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THE PREPARATION OF LUBRICATING OIL FROM
HYDROGENATION PRODUCTS BY THERMAL CRACKING
AND POLYMERIZATION OF THE CRACKED PRODUCTS

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THE PREPARATION OF LUBRICATING OIL FROM HYDROGENATION PRODUCTS,
BY THERMAL CRACKING AND POLYMERIZATION OF THE CRACKED PRODUCTS

The purpose of this work is to obtain high-value lubricating oils from suitable and available hydrogenation products; the cost problem made it of interest to arrange the experiments so as to be applicable mainly to automobile motor oils.

OPERATING METHOD

The initial products, consisting mostly of saturated or only small amounts of olefinic components, were subjected to a de-hydrogenation treatment, and the reaction products resulting from this treatment were polymerized by means of aluminum chloride or other substances of similar characteristics.

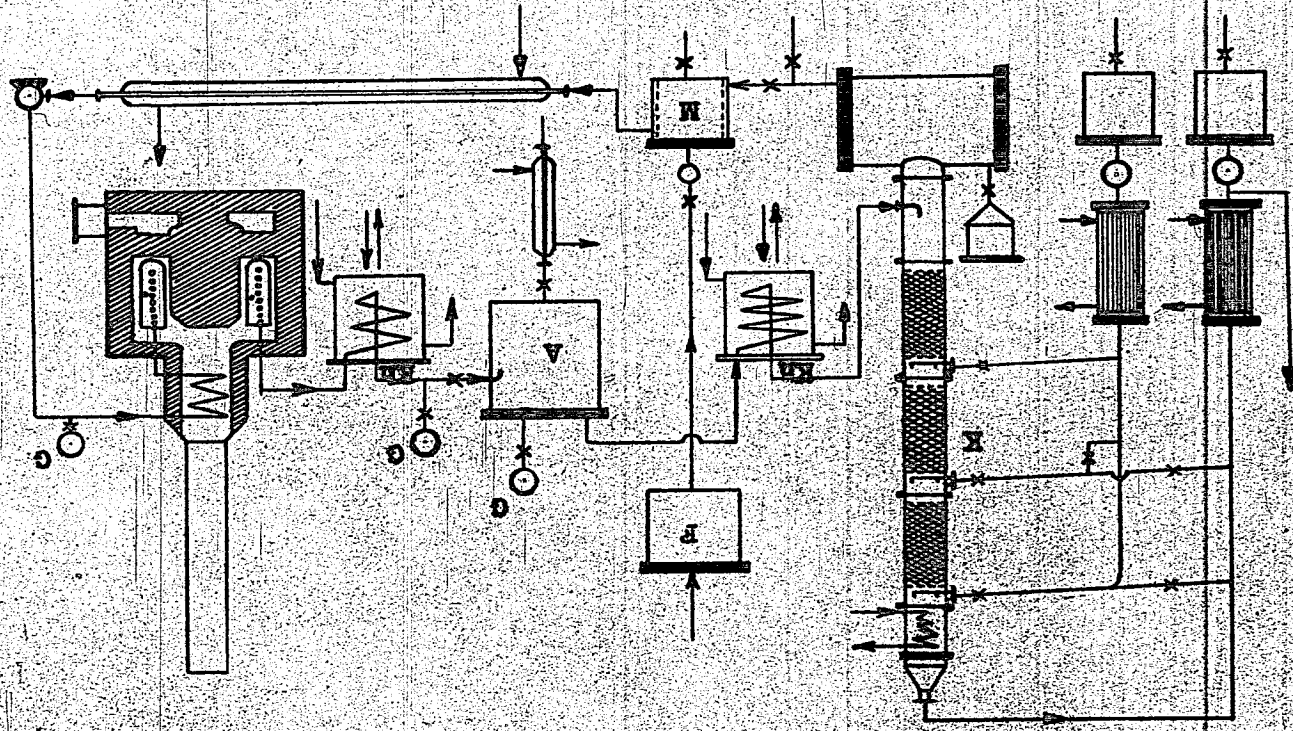
I. Preparation of the Olefins

a. By Chlorination and De-chlorination

Chlorination and de-chlorination for the purpose of preparing olefins was attempted in two-stage and one-stage operation (i.e. substitution of chlorine and splitting off of hydrogen chloride, all in a single step). This procedure did not lead to the desired end when the hydrocarbons of the gasoline and middle-oil range were used, inasmuch as the olefinic reaction products were obtained with unsatisfactory yields and with a residual chlorine content of about 1.5 - 7%. The polymerization of these products gave only fairly good yields of poor quality lubricating oils, and therefore the method of chlorination and decoloration was abandoned in favor of the thermal cracking process.

b. Thermal Cracking under Pressure

In contrast to the usual normal-pressure cracking process used in Oppau, we used pressure cracking, and were successful. As will become apparent from the results tabulated further on, the pressure cracking method has certain advantages, especially when the initial stock consists of mixed-base material (i.e. paraffinic-naphthenic). The unit operates roughly on the Carburol principle. The liquid (or, if one deals with solid paraffins, the liquefied) initial products are added, under pressure and with a high rate of thru-put (.8 - 2 m/sec, based on the cold oil), to a high-pressure tube unit (6 mm) which has been heated to the cracking temperature. The high pressure unit is built of V 17 f material (S) (length = 18-35m). After partial cooling (high pressure cooler K_h , low pressure cooler K_n), the product is passed into a column K so that the remaining heat content of the cracking products will be sufficient for the particular fractionation which is desired. The cracked gases and the



EXPERIMENTAL CRACKING UNIT No. 907X

ILLUSTRATION 1

olefinic crack products of the gasoline range are taken from the head of the column; the cracked oils of the middle oil range are taken from the lower parts of the column, provided that these cracked oils are desired as primary product; the least cracked higher boiling components are re-passed into the sump at the bottom of the column by means of a pumping unit P consisting of 2 six-stage Bosch pumps. The cracking coil is heated in the furnace (O), over a lead bath (B). This method of heating is very convenient since, despite pressure and heat-value variations in the heating-gas, the cracking temperature can be kept constant and disturbing over-heating effects are avoided. For the purpose of utilizing more thoroughly the heat of the outgoing combustion gases, a 16 meter long preheater coil (V) is fitted in front of the cracking coil inside the furnace, at the base of the chimney.

For continuous operation tests, the cracked products are released into an insulated intermediate catch pot A before they enter the column. The temperature of this intermediate catch pot is regulated by the high-pressure cooling unit in such a manner that the highest boiling, hydrogen-lean tar components will be condensed and can be drawn off in the liquid phase. The fresh product is taken from a storage tank F and mixed with the cycle oil coming from the column, in a heatable mixing tank M. When dealing with fatty paraffins, the conduits and containers carrying the product are fitted, as far as necessary, with steam-heated jackets.

About 30 kg of product can be processed in our unit every hour; the maximum container capacity is 300 kg. The operating pressure is about 5 - 100 atmospheres as measured in front of the cracking coil. The pressure drop inside the cracking coil depends on the latter's length and on pressure, through put and temperature; it amounts to about 5 - 40 atm.

RESULTS

In the high pressure cracking process too, the olefinic cracked products vary in quantity, depending on the operating conditions (Tables I - V). However, the olefin content decreases, both in the gaseous and in the liquid cracked products, with increasing pressure and contact time. On the other hand, the drawback of having a smaller content of unsaturated hydrocarbons is more or less compensated by the advantage of having a higher yield of cracking distillate and, at the same time, a smaller gas loss. Another advantage is the fact that - at least with the higher boiling products - the cracking can be achieved, to a great extent, in the liquid phase; this means that there is less danger of overheating (by improved heat conduction through the tube walls); thus, there is the advantage - among others - of a smaller coking tendency. There are other advantages of the high pressure process as compared to the normal-pressure cracking process, especially with liquid initial products; these advantages, which make themselves felt in the quality of the lubricating oils, will be shown later.

From a technical point of view, it can be said that the apparatus required for high pressure thermal cracking can be rapidly and reliably adjusted, whenever the most favorable cracking conditions are desired for a certain given initial stock, these adjustments are made by changes in temperature, through-put and pressure, either singly or simultaneously.

As already mentioned, the cracking distillates were drawn off, in several cases, in fractions. (See also the report of Dr. Bahr and Kolb: "Diesel Oil from Low Temperature Hydrogenation Residue boiling over 300° and of its Components by Cracking"; report is dated 24 October 1938). The results (shown later in this report) obtained by this type of separate processing of the cracking product components into lubricating oils, show that there are several advantages. However, the pour point sets an upper limit: it will be convenient not to exceed a terminal boiling point of 330°.

Examples from the Cracking Experiments

1. Effect of Temperature on Cracking is shown in Tables I and II, following.
2. Effect of pressure on cracking is shown in Tables III and IV, following.

Comparison of cracking under pressure with normal pressure cracking.

Different initial products:

From the tables above (see following pages) the following essential facts appear:

1. With increasing cracking temperature (the pressure remaining constant), the gas loss increases; at the same time, the olefin content of the cracked products increases.
2. With increasing operating pressure, the gas loss and the olefin content of the cracked products decreases.
3. The higher olefin content of the cracked products as obtained by the pressure-less cracking process is more or less compensated by the higher yield of liquid cracked products and by the more favorable product distribution as obtained by cracking under pressure.

TABLE I

STOCK: RESIDUE 6434; CONTINUOUS CRACKING PROCESS

| CRACKING CONDITIONS | | | | R E A C T I O N P R O D U C T S | | | | | | | | |
|---------------------|----------------|--------------------|------------------------|---------------------------------|--------------------------|---------------|-----|-------------|------------------------------|-------------------|--------------------|-----|
| Temp. °C. | Press. Atm. | Thruput lit/hr. | Conversion/ Pass. % | Cracked Distillates | | | | Cracked Gas | | TAR | | |
| | | | | % of Conversion | Iodine No. (Hanus) | Boiling Range | | | % of Conversion | Vol. % Olefins | % of Conversion | |
| | | | | | | IBP | 50% | EP | d ₂₀ ^o | | | |
| 500 | 40/30 | 155 | 1.2 | 61.8 | 138 | 40 | 128 | 192 | 0.733 | 29.2 | 37.5 | 9.0 |
| 520 | 40/30 | 155 | 4.5 | 74.2 | 153 | 38 | 145 | 194 | 0.745 | 23.7 | 39.2 | 6.1 |
| 538 | 40/30 | 155 | 5.2 | 66.2 | 169 | 40 | 137 | 187 | 0.744 | 32.6 | 39.8 | 1.2 |
| 550 | 40/30 | 155 | 11.2 | 74.8 | 162 | 44 | 153 | 202 | 0.756 | 24.8 | 40.0 | 0.4 |

TABLE II

STOCK: L.T.H. RESIDUE ABOVE 300°; CONTINUOUS CRACKING

| <u>CRACKING CONDITIONS</u> | | | | <u>R E A C T I O N P R O D U C T S</u> | | | | | | | | | | | | |
|----------------------------|------------------------------|----------------------------------|---|--|---|---|-----|-----|----------------------------------|---|---|-----|-----|----------------------------------|----------------------------------|--------------------------------|
| <u>Temp.</u> <u>°C.</u> | <u>Press.</u> <u>Atm.</u> | <u>Thruput</u> <u>lit/hr.</u> | <u>Conversion</u> <u>per Pass, %</u> | <u>Cracked Middle Oil</u> | | | | | <u>Cracked Gasoline</u> | | | | | <u>Tar</u> | <u>Cracked Gas</u> | |
| | | | | <u>% of</u> <u>Conversion</u> | <u>Iodine</u> <u>No.</u> <u>(Hanus)</u> | <u>Boiling Range</u> <u>IBP 50% EP</u> | | | <u>% of</u> <u>Conversion</u> | <u>Iodine</u> <u>No.</u> <u>(Hanus)</u> | <u>Boiling Range</u> <u>IBP 50% EP</u> | | | <u>% of</u> <u>Conversion</u> | <u>% of</u> <u>Conversion</u> | <u>Vol. %</u> <u>Olefin</u> |
| 485 | 50 | 175/225 | 6.2 | 53.8 | 85 | 196 | 271 | 330 | 14.2 | 164.5 | 55 | 120 | 185 | 26.3 | 5.7 | 33.0 |
| 500 | 50 | 225 | 6.6 | 63.1 | 89 | 195 | 266 | 324 | 20.7 | 155 | 46 | 117 | 183 | 7.0 | 9.3 | 30.5 |
| 510 | 50 | 225 | 7.5 | 55.7 | 78 | 198 | 256 | 326 | 23.5 | 157 | 44 | 119 | 180 | 10.8 | 10.0 | 27.0 |

TABLE III

STOCK: L.T.H. RESIDUE ABOVE 300°; CONTINUOUS CRACKING
 L.T.H. RESIDUE ABOVE 300°; FREED FROM PARAFFINS (x)

| <u>CRACKING CONDITIONS</u> | | | | <u>R E A C T I O N P R O D U C T S</u> | | | | | | | | | | | | | | |
|------------------------------|----------------------------|----------------------------------|---|--|---|----------------------|------------|-----------|----------------------------------|---|----------------------|------------|-----------|----------------------------------|----------------------------------|---------------------------------|--------------------|--|
| <u>Press.</u> <u>Atm.</u> | <u>Temp.</u> <u>°C.</u> | <u>Thruput</u> <u>lit/hr.</u> | <u>Conversion</u> <u>per Pass, %</u> | <u>Cracked Middle Oil</u> | | | | | | <u>Cracked Gasoline</u> | | | | | | <u>Tar</u> | <u>Cracked Gas</u> | |
| | | | | <u>% of</u> <u>Conversion</u> | <u>Iodine</u> <u>No.</u> <u>(Hanus)</u> | <u>Boiling Range</u> | | | <u>% of</u> <u>Conversion</u> | <u>Iodine</u> <u>No.</u> <u>(Hanus)</u> | <u>Boiling Range</u> | | | <u>% of</u> <u>Conversion</u> | <u>% of</u> <u>Conversion</u> | <u>Vol. %</u> <u>Olefins</u> | | |
| | | | | | | <u>IBP</u> | <u>50%</u> | <u>EP</u> | | | <u>IBP</u> | <u>50%</u> | <u>EP</u> | | | | | |
| 30 | 495 | 225 | 9.7 | 54.2 | 73.5 | 198 | 254 | 310 | 26.0 | 162 | 53 | 121 | 186 | 6.0 | 14.0 | 34.0 | | |
| 50 | 495 | 225 | 6.6 | 55.3 | 79 | 195 | 257 | 313 | 26.3 | 150 | 40 | 113 | 177 | 6.7 | 11.5 | 30.5 | | |
| 80 | 495 | 200/225 | 7.7 | 57.7 | 82 | 195 | 265 | 333 | 23.5 | 156 | 45 | 122 | 181 | 8.7 | 10.6 | 24.5 | | |
| x 50 | 475 | 220 | 7.7 | 60.3 | 92 | 220 | 256 | 318 | 22.0 | 168 | 51 | 123 | 189 | 7.9 | 10.0 | 21.5 | | |
| x 80 | 475 | 200 | 10.2 | 65.3 | 79 | 192 | 258 | 322 | 19.5 | 134.5 | 56 | 130 | 184 | 5.9 | 9.3 | 18.2 | | |

TABLE IV
 COMPARISON OF CRACKING UNDER PRESSURE WITH CRACKING AT NORMAL PRESSURE
 DIFFERENT INITIAL PRODUCTS

| S T O C K | Press. (Atm. exc.) | Temp. °C. | Conver- sion % by Wt. | R E A C T I O N | | | | | | | | | P R O D U C T S | | |
|-------------------------------|-----------------------|--------------------|-----------------------------|-------------------------|--------------------------|-----------------------------|-------------------------|--------------------------|-----------------------------|-------------------------|-------------------|------------|-----------------|--------------|----------------|
| | | | | Cracked Middle Oil | | | Cracked Gasoline | | | Cracked Gas | | | | | |
| | | | | % of Conver- sion | Iodine No. (Hanus) | Boiling Range IBP 50% EP | % of Conver- sion | Iodine No. (Hanus) | Boiling Range IBP 50% EP | % of Conver- sion | Vol. % Olefins | | | | |
| L.T.H. Residue above 300° | 0 50 | - 520 | 67.7 85.5 | 23.2 64.1 | 104 80 | 198 180 | 254 260 | 321 326 | 28.4 24.2 | 250 152 | 34 48 | 103 124 | 181 190 | 48.4 11.7 | - 26.0 |
| Total Cracked Distillate | | | | | | | | | | | | | | | |
| L.T.H. Soft Paraffin | 0 26/18 | 510 505/510 | 62 68 | - - | - - | - - | - - | - - | 64.5 82.3 | 200 127 | 45 62 | 190 205 | 312 310 | 35.5 17.7 | ab 55 37.5 |
| L.T.H. Soft and Hard Paraffin | 0 16/5 | 500/510 560/570 | 60 49.3 | - - | - - | - - | - - | - - | 55.8 74.4 | 255 200 | 42 38 | 126 157 | 234 234 | 44.2 25.6 | ab 56 ab 42 |

TABLE V

CRACKING UNDER PRESSURE WITH DIFFERENT STOCKS

| S T O C K | | C R A C K I N G | | | R E A C T I O N P R O D U C T S | | | | | | | | |
|--------------------------------------|------------------------------|-----------------|-------------|---------------------|------------------------------------|---------------------|--------------------|---------------|------------|-----|---------------------|----------------|---------------------|
| Name or Description | After-Treatment | Temp. °C. | Press. Atm. | Conversion % by Wt. | Cracked Distillate | | | | | | Cracked Gas | | |
| | | | | | Fraction | Wt. % of Conversion | Iodine No. (Hanus) | Boiling Range | | | Wt. % of Conversion | Vol. % Olefins | Wt. % of Conversion |
| | | | | | | | | IBP | 50% | EP | | | |
| Hard Paraffin Riebeck | - | 500 | 30 | 75.8 | Total | 82.7 | 171 | 34 | 123 | 245 | 17.3 | 39.6 | - |
| Kogasin II | - | 515 | 30 | 85.5 | Total | 71.0 | 185 | 38 | 130 | 224 | 29.0 | 40.8 | - |
| Residue 5058 (d = .80) | - | 530 | 30 | 65.8 | Total | 75.2 | 170 | 46 | 161 | 219 | 24.8 | 40.2 | - |
| Residue 5058 (d = .82) | Topped (fraction 220-260°) | 525 | 30 | 57.8 | Total | 74.4 | 173 | 28 | 132 | 206 | 25.6 | 38.8 | - |
| Residue 5058 (d = .84) | - | 550 | 30 | 76.8 | Total | 69.4 | 170 | 33 | 133 | 212 | 30.6 | 21.2 | - |
| Residue 6434 (d = .807) | - | 520 | 40/30 | 50.0 | Total | 74.2 | 153 | 38 | 145 | 194 | 23.7 | 39.2 | 2.1 |
| Residue 6434 (d = .807) (d = .815) | Topped (fraction above 240°) | 560 | 20 | 80.7 | Total | 69.5 | 190 | 31 | 142 | 214 | 30.5 | 40.5 | - |
| Gasoline from pre-hydrogenation | Topped (above 70°) | 560 | 30 | ab. 75 | Total | 70.5 | 208 | 34 | 137 | 233 | 29.5 | 44.8 | - |
| LTH Diesel Oil I | - | 630 | 30 | 63.0 | Total | 52.0 | 138 | 31 | 75 | 180 | 48.0 | 42.3 | - |
| LTH Diesel Oil I | - | 520 | 20 | 41.8 | Total | 64.4 | 188 | 35 | 125 | 230 | 35.6 | 32.2 | - |
| LTH Diesel Oil I | - | 520 | 30 | 80.0 | Total | 74.8 | 138 | 56 | 175 | 270 | 25.2 | 30.8 | - |
| LTH Diesel Oil II de-paraffinized | - | 540 | 30 | ab. 65 | Total | 73.9 | 179 | 30 | 132 | 267 | 26.1 | 29.2 | - |
| LTH Diesel Oil II de-paraffinized | - | 590 | 15 | 53.7 | Total | 64.7 | 205 | 29 | 132 | 265 | 35.3 | 40.2 | - |
| LTH Product above 300° | - | 505 | 50 | 39.1 | Total | 84.7 | 165 | 35 | 128 | 205 | 15.3 | 29.4 | - |
| LTH Product above 300° | - | 495 | 30 | - | (Middle Oil 55.3 Gasoline 26.3) | 79 150 | 195 40 | 257 113 | 313 177 | | 11.5 | 30.5 | 6.7 |
| LTH Product above 300° | Deparaffinized | 520 | 50 | - | (Middle Oil 60.3 Gasoline 22.8) | 92 168 | 220 51 | 256 123 | 318 189 | | 10.0 | 21.5 | 7.9 |
| LTH Soft Paraffin (ab. 87% Paraffin) | - | 505 | 30 | 82.9 | Total | 80.8 | 162 | 36 | 144 | 264 | 19.2 | 36.8 | - |
| LTH Soft Paraffin (ab. 87% Paraffin) | - | 485/ 495 | 35/ 20 | - | (Middle Oil 48.4 Gasoline 30.0) | 95 168 | 145 47 | 250 136 | 320 250 | | 12.1 | 38.5 | 9.5 |
| LTH Soft and Hard Paraffin | - | 560/ 570 | 16/ 5 | - | Total | 73.4 | 200 | 38 | 157 | 234 | 25.4 | ab. 42 | 1.2 |
| Hot Separator Condensate Oil | - | 510 | 40/35 | - | Total | 32.2 | 131 | 50 | 142 | 190 | 18.0 | 13.2 | 49.8 |
| Ruhland (50-420°) | - | 510 | 30/22 | - | Total | 86.5 | 125 | 44 | 177 | 237 | 13.5 | 47.8 | - |
| LTH Hard Paraffin | - | ab. 500 | 30/5 | 36.4 | Total | 77.2 | 170 | 35 | 134 | 238 | 22.8 | 42.2 | - |

TABLE VI
POLYMERIZATION OF CRACKED DISTILLATES OF THE PRESSURE CRACKING AND CONVERSION INTO LUBE OILS
EXPERIMENTS WITH DIFFERENT STOCKS

| S T O C K | CRACKED DISTILLATE | CRACKED GAS | | | | | | P O L Y M E R I Z A T I O N | | | | LUBE OIL YIELDS | |
|--|--------------------|---------------------|--------------------|---------------|------|------|--|-----------------------------|--------------------------------------|----------|-----------------|--------------------------------|-------------------------------|
| | | % Wt. of Conversion | Iodine No. (Hanus) | Boiling Range | | | % Wt. of Conversion Ind. C ₃ O, Olefins | Temp., °C. | Additions, % by Wt. | | Cracked Gas | % by Wt. of Cracked Distillate | % by Wt. of Stock (Converted) |
| | | | | TBP | 50% | EP | | | AlCl ₃ | Diluents | | | |
| 1. Hard Paraffin Risbeck | 82.7 | 171 | 34 | 123 | 24.5 | 17.3 | - | 120 | 8 | 40 | - | 51.9 | 43.0 |
| 2. L.T.H. Hard Paraffin | 77.2 | 170 | 35 | 134 | 238 | 22.8 | 8.2 | 120 | 10 | 40 | - | 36.8 | 28.4 |
| 3. L.T.H. Diesel Oil I | 67.5 | 168 | 30 | 154 | 265 | 32.5 | 13.2 | 120 | 10 | 0 | - | 28.5 | 19.3 |
| 4. L.T.H. Diesel Oil I | 67.5 | 160 | 30 | 154 | 265 | 32.5 | 13.2 | 120 | 10 | 0 | 24.5 of Product | 25.5 | 17.3 |
| 5. L.T.H. Diesel Oil II | 64.7 | 205 | 29 | 132 | 265 | 35.3 | 12.8 | 120 | 5 | 40 | - | 48.3 | 31.3 |
| 6. Deparaffinized | 64.7 | 205 | 29 | 132 | 265 | 35.3 | 12.8 | 120 | 10 | 0 | 35.0 of Product | 43.1 | 27.9 |
| 7. Residue 5058 d = 0.80 | 75.2 | 170 | 46 | 161 | 219 | 24.8 | 9.4 | 120 | 10 | 0 | 44.0 of Product | 30.0 | 22.6 |
| 8. Residue 5058 d = 0.84 | 69.4 | 170 | 33 | 133 | 212 | 30.6 | 9.3 | 150 | 5 | 0 | - | 26.5 | 18.4 |
| 9. Residue 6434 AP = 69.7°; d = .80 | 73.4 | 169 | 40 | 128 | 190 | 26.6 | - | 120 | 5 | 40 | - | 36.2 | 26.6 |
| 10. AP = 70.8°; d = 0.81 | 74.3 | 182 | 33 | 135 | 212 | 25.7 | - | 120 | 5 | 40 | - | 35.5 | 26.4 |
| 11. AP = 71.8°; d = 0.807 | 66.6 | 189 | 37 | 134 | 224 | 33.4 | - | 135 | 5 | 40 | - | 39.3 | 26.2 |
| 12. Above 240°; AP = 74.0 | 70.5 | 208 | 34 | 137 | 233 | 29.5 | - | 150 | 5 | 40 | - | 48.0 | 33.8 |
| 13. Gasoline from Prehydrogen | 52.0 | 138 | 31 | 75 | 180 | 48.0 | - | 90 | 5 | 40 | - | 17.8 | 9.3 |
| 14. L.T.H. Residue Above 300° 40% Paraffin | 84.7 | 165 | 35 | 128 | 205 | 15.3 | - | 120 | 5 | 40 | - | 36.6 | 30.8 |
| L.T.H. Residue Above 300° 36% Paraffin | (56.7) | 77 | 195 | 260 | 326 | 9.9 | - | 90/150 | 8 | 40 | - | (24.5) | (13.9) |
| 15. L.T.H. Residue Above 300° De-paraffinized | (22.3) | 153 | 48 | 124 | 190 | - | - | 110 | 8 | 0 | - | (32.6) | (7.3) |
| 16. L.T.H. Soft Paraffin (22 June '38) | (65.3) | 79 | 192 | 258 | 322 | 9.3 | - | - | - | - | - | - | - |
| 17. L.T.H. Soft Paraffin (22 June '38) | (19.5) | 135 | 56 | 130 | 184 | - | - | 110 | 8 | 0 | - | 26.5 | 5.2 |
| 18. L.T.H. Soft and Hard Paraffin Mixture | 84.8 | 133 | 47 | 196 | 308 | 12.7 | - | 120 | 5 | 40 | - | 43.3 | 36.7 |
| 19. L.T.H. Soft and Hard Paraffin Mixture | 84.8 | 133 | 47 | 196 | 308 | 12.7 | - | 120 | 2 + 4 AlCl ₃ Sludge | 40 | - | 45.2 | 38.3 |
| 20. Condensate Oil Ruhland | 73.4 | 200 | 38 | 157 | 234 | 25.4 | - | 90/150 | 8 | 40 | - | 49.5 | 36.4 |
| | 80.0 | 150 | 43 | 145 | 218 | 20.0 | - | 90/150 | 8 | 40 | - | 45.2 | 36.2 |
| | 86.5 | 124 | 40 | 175 | 237 | 13.5 | - | 120 | 5 | 40 | - | 33.0 | 28.6 |

TABLE VI (CONT'D)

| S T O C K | A N A L Y S I S | | | | | | |
|---|---------------------------|--------|-------------------|--------------------|-------------------|--------|--------------------------|
| | Viscosity OE. at 50°C. | V.I. | Pour Point °C. | Flash Point °C. | Hard Asphalt % | Coking | Specific Wt. at 20°C. |
| 1. Hard Paraffin Riebeck | 10.2 | +115 | -18 | 202 | 0.0 | 0.13 | - |
| 2. L.T.H. Hard Paraffin | 9.8 | +100 | -27 | 196 | 0.0 | 0.12 | 0.865 |
| 3. L.T.H. Diesel Oil I | 8.9 | +33.5 | -32 | 182 | 0.0 | 0.14 | 0.898 |
| 4. L.T.H. Diesel Oil I | 14.5 | +4.5 | -30 | 192 | 0.0 | 0.21 | 0.904 |
| 5. L.T.H. Diesel Oil II | 25.0 | +10.5 | -23 | 192 | 0.0 | 0.14 | 0.913 |
| 6. Deparaffinized | 20.0 | -1 | -26 | 190 | 0.0 | 0.18 | 0.913 |
| 7. Residue 5058 d = 0.80 | 26.7 | +9 | -18 | 197 | 0.0 | 0.35 | 0.906 |
| 8. Residue 5058 d = 0.84 | 14.0 | -14.5 | -30 | 182 | 0.0 | 0.27 | 0.917 |
| 9. Residue 6434 AP = 69.7°; d = .80 | 20.6 | +12.5 | -25 | 194 | 0.0 | 0.25 | 0.894 |
| 10. AP = 70.8°; d = 0.81 | 17.2 | +57 | -28 | 188 | 0.0 | 0.16 | 0.890 |
| 11. AP = 71.8°; d = 0.807 | 23.4 | +33 | -25 | 196 | 0.0 | 0.36 | 0.905 |
| 12. Above 240°; AP = 74.0 | 10.4 | +75.5 | -39 | 196 | 0.0 | 0.24 | 0.883 |
| 13. Gasoline from Prehydrogen | 621.1 | ? | ab. +20 | 196 | - | - | 0.942 |
| 14. L.T.H. Residue Above 300° 40% Paraffin | 9.5 | +79 | -30 | 207 | 0.0 | 0.09 | 0.868 |
| 15. L.T.H. Residue Above 300° 36% Paraffin | 10.0 | +79 | -32 | 228 | 0.0 | 0.58 | 0.902 |
| 15. L.T.H. Residue Above 300° Deparaffinized | 9.2 | +77 | -40 | 199 | 0.0 | 0.05 | 0.870 |
| 16. L.T.H. Soft Paraffin (22 June '38) | 11.4 | +20 | -33 | 208 | 0.0 | 0.12 | 0.887 |
| 17. L.T.H. Soft Paraffin (22 June '38) | 11.5 | +112.5 | -23 | 216 | 0.0 | 0.33 | 0.865 |
| 18. L.T.H. Soft and Hard Paraffin Mixture | 11.1 | +102 | -41 | 232 | 0.0 | 0.51 | 0.873 |
| 19. L.T.H. Soft and Hard Paraffin Mixture | 12.7 | +100 | -42 | 196 | 0.0 | 0.76 | 0.877 |
| 20. Condensate 211-Ruhland | 10.4 | +101 | -46 | 195 | 0.0 | 0.16 | 0.869 |
| | 12.5 | +102 | -44 | 219 | 0.0 | 0.19 | 0.858 |

II. Polymerization of the Olefinic Products into Lubricating Oils

As a rule, the polymerization of the olefinic cracked distillate was effected by means of aluminum chloride (3-10% by weight of the total cracked product). In a few exceptional cases, sulfuric acid, phosphoric acid and boron fluoride were also used, but it was found that, for our purpose, aluminum chloride was far superior to all other polymerizing agents. The addition of diluents in form of saturated hydrocarbon oils, practiced in Ludwigshafen, (mostly these oil diluents are taken from the first runnings of the lube oil distillation), was found to be most practical: better lube oil yields could be obtained, apparently due to a repression of depolymerization. The operating temperature of the polymerization process was, in general, kept between 90 and 180°, mostly around 120°. Temperatures above 120° were, as a rule, applied only with stocks which had a tendency to form highly viscous lube oils. - Barring a few exceptions, all polymerizations were carried out on laboratory scale.

METHOD OF POLYMERIZATION AND AFTER-TREATMENT

The cracked distillate was diluted (in most cases, the diluent amounted to 40% by vol. of the cracked distillate); then, aluminum chloride was added in small quantities at a time, for a period of one hour, under constant and thorough stirring and without outside heating. Towards the end of the polymerizing-agent addition, the temperature was gradually brought to the desired level by outside heating, and it was then maintained at this level until a sample of the oily upper layer showed an Iodine Number value of 20. Stirring continued.

Only the light-colored upper layer of the polymerization product was used for processing into lubricating oil; the black-brown, viscous lower layer which, besides the condensation products, also contains more or less highly unsaturated oil components, was not taken into consideration unless it could be used for further polymerization. The upper layer was then freed from aluminum chloride and hydrochloric acid by washing with water and lye; after completion of this treatment, it was subjected to distillation in vacuo (.5 - 2 mm) until the distillation residue showed a viscosity of about 10⁰E at 50°C. Many lube oils, especially those of poorer quality, did not meet (with 10⁰E at 50°) the flash-point requirements (above 185°C); therefore, in these cases, we aimed at oils of higher viscosity. The residue above, say, 120 - 160 (at the above mentioned pressures) was regarded as lubricating oil and subjected to examination after a one-hour treatment with 2-5% bleaching earth. The distillate, which consisted of saturated gasoline, middle oil and spindle oil, was used as diluent for further polymerization tests.

The lube oil yield varied considerably, depending on the type of stock, olefin content and boiling range of the cracked product, and on the polymerization reaction conditions. (See Tables VI - XI). As a rule, solid paraffins gave more lube oil than middle oil; and the latter in turn gave more lube oil than gasolines; this is due to the fact that the amount of heat required for the achievement of a sufficiently high olefin content in the cracked distillate, and the gas loss which it entails, is usually higher in the gasolines. To this we must also add the overlapping of the boiling points of the stock and the cracked product. The yields obtained in Ludwigshafen from cracked products of normal pressure cracking, were not equalled, at least not with solid paraffin. It is quite probable that the oil yields obtained in our experiments could have been improved by a more suitable choice of reaction conditions; with the exception of the experimental series given in Table VII - X, we did not study this particular question any further.

As a whole, the polymerization of cracked products obtained under pressure from solid paraffins, led to lube oils of equal and sometimes superior quality. As can be seen from Table II, pressure cracking is definitely superior to pressure-less cracking in the case of the processing of Leuna mixed-base products (LTH-product, for instance). The normal pressure cracking method leads, at least in the case of the gasoline range cracked products, to viscous and resin-like oil; in contrast to this, the cracked products obtained by pressure cracking give oils of higher quality and of the desired viscosity. From the point of view of the initial stock, it can be said that, polymerization conditions being the same, the lube oil yields are approximately constant; this is due to the fact that the diminished olefin content of the pressure-cracking distillates is compensated by the higher liquid-phase yield.

From Tables VII - X it can be seen that the oil yield and, to a certain extent also the oil quality, can be materially influenced by the choice of polymerization conditions. The following overall results were established:

1. Polymerization temperatures exceeding 120° diminish the oil yield considerably, and also decrease the viscosity of the oils. However, when a higher flash point is desired, and if otherwise oils of high viscosity would be obtained such higher temperatures are practicable (See Table VII).
2. Addition of diluents in form of saturated hydrocarbon oils is advantageous in all cases; the yield is increased without appreciable effect on the quality of the oil (Table VIII).
3. The oil yield increases with decreasing amounts of condensing agent (examined down to 3% AlCl₃). See Table IX*.

*Table IX is missing.

TABLE VII

POLYMERIZATION OF PRESSURE CRACKING DISTILLATES TO LUBE OILS
EFFECT OF THE TEMPERATURE OF POLYMERIZATION

| S T O C K | CRACKED DISTILLATE | | | POLYMERIZATION | | | | LUBE OIL YIELDS WEIGHT % OF: | | A N A L Y S I S | | | | | |
|--|------------------------|--------------------------|-----------------------------|----------------|--|----|-----------------------|---------------------------------|------------------------|-----------------|-------------|----------------|--------------------|-------------|---------------------|
| | Wt. % of Conversion | Iodine No. (Hanus) | Boiling Range IBP 50% KP | Temp. °C. | Additions, Wt. % AlCl ₃ Diluents | | Cracked Distillate | Converted Stock | Visc. Ck. at 50° | V.I. | Four Pt. | Flash Point | Hard Asph. % | Coking % | Spec. Wt. 20° |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction 100-200° | 90 | 10 | 40 | 54.5 | 16.8 | 22.6 | +112 | - | - | 0.0 | 0.1 | - |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction 100-200° | 120 | 10 | 40 | 57.3 | 17.7 | 14.9 | +109 | -42 | 204 | 0.0 | 0.1 | - |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction 100-200° | 150 | 10 | 40 | 51.0 | 15.8 | 11.5 | +113.5 | -41 | 201 | 0.0 | 0.1 | - |
| Residue 6434 AP = 70.8; d = .81 | 74.3 | 182 | 33 135 212 | 120 | 5 | 40 | 35.5 | 26.4 | 17.2 | +57 | -28 | 188 | 0.0 | 0.16 | 0.890 |
| Residue 6434 AP = 70.8; d = .81 | 74.3 | 182 | 33 135 212 | 135 | 5 | 40 | 34.8 | 25.9 | 14.4 | +52 | -30 | 188 | 0.0 | 0.19 | 0.890 |
| Residue 6434 AP = 70.8; d = .81 | 74.3 | 182 | 33 135 212 | 150 | 5 | 40 | 31.5 | 23.4 | 10.4 | +54 | -32 | 195 | 0.0 | 0.23 | 0.887 |
| Hard Paraffin Riebeck | 25.2 | 266 | Fraction below 100° | 90/ 110 | 10 | 40 | 53.5 | 13.5 | 24.8 | +80.5 | - | - | - | - | - |
| Hard Paraffin Riebeck | 25.2 | 266 | Fraction below 100° | 120 | 10 | 40 | 51.5 | 13.0 | 18.5 | +87 | -37 | 196 | 0.0 | 0.1 | - |
| L.T.H. Hard and Soft Paraffin Mixture | 75.6 | 156 | 48 164 269 | 60 (150) | 8 | 40 | 43.3 | 32.7 | 12.3 | +104 | -42 | 208 | 0.0 | 0.37 | 0.873 |
| L.T.H. Hard and Soft Paraffin Mixture | 75.6 | 156 | 48 164 269 | 90 (150) | 8 | 40 | 44.3 | 33.5 | 14.4 | +105 | -38 | 215 | 0.0 | 0.48 | 0.875 |
| L.T.H. Hard and Soft Paraffin Mixture | 75.6 | 156 | 48 164 269 | 150 | 8 | 40 | 33.7 | 25.5 | 9.9 | +102 | -37 | 236 | 0.0 | 0.20 | 0.864 |

TABLE VIII
POLYMERIZATION OF PRESSURE CRACKING DISTILLATES TO LUBE OIL
EFFECT OF DILUENT ON LUBE OIL YIELD

| S T O C K | CRACKED DISTILLATE | | | | | POLYMERIZATION | | | | LUBE OIL YIELDS WEIGHT % OF: | | A N A L Y S I S | | | | | |
|--|------------------------|--------------------------|------------------------|-----|-----|----------------|-------------------|----------|------------------------|---------------------------------|------------------------|-----------------|-------------|----------------|--------------------|-------------|---------------------|
| | Wt. % of Conversion | Iodine No. (Hanus) | Boiling Range | | | Temp. °C. | Additions, Wt. % | | Cracked Distillates | Converted Stock | Visc. °E. at 50° | V.I. | Pour Pt. | Flash Point | Hard Asph. % | Coking % | Spec. Wt. 20° |
| | | | IBP | 50% | EP | | AlCl ₃ | Diluents | | | | | | | | | |
| Residue 6434 | 74.3 | 182 | 33 | 135 | 212 | 120 | 5 | - | 33.6 | 25.0 | 11.1 | +55 | -23 | 203 | 0.0 | 0.16 | 0.889 |
| Residue 6434 | 74.3 | 182 | 33 | 135 | 212 | 120 | 5 | 40 | 35.5 | 26.4 | 17.2 | +56.5 | -28 | 188 | 0.0 | 0.16 | 0.890 |
| L.T.H. Soft Paraffin | 84.8 | 133 | 47 | 196 | 308 | 120 | 5 | - | 40.3 | 34.2 | 11.9 | +112 | -35 | 229 | 0.0 | 0.34 | 0.868 |
| L.T.H. Soft Paraffin | 84.8 | 133 | 47 | 196 | 308 | 120 | 5 | 40 | 43.3 | 36.7 | 11.5 | +112.5 | -23 | 216 | 0.0 | 0.33 | 0.865 |
| L.T.H. Soft Paraffin | 84.8 | 133 | 47 | 196 | 308 | 120 | 5 | 80 | 47.5 | 40.3 | 9.7 | +111.5 | -30 | 208 | 0.0 | 0.46 | 0.873 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 | - | 40.5 | 30.5 | 11.3 | +97.5 | -42 | 220 | 0.0 | 0.20 | 0.87 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 | 40 | 41.7 | 31.5 | 9.6 | +102 | -44 | 213 | 0.0 | 0.23 | 0.872 |
| L.T.H. Soft and Hard Paraffin Mixture | 49.1 | 133 | Fraction above 130° | | | 120 | 5 | - | 36.8 | 16.1 | 9.7 | +107 | -46 | 222 | 0.0 | 0.26 | 0.87 |
| L.T.H. Soft and Hard Paraffin Mixture | 49.1 | 133 | Fraction above 130° | | | 120 | 5 | 40 | 43.3 | 21.3 | 11.1 | +107 | -47 | 237 | 0.0 | 0.39 | 0.87 |

TABLE X

POLYMERIZATION OF PRESSURE CRACKING DISTILLATES TO LUBE OIL
THE EFFECT OF ALUMINUM CHLORIDE ADDITIONS

| S T O C K | CRACKED DISTILLATE | POLYMERIZATION LUBE OIL | | | | | | | | | | A N A L Y S I S | | | | | |
|---------------------------------------|--------------------|-------------------------|--------------------|---------------|-----|-----|--|------------------|--------------------|---------------------|------|------------------|------|----------|-------------|--------------|----------|
| | | % by Wt. of Conversion | Iodine No. (Hanus) | Boiling Range | | | Temp. °C. | Additions, % Wt. | | Yields % by Wt. of: | | Visc. °S at 50°C | V.I. | Four Pt. | Flash Point | Hard Asph. % | Coking % |
| | | | IBP | 50% | EP | | AlCl ₃ | Diluent | Cracked Distillate | Converted Stock | | | | | | | |
| Residue 6434 AP = 71.8; d = .807 | 66.6 | 189 | 37 | 134 | 224 | 135 | 3 | 40 | 43.2 | 28.8 | 26.1 | +34.5 | -23 | 206 | 0.0 | - | 0.905 |
| Residue 6434 AP = 71.8; d = .807 | 66.6 | 189 | 37 | 134 | 224 | 135 | 5 | 40 | 39.3 | 26.2 | 23.5 | +33 | -25 | 196 | 0.0 | 0.36 | 0.905 |
| Residue 6434 AP = 71.8; d = .807 | 66.6 | 189 | 37 | 134 | 224 | 135 | 4 + 1 ZnCl ₂ | 40 | 36.5 | 24.3 | 25.0 | +36 | -24 | 198 | 0.0 | 0.33 | 0.903 |
| Residue 6434 AP = 71.8; d = .807 | 66.6 | 189 | 37 | 134 | 224 | 135 | 5 + 1 Zn Dust | 40 | 42.5 | 28.4 | 24.9 | +26.5 | - | 201 | 0.0 | - | 0.906 |
| Residue 6434 AP = 71.8; d = .807 | 66.6 | 189 | 37 | 134 | 224 | 135 | 5 + 1 Al activated | 40 | 41.0 | 27.3 | 20.2 | +26 | - | 195 | 0.0 | 0.3 | 0.902 |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction 100-200° | | | 120 | 10 | 40 | 57.3 | 17.7 | 15.0 | +109 | -42 | 204 | 0.0 | 0.10 | - |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction 100-200° | | | 120 | 10 + 5 Al activated | 40 | 61.4 | 19.0 | 15.7 | +105.5 | -39 | 209 | 0.0 | 0.2 | - |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 | 40 | 38.3 | 29.0 | 9.7 | +107 | -46 | 222 | 0.0 | 0.26 | 0.873 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 + 0.5 P ₂ O ₅ | 40 | 42.5 | 32.1 | 10.0 | +101.5 | -43 | 214 | 0.0 | 0.29 | 0.871 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 + 0.5 CaO | 40 | 41.5 | 31.4 | 11.7 | +97.5 | -46 | 225 | 0.0 | 0.30 | 0.873 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 + 0.5 HFO ₃ | 40 | 40.3 | 30.5 | 12.9 | +86 | -4 | 225 | 0.0 | 0.27 | 0.874 |
| L.T.H. Soft and Hard Paraffin Mixture | 75.6 | 156 | 48 | 164 | 269 | 120 | 5 + 2 Silica Gel | 40 | 43.0 | 32.5 | 10.0 | +97 | -37 | 207 | 0.0 | 0.29 | 0.873 |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 7 | 0 | 27.0 | 16.9 | 12.9 | +14 | - | - | - | - | 0.907 |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 7 + 1 TiCl ₄ | 0 | 27.0 | 16.9 | 16.8 | +11 | - | - | - | - | 0.916 |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 7 + 1 Zn Dust | 0 | 25.5 | 16.0 | 29.1 | -12 | - | - | - | - | - |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 7 + 1 FeCl ₃ | 0 | 27.5 | 17.2 | 17.2 | +7 | -25 | 188 | 0.0 | 0.34 | 0.915 |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 7 + 1 ZnCl ₂ | 0 | 30.1 | 18.8 | 15.2 | +13 | - | - | - | - | 0.913 |
| L.T.H. Diesel Oil I | 62.5 | 172 | 32 | 138 | 255 | 120 | 8 + 0.1 HgCl ₂ | 0 | 28.0 | 17.5 | 11.3 | +17 | -30 | 179 | 0.0 | 0.15 | 0.904 |

TABLE XI

POLYMERIZATION OF NORMAL PRESSURE AND OF HIGH PRESSURE CRACKED DISTILLATES TO LUBE OIL

| S T O C K | CRACKING | | POLYMERIZATION | | Yields | | L U B E O I L A n a l y s i s | | | | | |
|-------------------------------|-----------------------|--|----------------|-------------------------------|--------------------------------------|-----------------------------------|-------------------------------|------|-------------|----------------|-------------|------|
| | Press. (Atm. exc.) | Cracked Distillate % by Wt. of Conversion | Temp. °C. | AlCl ₃ % by Wt. | % by Wt. of Cracked Distillate | % by Wt. of Converted Stock | Visc. OR at 50°C. | V.I. | Pour Pt. | Flash Point | Coking % | |
| L.T.H. Product above 300 | 0 | (Middle | | | | | | | | | | |
| | | (Oil 23.2 | 90/150 | 8 | 35.6 | 23.6 | 10.5 | 57.5 | -42 | 218 | 0.77 | |
| | (Gasoline 28.4 | 90/150 | 8 | 54.0 | | | 57.6 | 55.5 | -19 | 202 | 0.76 | |
| | 50 | (Middle | | | | | | | | | | |
| | | (Oil 64.1 | 90/150 | 8 | 24.1 | 28.7 | 10.0 | 80 | -32 | 228 | 0.58 | |
| | | (Gasoline 24.2 | 90/150 | 8 | 33.3 | | | 9.5 | 77 | -42 | 212 | 0.15 |
| L.T.H. Soft Paraffin | 0 | Total | 64.5 | 120 | 5 | 63.1 | 40.7 | 9.9 | 102.5 | -9 | 201 | 0.43 |
| | 26/18 | Total | 82.3 | 120 | 5 | 46.0 | 37.9 | 10.5 | 112 | -30 | 215 | 0.30 |
| L.T.H. Soft and Hard Paraffin | 0 | Total | 55.8 | 90/150 | 8 | 65.2 | 35.9 | 14.5 | 99.5 | -40 | 205 | 0.21 |
| | 16/5 | Total | 74.4 | 90/150 | 8 | 55.1 | 41.0 | 15.0 | 101 | -43 | 220 | 0.31 |

For further details concerning the cracked distillates, see Table IV

TABLE XII

POLYMERIZATION OF PRESSURE CRACKING DISTILLATES TO LUBE OIL
EFFECT OF THE BOILING RANGE OF THE CRACKED DISTILLATE ON THE QUALITY OF THE LUBE OIL

| S T O C K | CRACKED DISTILLATE | | | POLYMERIZATION | | | LUBE OIL | | A N A L Y S I S | | | | | |
|--------------------------------------|------------------------|--------------------|---------------------------------------|----------------|--|--------------------|--|-----------------|--------------------|------|----------|-------------|--------------|----------|
| | % by Wt. of Conversion | Iodine No. (Hanus) | Boiling Range IBF 50% EP | Temp. °C. | Additions, % Wt. AlCl ₃ Diluent | Cracked Distillate | Yields % by Wt. of: Cracked Distillate | Converted Stock | Visc. °S. at 50°C. | V.I. | Pour Pt. | Flash Point | Hard Asph. % | Coking % |
| Hard Paraffin Riebeck | 25.2 | 266 | Fraction below 100° | 120 | 10 40 | 51.5 | 13.0 | 18.5 | +87 | -37 | 196 | 0.0 | 0.1 | - |
| Hard Paraffin Riebeck | 30.8 | 146 | Fraction below 100° | 120 | 10 40 | 57.3 | 17.7 | 15.0 | +109 | -42 | 204 | 0.0 | 0.1 | - |
| L.T.H. Soft Paraffin of 22 June 1938 | 82.8 | 134 | Total Product 52 184 297 | 120 | 5 40 | 45.8 | 38.0 | 10.5 | +116 | -42 | 220 | 0.0 | 0.65 | 0.864 |
| L.T.H. Soft Paraffin of 22 June 1938 | 8.7 | 235 | Fraction below 80° | 120 | 5 40 | 44.3 | 3.9 | 15.9 | +98 | -34 | 195 | 0.0 | 0.03 | 0.856 |
| L.T.H. Soft Paraffin of 22 June 1938 | 20.6 | 182 | Fraction below 130° | 120 | 5 40 | 49.0 | 10.1 | 11.0 | +104 | -34 | 206 | 0.0 | 0.08 | 0.859 |
| L.T.H. Soft Paraffin of 22 June 1938 | 31.9 | 175 | Fraction below 180° | 120 | 5 40 | 46.2 | 14.8 | 14.3 | +107.5 | -43 | 221 | 0.0 | 0.17 | 0.863 |
| L.T.H. Soft Paraffin of 22 June 1938 | 67.7 | 110 | Fraction above 80° | 120 | 5 40 | 48.0 | 32.5 | 9.6 | +118 | -26 | 200 | 0.0 | 0.69 | 0.865 |
| L.T.H. Soft Paraffin of 22 June 1938 | 60.5 | 105 | Fraction above 130° | 120 | 5 40 | 48.5 | 29.4 | 9.3 | +121 | -25 | 200 | 0.0 | 0.61 | 0.862 |
| L.T.H. Soft Paraffin of 22 June 1938 | 49.8 | 95 | Fraction above 180° | 120 | 5 40 | 47.5 | 23.7 | 10.2 | +122 | -18 | 205 | 0.0 | 0.92 | 0.869 |
| L.T.H. Soft Paraffin of 22 June 1938 | 50.0 | 148 | Fraction 80-270 | 120 | 5 - | 39.8 | 19.9 | 12.6 | +117 | -44 | 217 | 0.0 | 0.19 | 0.862 |
| L.T.H. Soft Paraffin of 22 June 1938 | 45.4 | 120 | Fraction 130-270 | 120 | 5 - | 38.5 | 17.5 | 10.3 | +122.5 | -37 | 212 | 0.0 | 0.31 | 0.858 |
| L.T.H. Soft Paraffin of 22 June 1938 | 43.0 | 108 | Fraction 180-280 | 120 | 5 - | 35.5 | 15.3 | 10.0 | +124 | -28 | 225 | 0.0 | 0.37 | 0.859 |
| L.T.H. Product above 300° | 64.1 | 152 | Cracked Middle Oil 90/180 260 326 150 | 90/150 | 8 - | 24.1 | 28.7 | 10.0 | +80 | -32 | 228 | 0.0 | 0.58 | - |
| L.T.H. Product above 300° | 24.2 | 80 | Cracked Gasoline 48 124 190 | 90/150 | 8 - | 33.3 | | 9.5 | +77 | -42 | 212 | 0.0 | 0.15 | - |

4. Certain additions of condensing agents give a considerable lube-oil yield increase; especially effective are the additions of metallic aluminum (in form of dust or "gravel", preferably activated), silica gel and, under certain circumstances also zinc dust or zinc chloride; phosphorus pentoxide was also found to be advantageous in one instance. However, the increased yield is often obtained at the expense of a viscosity index drop (Table X).

The choice of a particular set of polymerization conditions affects mainly the lube-oil yields; the boiling range of the cracked distillates, on the other hand, affects mainly the lube-oil quality. The highest quality carriers are the higher boiling cracked product fractions, if the viscosity index be used as standard for comparison. As shown by the results tabulated in Table XII, the lube-oils obtained by the polymerization of cracked distillates of different boiling range, can show V.I. differences amounting to more than 25 V.I. units!

Experiments were made for the purpose of utilizing, either directly or by further processing, the by-products which are formed during the preparation of lubricating oils. The following results were obtained:

1. Copolymerization of the Olefin-Containing Cracked Gases

Passing the cracked gases (which contain anywhere from 20-45% olefins, depending on the experimental conditions) through during the normal pressure polymerization process, showed that propylene and the butylenes (ab. 15-30% by volume of the cracked gas) are taken up almost completely, whereas practically no ethylene is taken up. The lube oil yield is not appreciably affected, but in most cases the oils are more viscous and their viscosity index is lowered (See Table VI).

2. Further Processing of the Cracking Residue Oils

Discontinuous cracking of any initial stock results, after progressive cracking, in the formation of a cycle product whose characteristic values (Iodine number, specific weight, aniline point, hydrogen content, etc.) will slowly draw farther and farther apart from the corresponding values of the fresh stock. If it is processed, by further cracking, into a lube-oil, this will be of poorer quality (Table XIII). Therefore, in continuous operation experiments, the cycle oil must not be permitted to exceed a certain level; this can be done by continuous drawing off of some cycle oil during the process. The hydrogen-lean and cyclized product must be passed back to the hydrogenation, unless one prefers to subject it to further cracking for the obtaining of antiknock gasoline. Residue No. 6434, when subjected to discontinuous cracking, gave cracked gasolines which, despite their practically equal boiling range and olefin content, gave

antiknock values which increased progressively with the experiment (68 - 72).

3. Re-Cracking of the Lube Oil First Runnings (Table XIII)

The gasolines, middle oils and spindle oils which are obtained (besides lube oil) by the polymerization process, can again be cracked. The lube oils which are thus obtained are of inferior quality. It is therefore not advisable to take such first runnings in any considerable amounts and crack them together with the initial product for the purpose of getting lube oil. The components boiling, say, above 200°C, can be conveniently utilized as high quality Diesel oil, since oils stemming from paraffins have excellent ignition capacity and low pour points (down to -70° and less) (See report Dr. Bahr and Kolb, dated 24 October 1938, loc. cit.).

4. Processing of the Oil-Components of the AlCl₃ Sludge

The undecomposed aluminum chloride sludge can be used again as condensing agent, either alone or in mixture with fresh aluminum chloride. However, the quality of the lube oil is affected in some cases (See exp. 17, Table 6). The olefinic oils obtained by decomposing the aluminum chloride sludge with water have, to a greater or lesser extent, the characteristics of drying oils. A factor which would render difficult their use as such, either alone or in mixture with others, is their dark color. By hydrogenation, not only gasoline and middle oil, but also a usable lube-oil can be obtained. Depending on the conditions of hydrogenation, the following products could be recovered from the stock shown below:

| | | |
|------------------------------|------------------|----------------------------------|
| from: Hard-paraffin Riebeck: | ab. 50% lube-oil | (VI = 80-100; I-No = 2-8) |
| Residue 5058 | : ab. 60-70% | " (VI = 5 - 45, I-No 10-45) |
| Residue 6434 | : ab. 25% | " (VI = 50 - 80, I-No 0-10)2) |

2) Note: At higher lube oil I-number, the lube oil yield increases up to about 50%, the VI drops down to about 30.

These lubricating oils correspond essentially to those obtained from the upper layer of the polymerized product; in some cases, they are even superior to them.

5. Processing of the Lube Oil First Runnings

(By chlorination and condensation of the chlorides with cracked distillates under the influence of aluminum chloride and activated aluminum.)

Nicely fluorescent lube-oils are obtained with high yield. However, their viscosity index is greatly lowered as compared to that of the oils obtained from the cracked distillate alone; furthermore, it has not been possible to free them entirely from chlorine.

III. Experiments for the Improvement of the Lube Oils

Experiments for the improvement of the quality of the lubricating oils can be made with the initial stock, the intermediate products and the end product.

As to the dependence of the oil-quality on the conditions of polymerization and on the cracked products (and their fractions), the results are given in Tables VII - XII. Exhaustive experiments for the improvement of the finished lubricating oils (for instance by extraction), have not been made. Preliminary "orienting" experiments with oils of inferior quality (i.e. of poor viscosity index) gave no particularly outstanding results which might have warranted further investigation. Apparently, the synthetically prepared lube oil consists of uniformly built molecules which, in contrast to the petroleum lubricants, cannot be decomposed (by suitable methods) into components of different characteristic properties. Therefore, if mixed-base initial stock should be used, its decomposition would be more promising.

1. Extraction

It is known, and it has also been very clearly confirmed in our tests, that the paraffin base of the initial stock is the most necessary prerequisite for a high quality oil*. The hydrogenation products examined during the course of these experiments meet this requirement only partially; the extent to which they lead to inferior quality oils can be attributed to their high naphthenic content.

* See: Reports of the Ammonia Lab., Oppau. - More recent observations have also established structural effects in the paraffin or olefin molecule; these effects can be more or less pronounced.

TABLE XIII

POLYMERIZATION OF CRACKED DISTILLATES FROM CRACKING RESIDUE OILS INTO LUBE OIL
 POLYMERIZATION OF CRACKED DISTILLATES FROM LUBE OIL FIRST RUNNINGS INTO LUBE OIL

| S T O C K | CRACKED DISTILLATE | | | | | POLYMERIZATION | | LUBE OIL | | A N A L Y S I S | | | | | |
|--|------------------------|--------------------|-----------------------------|-----|-----|----------------|----------------------------|---------------------------|-----------------------------|--------------------|------|----------|-------------|----------|------------------|
| | % by Wt. of Conversion | Iodine No. (Hanus) | Boiling Range IBP 50% EP | | | Temp. °C. | % by Wt. AlCl ₃ | Yield, Cracked Distillate | % by Wt. of Converted Stock | Visc. °S. at 50°C. | V.I. | Pour Pt. | Flash Point | Coking % | Spec. Wt. at 20° |
| Residue 5058 d = .80, original | 75.2 | 170 | 46 | 161 | 219 | 120 | 10 | 30.0 | 22.6 | 26.7 | +9 | -18 | 197 | 0.35 | 0.906 |
| Cracked Residue Oils 14.8% by Wt. of Original | 67.5 | 170 | 32 | 125 | 210 | 120 | 10 | 27.2 | 18.4 | 44.6 | -107 | -13 | 183 | 0.21 | - |
| Lube Oil First Runnings above 180°F. | 66.9 | 182 | 37 | 144 | 203 | 120 | 5 | 31.5 | 21.1 | 48.2 | -31 | -15 | 200 | - | 0.905 |
| Lube Oil First Runnings below 180°F. | 50.5 | 150 | 31 | 80 | 134 | 90 | 5 | 20.8 | 10.5 | 58.7 | -40 | - | 169 | - | 0.911 |
| Hard Paraffin Riebeck, original | 82.7 | 171 | 34 | 123 | 245 | 120 | 8 | 51.9 | 43.0 | 0.2 | +115 | -18 | 202 | 0.13 | - |
| Cracked Residues 18% by Wt. of Original | 77.8 | 180 | 34 | 150 | 252 | 120 | 10 | 33.5 | 26.1 | 7.9 | +89 | - | 209 | - | 0.873 |
| Lube Oil First Runnings under 180° | 46.7 | 150 | 32 | 84 | 143 | 90 | 5 | 27.5 | 12.9 | 34.9 | +35 | - | 190 | - | 0.892 |

Extraction experiments with solvents such as methanol, SO₂-containing methanol, furfural, benzyl-alcohol, Chlorex (BB'-dichloro-diethyl ether), glycol monoacetate etc., showed that it is relatively easy to separate the paraffins from the phenols, aromatics and cyclo-olefins, but that it is not possible (or only to a very small extent), to separate them from the naphthenes. Even the multi-stage extraction of pure naphthenic/paraffinic mixtures gave selectivity effects which could only be noticed by a very small difference of a few degrees centigrade in the aniline point. And even this difference can be questionable, since it may be caused by the simultaneous shifting of the boiling range between "refined-" and "extract-" component. It appears that the higher-boiling oils which as such would have a greater tendency towards extraction, contain naphthenes with rather long aliphatic side chains which have a "paraffinic" behaviour towards the selective extracting agents. It is for this reason that the Leuna gas phase middle oils cannot readily be decomposed into paraffinic and non-paraffinic components whereas this can be easily done with the aromatic A-middle oils.

2. "Selective" Cracking

It is a known fact that paraffins are split more easily than naphthenes, and naphthenes more easily than aromatics*.

As far as we know, no attempt has yet been made to crack the paraffinic components of a mixed-base hydrocarbon oil, by mild cracking at the lowest possible temperature, with the purpose of getting better quality oils than are obtained by the usual drastic cracking methods. As will appear from the experiments described further on, such selective effects can be obtained, to a certain extent, when using a lead bath as heat-carrying medium, and operating at high throughput rates and low temperatures.

The model-substance chosen by us was residue No. 6434 and stripped charge oil with about 10 - 15% paraffin hydrocarbons.

Experiment 1: 120 kg of residue 6434 were cracked batch-wise at 520°, at a pressure of 40 atm and a throughput rate of 155 liters/hr.; no fresh product was added, and the non-cracked or insufficiently cracked oil-components were refluxed. The cracked distillates were drawn off by stages, examined individually and then subjected to polymerization (Table XIV).

Experiment 2: Batches of 60 kg of residue 6434 were cracked continuously in separate experiments; the pressure was 40 atm, and the throughput 155 liters/hr.; the converted product was replaced, and the temperature conditions were varied. Un-

* Trusty, Nat. Petr. News, 27, No. 45, 34-38; Refiner, 11, No. 9, p. 174

cracked or insufficiently cracked oil components were refluxed. The cracked distillate was drawn off by stages, examined individually and then subjected to polymerization (Table XV).

Experiment 3: 140 kg of stripped charge oil were cracked at 510°, 40 atm. pressure and at a throughput rate of 210 liters/hr.; the process was discontinuous and no fresh product was added during the experiment; the uncracked or insufficiently cracked oil components were refluxed. The cracked distillates were drawn off by stages, examined individually and then subjected to polymerization (Table XVI).

From Tables XIV, XV and XVI, the following conclusions may be drawn:

1. Discontinuous (i.e. batch-wise) cracking of the above mentioned mixed-base stocks gives, despite the fact that the experimental conditions remain the same, a type of cracked distillates which, upon polymerization, yield lubricating oils whose quality declines as the cracking progresses.
2. The "selective" effect of milder cracking temperatures is noticed in the continuous experiments, inasmuch as the cracking gives better oils at lower temperatures, poorer ones at higher temperature.
3. The lube-oil yield, based on the conversion of fresh product, in general remains approximately constant, regardless of whether the operation is continuous or discontinuous.
4. As the cracking progresses (i.e. as the cracking temperature increases), the drop in oil quality can be noticed by the decreasing viscosity index and flash point, and quite often, by the increase in pour point and coking test.

The processing of the mixed-base stocks which, upon cracking the high conversion, yield oils of poor or only fair viscosity index, could be operated so that the cracking occurs with a lower overall conversion and with lowest conversion per pass. The remaining residual oils of low paraffin content (as compared to the initial paraffin content) could then be converted into antiknock gasolines either by further cracking or by hydrogenation.

TABLE XIV
DISCONTINUOUS CRACKING OF RESIDUE 6434, AT 520°C. AND 40 ATM., AND POLYMERIZATION
OF THE CRACKED DISTILLATE INTO LUBE OIL

| CRACKING | | | CRACKED DISTILLATE | | | | | | | | CRACKED GAS | | LUBE OIL | | | | | | |
|--------------|----------------|-----------------------------|--------------------|---------------------|-------------------------|--------------------------|---------------|-----|-----|---------------------|-------------------------|-------------------|----------------------------|-------------------------|----------------------|-------|-------------|----------------|-------------|
| Temp. °C. | Press. Atm. | Conver- sion % by Wt. | No. | Prod- uct Kg. | % of Conver- sion | Iodine No. (Hanus) | Boiling Range | | | Aniline Pt., °C. | % of Conver- sion | Vol. % Olefins | Yield, % by wt. of: | | | | | | |
| | | | | | | | IBP | 50% | BP | | | | Cracked Distil- late | Con- verted Stock | Visc. at 50°C. | V.I. | Pour Pt. | Flash Point | Coking % |
| 520 | 40/38 | 7.7 | 1 | 7.6 | 82.5 | 75 | 46 | 144 | 186 | 0.757 | 43.4 | 17.5 | 12 | 9.9 | 10.2 | +78 | -38 | 227 | 0.005 |
| 520 | 40/38 | 14.1 | 2 | 5.95 | 77.2 | 121 | 40 | 150 | 184 | 0.748 | 42.2 | 22.8 | 22.5 | 17.4 | 10.8 | +71.5 | -36 | 206 | 0.03 |
| 520 | 40/38 | 21.7 | 3 | 6.6 | 76.5 | 145 | 40 | 149 | 200 | 0.748 | 39.5 | 23.5 | 27 | 20.7 | 13.4 | +67 | -32 | 201 | 0.08 |
| 520 | 40/38 | 27.5 | 4 | 5.15 | 75.7 | 156 | 38 | 142 | 194 | 0.743 | 37.5 | 24.3 | 25 | 19.0 | 9.3 | +62 | -35 | 198 | 0.11 |
| 520 | 40/38 | 33.7 | 5 | 5.5 | 74.7 | 162 | 38 | 142 | 195 | 0.744 | 36.4 | 25.3 | 30.5 | 22.8 | 11.7 | +64 | -34 | 195 | 0.08 |
| 520 | 40/38 | 42.7 | 6 | 7.9 | 73.5 | 165 | 38 | 148 | 190 | 0.747 | 36.0 | 26.5 | 31 | 22.8 | 13.7 | +62 | -33 | 185 | 0.09 |
| 520 | 40/38 | 50.0 | 7 | 6.5 | 75.5 | 171 | 38 | 134 | 190 | 0.739 | 34.2 | 24.5 | 40 | 30.2 | 10.6 | +58 | -32 | 185 | 0.18 |

TABLE XV

CRACKING OF RESIDUE 6434 AT 40 ATM., AT INCREASING TEMPERATURES AND WITH REPLACEMENT OF THE CONVERTED PRODUCT BY FRESE STOCK - POLYMERIZATION OF THE CRACKED DISTILLATES TO LUBE OIL

| CRACKING | | C R A C K E D | | | | | D I S T I L L A T E | | | | CRACKED GAS | | L U B E O I L | | | | | | |
|-----------|-------------|---------------|-------------|------------------|--------------------|-------------------|---------------------|-----|-----------------|----------|------------------|-------------------|---|-----------------|---------------|-------|----------|-------------|----------|
| Temp. °C. | Press. Atm. | No. | Prod-uct Kg | % of Conver-sion | Iodine No. (Hanus) | Boiling Range IBP | 50% | EP | d ₂₀ | A.F. °C. | % of Conver-sion | % by Vol. Olefins | Yield, in % by wt. of: Cracked Distillate | Converted Stock | Visco. at 50° | V.I. | Pour Pt. | Flash Point | Coking % |
| 500 | 40 | 1 | 2.75 | ab 82.5 | 130.5 | 42 | 122 | 190 | 0.735 | 41.5 | ab 17.5 | - | 28.5 | ab 23.6 | 9.5 | +64 | -31 | 195 | Grade |
| 500 | 40 | 2 | 1.82 | ab 81.5 | 147 | 40 | 120 | 183 | 0.728 | 39.8 | ab 18.5 | 35.8 | 31.5 | ab 25.7 | 8.5 | +62.5 | -34 | 185 | 0.16 |
| 500 | 40 | 3 | 2.0 | 81.6 | 137 | 40 | 133 | 194 | 0.734 | 41.2 | 18.4 | 37.6 | - | - | - | - | - | - | - |
| 538 | 40 | 1 | 7.9 | ab 73 | 181 | 38 | 111 | 168 | 0.730 | 31.8 | ab 27 | ↓ | 36.7 | 26.8 | 9.8 | +60.5 | -35 | 183 | 0.07 |
| 538 | 40 | 2 | 11.8 | 71.2 | 173 | 44 | 137 | 186 | 0.744 | 33.2 | 28.8 | ↓ | 34.0 | 24.2 | 10.0 | +59.5 | -34 | 182 | 0.12 |
| 538 | 40 | 3 | 9.6 | 71.1 | 163.5 | 38 | 136 | 180 | 0.744 | 31.6 | 28.9 | ↓ | 34.4 | 24.5 | 11.1 | +56 | -31 | 188 | 0.12 |
| 540 | 40 | 4 | 10.1 | 71.3 | 171 | 40 | 140 | 190 | 0.744 | 31.8 | 28.7 | 39.8 | 36.4 | 26.0 | 10.0 | +53.5 | -30 | 182 | 0.12 |
| 550 | 40 | 1 | 42.9 | 74.9 | 160 | 47 | 150 | 197 | 0.758 | 32.4 | 25.1 | ↓ | 32.5 | 24.4 | 9.7 | +46 | -34 | 183 | - |
| 550 | 40 | 2 | 6.1 | 77.2 | 162 | 42 | 153 | 203 | 0.755 | 33.5 | 22.8 | ↓ | 33.6 | 25.2 | 12.7 | +49 | -36 | 188 | 0.09 |
| 545 | 40 | 3 | 11.7 | 75.9 | 160.5 | 42 | 155 | 207 | 0.757 | 33.8 | 24.1 | 40.0 | 30.6 | 23.3 | 10.9 | +41 | -31 | 183 | 0.10 |

TABLE XVI

DISCONTINUOUS CRACKING OF TOPPED CHARGE, AT 510° AND 40 ATM;
POLYMERIZATION OF THE CRACK DISTILLATES INTO LUBE OIL

| CRACKING | | | CRACKED DISTILLATE | | | | | | | CRACKED GAS | | LUBE OIL | | | | | | |
|--------------|----------------|-----------------------------|--------------------|--------------------|--------------------------|--------------------------|---------------|-----|-----|--------------------------|-------------------|-----------------------|--------------------|--------------------|------|-------------|----------------|-------------|
| Temp. °C. | Press. Atm. | Conver- sion % by Wt. | No. | Prod- uct Kg | % of* Conver- sion | Iodine No. (Hanus) | Boiling Range | | | % of* Conver- sion | Vol. % Olefins | Yield, wt. % of: | | Visc. at 50° | V.I. | Four Pt. | Flash Point | Coking % |
| | | | | | | | IBP | 50% | EP | d20° | | Cracked Distillate | Converted Stock | | | | | |
| 508 | 40 | 8.2 | 1 | 3.00 | 26.1 | 133 | 41 | 106 | 180 | 0.745 | 13.4 | 22.0 | 5.7 | 12.5 | +31 | -34 | 195 | 0.11 |
| 512 | 40 | 11.7 | 2 | 2.58 | 38.8 | 133.5 | 58 | 142 | 191 | 0.774 | 18.7 | 18.0 | 7.0 | 10.6 | -10 | -26 | 187 | 0.30 |
| 510 | 40 | 16.5 | 3 | 2.36 | 36.6 | 119.5 | 49 | 138 | 192 | 0.771 | 21.6 | 18.5 | 6.8 | 12.4 | -13 | -20 | 194 | - |
| 510 | 40 | 21.1 | 4 | 2.48 | 33.3 | 121 | 50 | 143 | 186 | 0.768 | 18.6 | 23.0 | 7.7 | 11.9 | -15 | -23 | 187 | 0.37 |
| 508 | 40 | 28.2 | 5 | 2.38 | 32.6 | 121 | 53 | 150 | 191 | 0.773 | 17.4 | 20.5 | 6.7 | 10.3 | -28 | -22 | 192 | - |

*The amount of tar taken out during the experiment, expressed in % by weight of the conversion, is calculated from the sum cracked distillate + cracked gas (% of conversion) subtracted from 100.

SUMMARY

1. It has been shown that the thermal pressure cracking of hydrogenation products can be used successfully for the preparation of olefinic cracked distillates.
2. These cracked distillates, when subjected to polymerization with aluminum chloride or similar substances, give useful automobile lubricants which meet all normal requirements.
3. Their properties are, in all cases, equal to those (oils) which are derived from the normal-pressure cracked distillates. With mixed-base initial stock, they are superior to the oils derived from the non-pressure cracking.
4. The lowered lube oil yield (based on the cracked distillate) which corresponds to the lower olefin content, is compensated by the higher cracked distillate yield which is obtained in the pressure cracking, as opposed to the non-pressure cracking.
5. The strongly unsaturated oils stemming from the aluminum chloride polymerization sludge, when subjected to hydrogenation, give lubricating oils of equal and sometimes superior quality (as compared to those obtained in the usual processes).
6. Experiments to subject only the paraffinic "raffinates" (obtained by extraction of paraffinic/naphthenic oils) to cracking and conversion into lube-oils, failed because these oils are not sufficiently decomposable.
7. However, by "selective" cracking of these oils, mainly paraffinic components could be cracked, at least to a certain extent.
8. These cracked distillates, when subjected to polymerization, give better lubricating oils than those derived from more drastic, and therefore less selective, operating methods.

This work was begun in June 1937 and concluded in October 1938.

Signed /BAHR/ /KOLB/

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Translated by: Bernard Rosenthal (Independent Translator)
Edited by: V. H. Kane (Chem. Eng., TCo.)