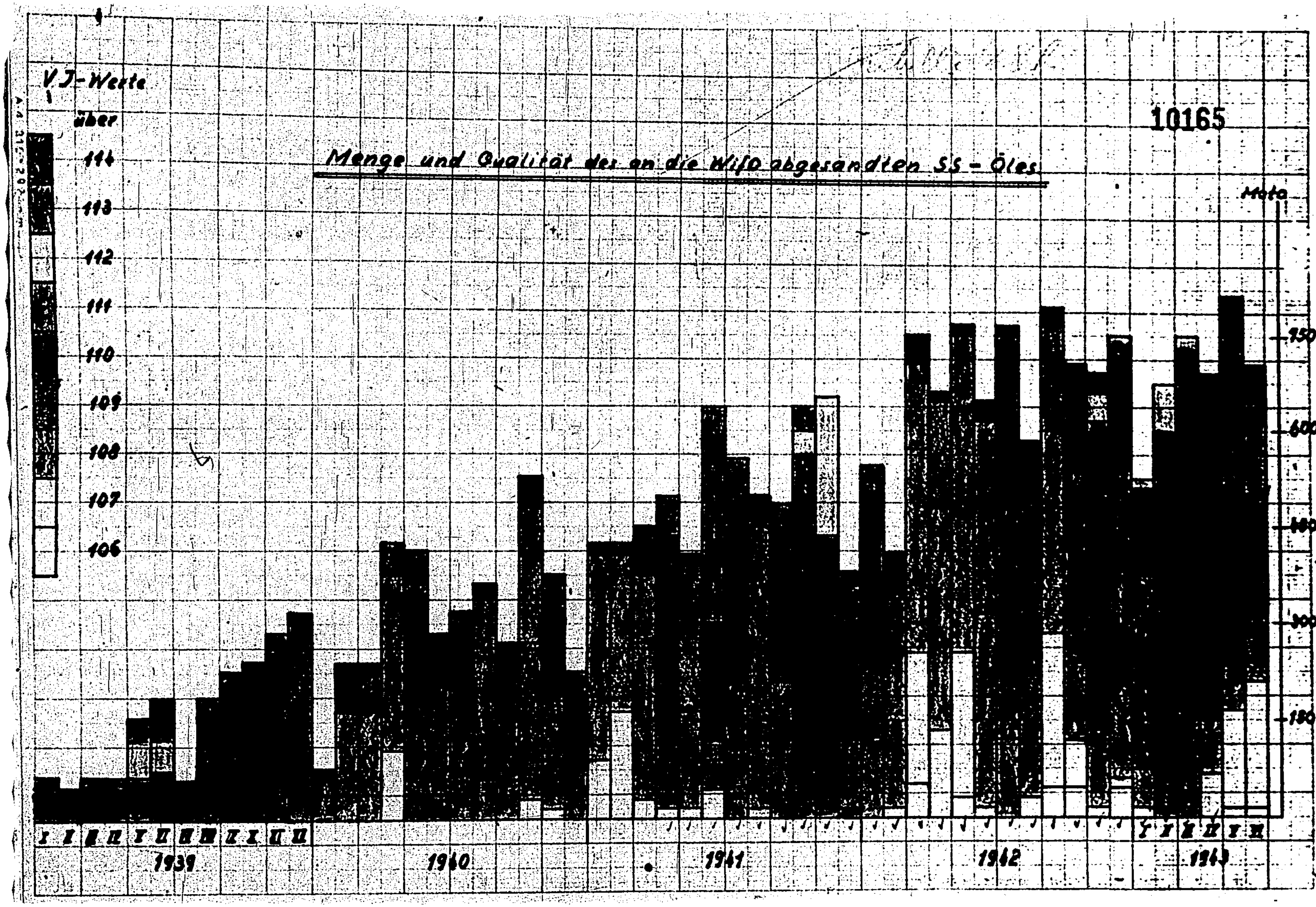
Table 70 again summarizes the properties of the ethylene lubricating oils described.

Table 68a.

Viscosity Indices of SS 906 Shipped to Wifo and Number of Tank Cars.

V.I.	Above	106	107	108	109	110	111	112	113	114	Total of Tank Cars
1939	No. of Cars	-	-	13	29	55	14	7	5	1	123
	%	-	-	10.6	23.6	44.7	11.4	5.7	4.1	0.8	
1940	No. of Cars	-	10	89	94	48	8	-	-	-	249
	%	-	4.0	35.8	37.8	19.3	3.2	-	-	-	
1941	No. of Cars	-	25	80	86	126	63	17	3	-	400
	%	-	6.2	20.0	21.5	31.5	15.7	4.2	0.7	-	
1942	No. of Cars	14	65	161	183	98	10	4	2	-	537
	%	2.6	12.1	30.0	34.0	18.3	1.9	0.7	0.4	-	
Jan. June 1943	No. of Cars	2	28	52	70	76	42	7	-	-	277
	%	0.7	10.1	18.8	25.0	27.4	15.2	2.3	-	-	

10165



Menge und Qualität des an die Wifo abgesandten SS-Öles

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Table 66

SS 900 - Production

		1938		1939		1940		1941		1942	
			%		%		%		%		%
Ethylene, total	t	700		2.799		5.121		8.512		11.440	
Ethylene recycle gas	t					278		309		not measured 1)	
Ethylene consumption	t					4.845		8.203			
Production referred to ethylene consumed											
SS 906	t	439	63.0	1.932	69.0	3.881	80.0	6.220	75.8	8.257	72.5
Overh'd distillate	t	19	2.7	113	4.0	238	4.9	526	6.4	708	6.2
R-Oil	t	73	10.0	231	8.3	406	8.4	729	8.9	505	4.4
Total Yield	t	531	75.7	2.267	81.3	4.525	93.3	7.475	91.9	9.470	83.1 2)
Consumption of materials referred to SS oil											
Aluminum chloride	t	39	9.0	151	7.8	291	7.5	454	7.3	621	7.5
Methanol	t	12	2.7	116	6.0	163	4.2	268	4.3	342	4.1
Hydrated lime	t	38	8.6			90	2.3	163	2.6	270	3.3
Bleaching clay	t	27	6.1	72	3.7	41	1.0	33	0.5	73	0.9
Power per 1000 kg SS oil											
Heating gas	m^3	265.000	600	750.000	390	890.000	228	1.290.000	206	1.273.000	158 3)
High pressure steam	t }	16.225	36 }	31.395	16.2	7.613	2.2	9.699	1.5	12.000	1.5
Low pressure steam	t }					41.067	10.5	50.406	8.1	34.818	4.3
Electric current	Kwh			379.530	222	600.130	154	845.800	136	894.420	111
Water	m^3	320.130	730	468.360	242	657.630	170			292.460	- 4)

1) Recycle gas not returned to 387 after 1942
2) Referred to total ethylene since recycle gas is no longer measured
3) At present, waste gas from 387
4) At present, water from 387.

Table 67 a/b

Autoclave	500 Ø (1000 liter)	800 Ø (4500 liter)
C_2H_4 / Furnace	470.0 kg = 100 %	2200 kg = 100 %
SS 906	362.9 kg = 77.2 %	1670 kg = 76.0 %
V-Oil	40.4 " = 8.6 %	150 " = 6.8 %
R-Oil	19.3 " = 4.1 %	160 " = 7.2 %
Machine oil	7.2 " = 1.5 %	- -
KT-Prod.	- -	20 " = 0.9 %
Resid. gas	- -	60 " = 2.7 %
Asphalt	14.2 " = 3.0 %	- -
Loss	26.1 " = 5.6 %	140 " = 6.4 %
For 2 charges / d For 80% operating factor furnace	28.200 kg/Month C_2H_4 17.5 Moto SS 906 = 210 Jato SS 906 /furhace	132.000 kg/Month C_2H_4 80 Moto SS 906 = 960 Jato SS 906/Furnace

SS-POLYMERIZATION IN 800 ø AUTOCLAVE (4500 LITERS).

(Confidential)

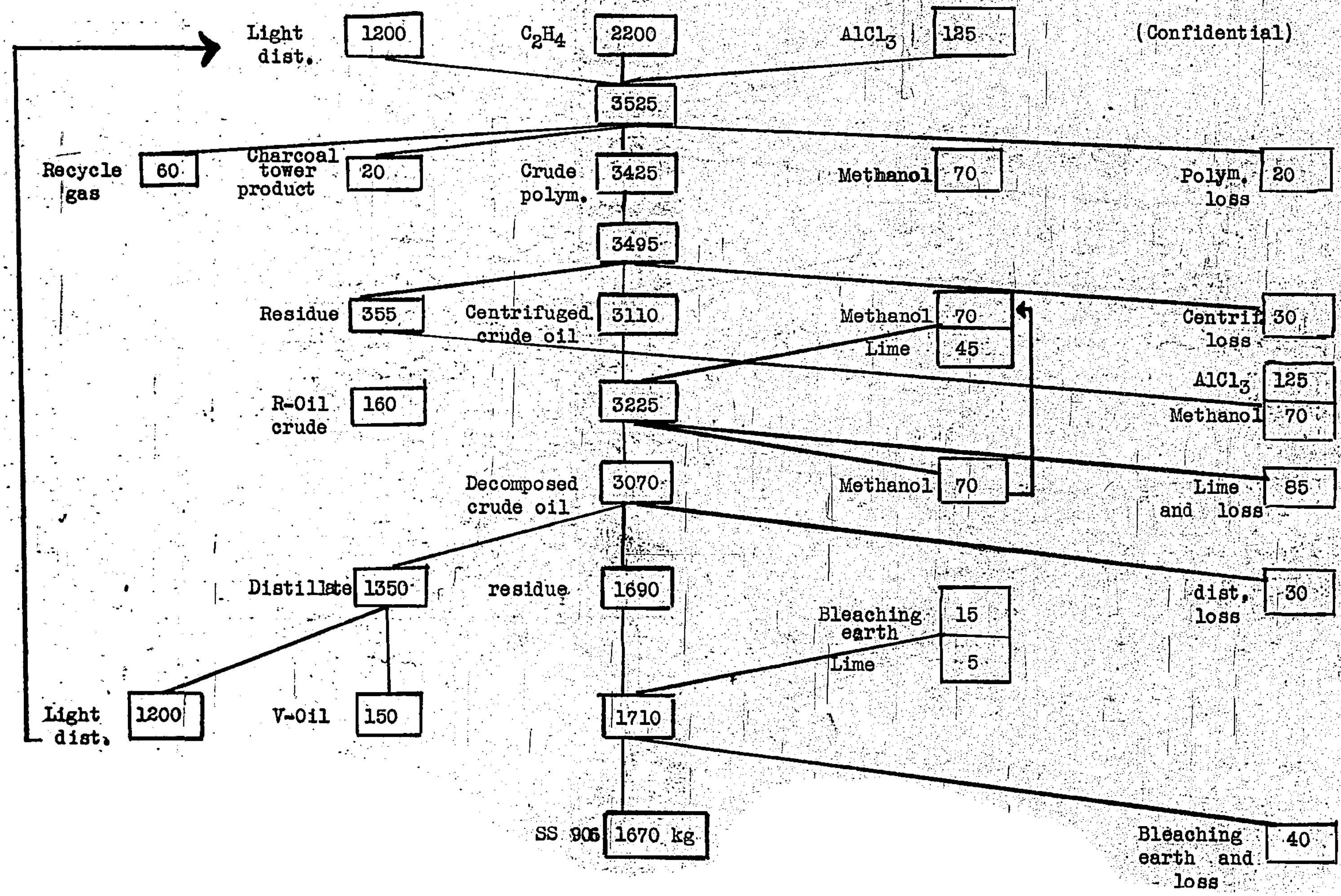


Table 67 a

SS-POLYMERIZATION IN 500 Ø AUTOCLAVE (1000 LITERS)

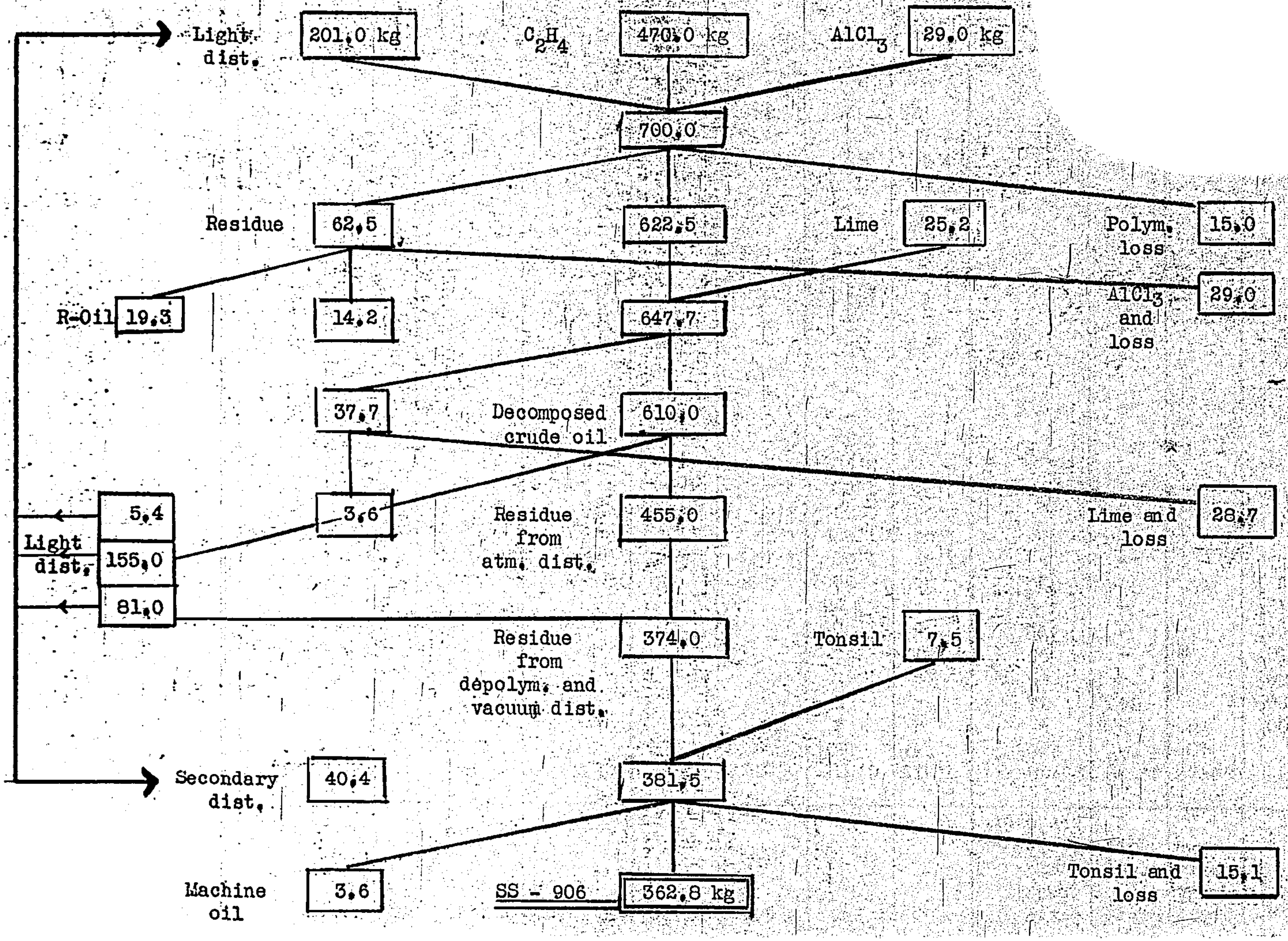
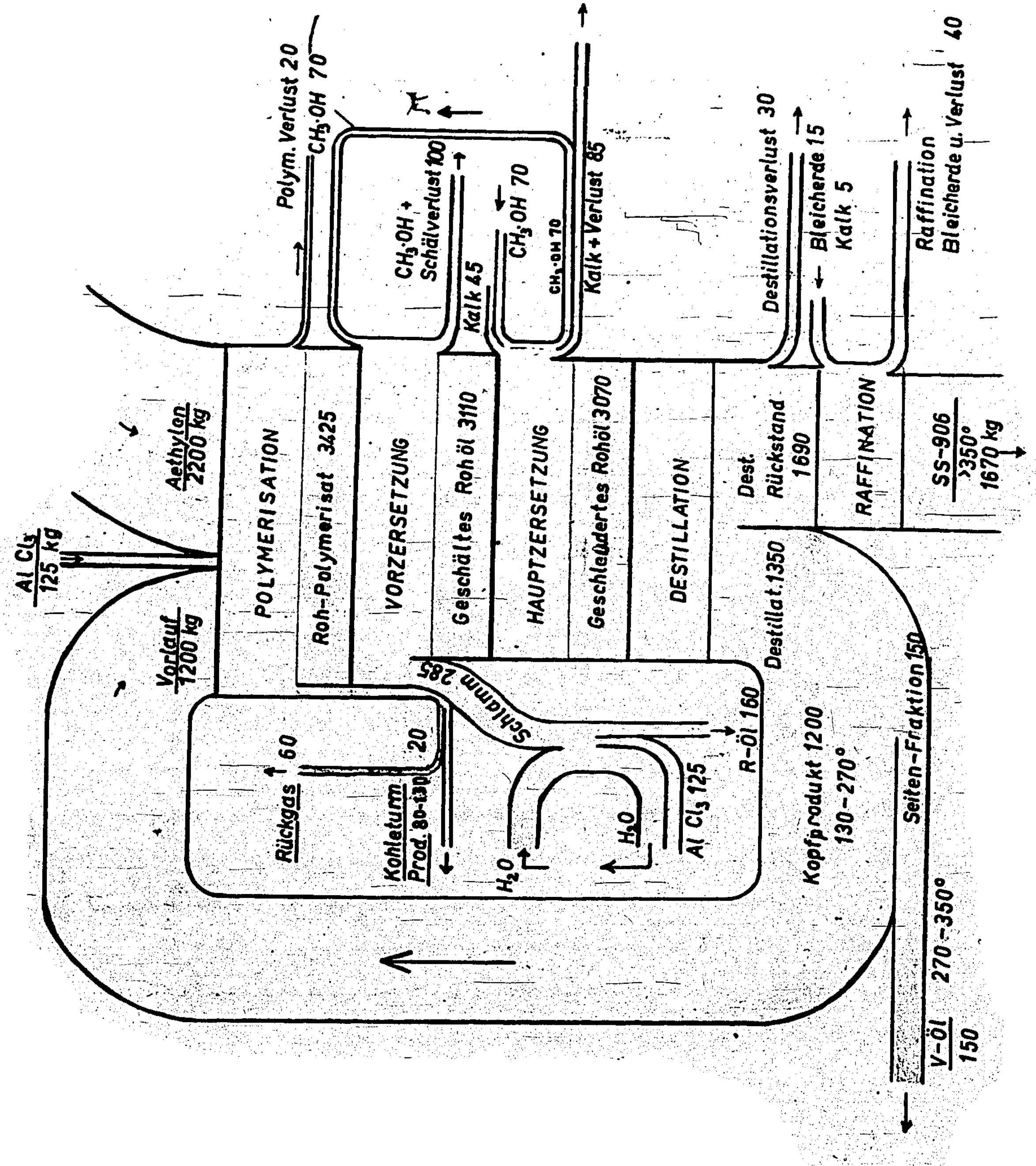


Table 70

	Char-coal tower prod.	Over-head from R-Oil	Over-head from dist.& stripper	V 105	V 120	V 140	V 160	V 120N	RR-Oil	Crd. polym.	SS 903	SS 906	R-Oil 180°
Density at 20°	0.690	0.778	0.778	0.812	0.815	0.817	0.822	0.811	0.960	0.824	0.850	0.853	0.857
Distillation	40°	74°	130°	230°	250°	270°	315	260	-	130	300	330	290
to 100°	72	9	-	-	-			-	-	-	-	-	-
- 150°		84	33	-	-			-	-	-	-	-	-
- 200°		-	88	-	-			-	-	13	-	-	-
- 250°		-	95	15	-			-	-	25	-	-	-
- 300°		-	98	63	55			56	-	32	-	-	
- 350°		-	-	90	93			-	-	45	11	13	20
End pt. at °C	140	174	300	360	360	360	360	330	-	-	-	-	-
Visc. E 99°	-	-	-	1.07	1.09	1.10	1.19	1.06	26.4	-	3.0	6.0	3.0
+ 50°				1.24	1.28	1.34	1.59	1.25	-		16	46	18
+ 38°				1.34	1.39	1.47	1.91	1.33	2622		30	92	34
+ 20°				1.58	1.69	1.88	3.02	1.58			92	352	106
0°					2.70	-	-	-		-	481	2325	646
-10°				-	-	-	14	3.3		-	1000	7280	1935
-20°				-	-	-	32	5.5		-	4000	(-15° 14320	6930
-25°				-	-	-	-	-			22100		14420
-30°				-	-	-		11.2					
-40°				-	14.9	-		24.3					
-45°				-	-	-		-					
-50°				63.8	99.6	150		70					
-60°	-	-	-	208	354	582		234		-			
Visc. Index	-	-	-	-	-	-	133	-	67		124	111	107
Bearing factor"m"	-	-	-	3.73	3.66	3.87	3.78	3.89	-	-	3.15	3.03	3.24
Pole Height	-	-	-	0.6	0.7	0.98	1.28	0.7	-	-	1.62	1.72	1.75
Solid. pt. °C	-73	-73	-73	-73	-73	-73	-70	-73	-1	-	-38	-36	-37
Flash pt. °C				105	120	146	163	123	188	58	190	230	179
Acid No.mg KOH/g	-	-	-	0.0	0.0	0.0	0.0	0.0	3.6	-	0.01	0.0	0.0
Sap. No." "	-	-	-	0.0	0.0	0.0	0.0	0.0	8.0	-	0.09	0.0	0.2
Conradson test	-	-	-	0.0	0.01	0.008	0.0	0.0	5.7		0.08	0.08	0.20
I-No. (Hanus)	3.3		1.4		4.1				137			8.5	32
Mol. wt.	101		155		238						640	826	327

R-Oil 155°	D-Oil V 140	VK$_{20}$	SV$_{15}$	Min. oil Comp. Int-ava	Red ring M45	RM$_4$f$_2$ Fl. Hydr. oil	Y-Journal oil, red	Ordnance oil, blue	K 16 Cold start oil	Breaking in oil	Torpedo oil
0.851	0.817	0.818	0.832	0.885	0.870	0.830	0.865	01886	0.886	0.896	0.916
270	270	-	250								
-		-									
-		-									
-		-									
-		-									
9		-	21								
33		-	60								
-	360	-	-								
	1.10	1.13	1.52	1.85	3.04	1.099	1.62	1.14	1.65	1.55	1.51
	1.34	1.38	3.04	7	18	1.327	3.75	1.42	4.2	3.5	3.2
	1.47	1.53	4.5	13	35	1.448	5.85	1.58	6.7	5.1	4.9
	1.88	1.98	9.6	39	118	1.807	13.2	2.09	16	12	12
-	-	-	33	209	-	-	-	-	-	-	-
358	-	-	-	594	2305	-	-	-	161	-	104
1018	-	-	175	(-15°	9460	-	-	-	457	-	294
				4060)							
1882	-	-	-			-	-	-	-	-	-
3580	-	-	-			-	-	-	1560	-963	-975
	-	-	1361			-	2738	81	6099		3830
	-	-				-	5610	-	13830		6883
	150	183				131		243			
	582	696				535		1111			
	-	-	150	93	108	-	141	-	133	142	127
	3.87	3.59	3.23	3.6	3.29	3.76	3.2	3.6	3.3	3.4	3.5
	0.98	0.8	1.22	2.0	1.69	1.19	1.30	1.29	1.46	1.39	1.51
-54	-73	-73	-67	-20	-32	-73	-60	-73	-33	-57	-58
155	146	124	124	224	228	133	133	127	199	182	215
0.059	0	0.0	0.0		0.0	0.22	0.0	0.0	0.0	0.47	0.17
0	0	0.0	0.0		0.0	42	81	(230)	141	148	181
0.15	0.008	0.006	0.01	0.25	0.20	0.20	0.11	0.31	0.17	0.28	0.16
14	0										


Al Cl3 125 kg
Aethylen 2200 kg
Vorlauf 1200 kg
POLYMERISATION
Polym. Verlust 20
CH3·OH 70
Roh-Polymerisat 3425
VORZERSETZUNG
CH3·OH + Schälverlust 100
Geschältes Rohöl 3110
Kalk 45
CH3·OH 70
CH3·OH 70
HAUPTZERSETZUNG
Kalk + Verlust 85
Geschleudertes Rohöl 3070
DESTILLATION
Destillationsverlust 30
Dest. Rückstand 1690
Bleicherde 15
Kalk 5
RAFFINATION
Raffination Bleicherde u. Verlust 40
SS-906 >350° 1670 kg
Destillat 1350
Kopfprodukt 1200 130-270°
Seiten-Fraktion 150
V-Öl 150 270-350°
Schlamm 285
R-Öl 160
Al Cl3 125
H2O
H2O
Rückgas 60
20
Kohletumm Prod. 80-130