

Naval Technical Mission,  
Reel 5820, Attachment V

THE ETHYLENE LUBE OIL SYNTHESIS;  
ITS DISCOVERY AND TECHNICAL DEVELOPMENT

by H. Zorn and coworkers

CONTENTS

|   | <u>Page</u> |
|---|-------------|
| Part I  |             |
| Discovery and Laboratory Scale Development. . . . .         | 1           |
| Polymerization of Propylene. . . . .                        | 2           |
| Polymerization of Ethylene . . . . .                        | 8           |
| Studies with Aluminum Alkyl Halide. . . . .                 | 12          |
| Catalytic Influence of Construction Material. . . . .       | 14          |
| Composition of Various Steels . . . . .                     | 16          |
| Quantity and Kind of Solvent. . . . .                       | 18          |
| Influence of Stirring Speed . . . . .                       | 21          |
| Influence of AlCl <sub>3</sub> Concentration. . . . .       | 21          |
| Temperature Effects . . . . .                               | 22          |
| Depolymerization. . . . .                                   | 24          |
| Material Balance of Process . . . . .                       | 25          |
| Part II   |             |
| Commercial Ethylene Polymerization Plants at Leuna. . . . . | 27          |
| A. The 700 Ton/Year SS 903 Plant . . . . .                  | 27          |
| Depolymerization . . . . .                                  | 29          |
| Vacuum Distillation. . . . .                                | 30          |
| B. The 3000 Ton/Year SS 906 Plant. . . . .                  | 30          |
| General Description of the Process. . . . .                 | 31          |
| I. Polymerization . . . . .                                 | 31          |
| a. Stirring. . . . .  | 31          |
| b. Autoclave Material. . . . .                              | 32          |
| c. Gas . . . . .  | 33          |
| The Water Absorption and Drying of Ethylene . . . . .       | 34          |
| d. Aluminum Chloride . . . . .                              | 36          |
| e. Initial Charge. . . . .                                  | 42          |
| f. Polymerization Course . . . . .                          | 43          |
| Operating Experience in the Polymerization Process. . . . . | 46          |
| Influence of Autoclave Construction on Process. . . . .     | 48          |
| II. Finishing the Crude Polymer . . . . .                   | 56          |
| a. Old Method. . . . .                                      | 56          |
| b. Present Method. . . . .                                  | 57          |
| c. Treating Procedure. . . . .                              | 60          |
| d. Corrosion Control . . . . .                              | 61          |
| III. Distillation. . . . .                                  | 62          |
| IV. Refining. . . . .                                       | 66          |
| V. Residual Oil Treatment. . . . .                          | 67          |
| VI. Experiments on After Treatment of SS Oil. . . . .       | 70          |
| VII. Survey of Leuna Production 1938/1943. . . . .          | 73          |
| VIII. Specifications for Products . . . . .                 | 76          |

ATTACHMENT V

THE ETHYLENE-LUBE OIL SYNTHESIS  
ITS DISCOVERY AND TECHNICAL DEVELOPMENT

by H. Zorn and coworkers

Part I deals with the discovery and laboratory scale development of lube oil synthesis from ethylene. This work, carried out in 1934-7, was the basis for the construction in 1936 of a pilot plant at Leuna for the production of 700 T/yr. of lube oil SS903. Part II is devoted to a discussion of this pilot plant. On the basis of results obtained on a semiplant scale, plants were erected in 1941 in Schkopau, Heydebreck, Moosbierbaum and Leuna.

Part I

The laboratory development of this process evolved from studies of the  $AlCl_3$ -catalyzed polymerization of gaseous olefins from high pressure hydrogenation of coal tar. Allenet's patent (DRP 402990) on the polymerization of olefins to liquid hydrocarbons by means of a suspension of  $AlCl_3$  in petroleum ether served as a starting point. McAfee's work (USP 1608329) also showed that lube oils were produced from olefins in cracked petroleum fractions. He recommended adding  $H_2$  with the cracked gases to increase catalyst life and suppress coke formation. The McAfee process was applied to coal tar fractions by Fabrik Weyl & Company (IRP 341686), and at Oppau it was applied to oil from high pressure hydrogenation of coal tar.

A semi-scale plant was constructed at Oppau in 1929 to polymerize olefins, which were obtained by cracking of hydro plant waste gases at  $800^\circ C$ . A lube oil of the following properties was obtained:

|                          |       |             |               |
|--------------------------|-------|-------------|---------------|
| Sp. Gr. ( $20^\circ C$ ) | 0.947 | V.I.        | -18           |
| Visc. °E $20^\circ C$    | 90.4  | M           | 4.37          |
| Visc. °E $38^\circ C$    | 20.5  | VP          | 4.61          |
| Visc. °E $50^\circ C$    | 9.3   | Flash Point | $193^\circ C$ |
| Visc. °E $99^\circ C$    | 1.8   | Pour Point  | $-19^\circ$   |
|                          |       | Kokstest    | 0.08          |

The work was discontinued in 1931 but was resumed in 1932-34. At that time the gas phase cracking of paraffin was being investigated, and it was found that liquid as well as gaseous olefins from this process could be converted to lube oils.

In preliminary experiments cracked gases were led into a 3-necked flask containing a stirred suspension of  $AlCl_3$  in ligroin. Absorption of olefins sets in even at low temperature, as shown in Table I:

| Date  | Exp.No. | Ligroin | $AlCl_3$ | Temp.      | Time | Feed | Resid. Gas | Absorbed Gas |
|-------|---------|---------|----------|------------|------|------|------------|--------------|
| 1932  | KV      | g.      | g.       | $^\circ C$ | hrs. | l.   | l.         | g.           |
| 11/15 | 9       | 200     | 50       | 80         | 3.5  | 151  | 114        | 41           |
| 11/3  | 7       | "       | "        | 70         | 4    | 153  | 94         | 47           |
| 10/28 | 5       | "       | "        | 50         | 4    | 150  | 105        | 59           |
| 11/1  | 6       | "       | "        | 50         | 6.5  | 150  | 103        | 61           |
| 12/21 | 12      | "       | "        | 40         | 2.25 | 152  | 112        | 59           |
| 12/19 | 11      | "       | "        | 30         | 4.75 | 150  | 110        | 27           |
| 11/11 | 8       | "       | 5x10     | 70         | 5.25 | 156  | 119        | 29           |

Olefins in the cracked gas were about 55%, in the residual gas about 35%. Recirculation of the residual gas led to no further absorption (Expt. No. 6). A material balance for Expt. 6 is as follows:

Table 2

|                                | Feed (150 l.)<br>Vol. % | Residual Gas (103 l.)<br>Vol. % |
|--------------------------------|-------------------------|---------------------------------|
| CO <sub>2</sub>                | 0.00                    | 0.00                            |
| O <sub>2</sub>                 | 0.00                    | 0.00                            |
| CO                             | 0.41                    | 0.11                            |
| H <sub>2</sub>                 | 3.14                    | 4.41                            |
| C <sub>2</sub> H <sub>4</sub>  | 35.50                   | 24.30                           |
| C <sub>3</sub> H <sub>6</sub>  | 12.10                   | 3.79                            |
| C <sub>4</sub> H <sub>8</sub>  | 4.20                    | 1.07                            |
| C <sub>5</sub> H <sub>10</sub> | 0.35                    | 0.85                            |
| CH <sub>4</sub>                | 23.15                   | 31.00                           |
| C <sub>2</sub> H <sub>6</sub>  | 16.33                   | 24.50                           |
| C <sub>3</sub> H <sub>8</sub>  | 3.67                    | 7.30                            |
| C <sub>4</sub> H <sub>10</sub> | 1.01                    | 1.81                            |
| C <sub>5</sub> H <sub>12</sub> | 0.06                    | 0.85                            |

Olefins Absorbed

|                               | g.   | % Absorption |
|-------------------------------|------|--------------|
| C <sub>2</sub> H <sub>4</sub> | 22.9 | 34           |
| C <sub>3</sub> H <sub>6</sub> | 26.8 | 79           |
| C <sub>4</sub> H <sub>8</sub> | 13.0 | 83           |

Table 3 shows some results obtained in 1934 in a somewhat larger apparatus under 2 atmospheres pressure:

Table 3

| Exp. No. | Ligroin l. | AlCl <sub>3</sub> g. | Duration hrs. | Gas Rate l./hr. | Temp. °C | Product° |      |      |
|----------|------------|----------------------|---------------|-----------------|----------|----------|------|------|
|          |            |                      |               |                 |          | g.       | E°99 | VI   |
| 90       | 7.6        | 1000                 | 16            | 720             | 70       | 2450     | 1.69 | 67.4 |
| 87       | 10         | 1000                 | 10            | 500             | 80       | 1920     | 1.59 | 39.2 |
| 88       | 10         | 1000                 | 6             | 400             | 80       | 1550     | 1.49 | 29.3 |
| 89       | 8.9        | 1000                 | 6             | 4000            | 70       | 1300     | 1.44 | 17.2 |

\* Product boiled above 170°C at 1 mm.

The varying quality of product in these runs led to the more fundamental study of polymerization of pure olefins.

Polymerization of Propylene

Propylene was first investigated because of its easy availability. The apparatus consisted of a 2 liter 3-neck glass flask equipped with stirrer, thermometer and condenser. Very efficient stirring (700 rpm) was obtained. Operating conditions were as follows:

Temp, 60-65°C  
 Flow Rate 32 l./hr.  
 Solvent 300 g.  
 AlCl<sub>3</sub> 30 g.

Table 4 shows how the properties of the propylene polymer are affected by the choice of solvent: (All polymer properties obtained on fraction boiling above 170°C at 1 mm.)

Table 4

| Exp. No. | Kind of Solvent  | Viscosity °E |      |      |
|----------|--|--------------|------|------|
|          |  | 38°          | 99°  | VI*  |
| 25       | Ligroin  | 51.2         | 2.54 | 10.1 |
| 46       | Petroleum  | 52.5         | 2.70 | 29.7 |
| 47       | Pet. Ether   | 51.2         | 2.52 | 5.8  |
| 48       | Normal Benzin  | 96.2         | 3.35 | 10.7 |
| 27       | Nitrobenzene   | 9.28         | 1.58 | 28.0 |
| 120      | Dichlorbenzol  | 93.2         | 3.34 | 16.0 |
| 24       | 60°/130° Hydrog. Cracked Paraffin                        | 85           | 3.37 | 31.4 |
| 45       | >200° Hydrog. Cracked Paraffin                           | 27.4         | 2.37 | 75.0 |
| 52       | Paraffin m.p. 52°  | 27.5         | 2.30 | 65.5 |
| 37       | >200°C Hydrog. Cracked Paraffin                          | 78.1         | 3.39 | 45.2 |
| 142      | Polymer from Run 45                                      | 122          | 4.26 | 46.3 |
| 124      | Forerunnings from C <sub>3</sub> H <sub>6</sub> -Polymer | 80.5         | 3.66 | 60   |
| 70       | n-C <sub>8</sub> H <sub>18</sub>                         | 90.3         | 3.53 | 37.4 |
| 71       | i-C <sub>8</sub> H <sub>18</sub>                         | 79.5         | 3.25 | 29.8 |
| 72a      | n-C <sub>12</sub> H <sub>26</sub>                        | 100          | 3.83 | 45.2 |
| 73       | i-C <sub>12</sub> H <sub>26</sub>                        | 91.5         | 3.58 | 40.0 |
| 58       | >150°C Hydrog. Cracked Paraffin                          | 28.2         | 2.32 | 65.2 |
| 58a      | Solvent Dist. from Run 58                                | 54.0         | 2.94 | 54.0 |
| 58b      | Solvent Dist. from Run 58a                               | 74.0         | 3.41 | 54.0 |

\* VI values were determined according to Dean & Davis, Chem. Met. Eng. 36, 618 (1929). Viscosities were measured in a Vogel-Ossag instrument.

Table 4 shows that VI of product seems to increase with increasing boiling point of hydrocarbon solvents. (Note the high VI obtained with hard paraffin as solvent.) The reason for the profound effect of solvent is the mixed polymerization (alkylation) of the solvent with olefin, the so-called conjoint polymerization of Ipatiev. Thus, the isoparaffins in Table 4 reacted more readily than the normal paraffins, while the VI's are lower for the more highly branched paraffins. This concept of lower VI for the more highly branched product explains the variation in VI with b.p. of paraffinic solvent, the comparison of iso and n compounds as solvents, and the use of polymer itself as solvent. In the latter case the branching of the C chain of the polymer is increased.

Influence of gas velocity, amount of AlCl<sub>3</sub>, amount of solvent and temperature on product quality are shown in Table 5, in which the solvent is a >125°C fraction from the hydrogenation of cracked wax recovered from a previous experiment.

Table 5

| Exp. No. | Solvent<br>l. | Temp.<br>°C | AlCl <sub>3</sub><br>g. | Gas Flow<br>l./hr. | Poly. Prod.<br>in 6 hr., g. | Viscosity °E* |       |      |
|----------|---------------|-------------|-------------------------|--------------------|-----------------------------|---------------|-------|------|
|          |               |             |                         |                    |                             | 38°           | 99°   | VI   |
| 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 |
| 40       | "             | "           | 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 |
| 56a      | 150           | "           | 30                      | "                  | 300                         | 44.7          | 2.68  | 51.8 |
| 58       | 300           | "           | "                       | "                  | 320                         | 28.2          | 2.32  | 65.2 |
| 57a      | 600           | "           | "                       | "                  | 313                         | 31.4          | 2.41  | 65.5 |
| 75       | 300           | 20          | "                       | "                  | 337                         |               | 17.3  | 72   |
| 74       | "             | 38          | "                       | "                  | 328                         | 61.2          | 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 |
| 91       | "             | 1/2 hr. 90° | 5-1/2 hr. 40°           | "                  | 281                         | 280           | 6.88  | 46   |
| 94       | "             | 40°         | 90°                     | "                  | 186                         | 49.5          | 2.68  | 36.3 |

\* Viscosities obtained on fraction b. >170°C at 1 mm.

This table shows that (1) propylene feed rate is without effect, (2) excessive quantity of AlCl<sub>3</sub> causes poor VI, (3) above a certain point quantity of solvent is unimportant, and (4) high temperatures produce less viscous polymers of poorer VI and poorer yield.

In Table 6 are listed experiments in which various types of promoters were added to the AlCl<sub>3</sub>. Conditions, except as noted, were similar to the "standard" conditions in Table 5.

Table 6

| Exp. No. | AlCl <sub>3</sub><br>g. | Promoter          |            | Temp.<br>°C | Poly. Prod.<br>in 6 hr., g. | Visc. of >170° Prod. |      |      |
|----------|-------------------------|-------------------|------------|-------------|-----------------------------|----------------------|------|------|
|          |                         | Kind              | Amount, g. |             |                             | 38°                  | 99°  | VI   |
| 80       | 30                      | ZnCl <sub>2</sub> | 6          | 40          | 303                         | 610(?)               | 14.5 | 71   |
| 84       | "                       | "                 | 15         | "           | 311                         | 263                  | 7.21 | 65   |
| 89       | "                       | "                 | 15         | 60          | 253                         | 101                  | 3.43 | 12.6 |
| 83       | "                       | NaCl              | 10         | 40          | 330                         | 202                  | 6.43 | 66   |
| 85       | "                       | "                 | 80         | "           | 327                         | 248                  | 6.94 | 65   |
| 102      | "                       | SiCl <sub>4</sub> | 1.5        | 60          | 279                         | 98.6                 | 3.61 | 31.4 |
| 103      | "                       | TiCl <sub>4</sub> | 1.5        | "           | 259                         | 117                  | 4.04 | 38.7 |
| 96       | "                       | FeCl <sub>3</sub> | 1          | "           | 268                         | 107                  | 3.83 | 36.2 |
| 121      | "                       | "                 | 15         | "           | 262                         | 170                  | 5.02 | 41.0 |
| 106      | "                       | Fe powder         | 30         | "           | 201                         | 101                  | 4.04 | 55.4 |
| 200      | "                       | "                 | 10         | "           | 216                         | 117                  | 4.48 | 63.0 |
| 204      | "                       | FeS               | 1          | "           | 204                         | 78.6                 | 3.37 | 25.9 |
| 155      | "                       | Tonsil AC         | 5          | "           | 127                         | 64.8                 | 2.92 | 26.5 |
| 131      | "                       | Hg                | 5          | "           | 328                         | 103.4                | 3.85 | 42.2 |

Evidently none of these additives improved the product and some were definitely deleterious. The effect of water on the catalytic action of  $\text{AlCl}_3$  was also investigated and is reported in Table 7.

Table 7

| Exp. No. | $\text{AlCl}_3$<br>g. | $\text{H}_2\text{O}$<br>g. | Temp.<br>°C | Duration<br>hrs. | Poly. Prod.<br>g. | Visc. of >170°C Prod. |      |         |
|----------|-----------------------|----------------------------|-------------|------------------|-------------------|-----------------------|------|---------|
|          |                       |                            |             |                  |                   | 38°                   | 99°  | VI      |
| 86       | 30                    | -                          | 60          | 6                | 350               | 126.2                 | 4.37 | 47.2    |
| 69       | "                     | -*                         | "           | "                | 288               | 122.5                 | 4.04 | 32.4    |
| 68       | "                     | 0.1                        | "           | "                | 318               | 94                    | 3.72 | 46.8    |
| 87       | "                     | 1.0                        | "           | "                | 296               | 134                   | 4.53 | 50.0    |
| 88       | "                     | 2                          | "           | "                | 271               | 88.1                  | 3.88 | 63.5    |
| 122      | "                     | 3                          | "           | "                | 276               | 97.5                  | 3.88 | 52.5)   |
| 123      | "                     | 4                          | "           | "                | 268               | 94.5                  | 3.61 | 36.1)** |
| 128      | "                     | 5                          | "           | 4-1/4            | 183               | 77.1                  | 3.27 | 36.6)   |

\* Solvent dried with Na.

\*\* Upon long standing a solid polymer of M.W. 1800 separated from oil.

Effect of pressure was studied in autoclaves and is reported in Table 8.

Table 8

| Exp. No. | Autoclave | Solvent<br>cc. | $\text{AlCl}_3$<br>g. | Temp.<br>°C | P, atm. | Yield<br>cc. | Props. of >170° Prod |      |
|----------|-----------|----------------|-----------------------|-------------|---------|--------------|----------------------|------|
|          |           |                |                       |             |         |              | E°99                 | VI   |
| 24       | 5 l. V2A  | 2000           | 125                   | 20-70       | -       | 2810         | 4.64                 | 43.0 |
| 27       | "         | "              | "                     | 60          | 4.5     | 4600         | 3.82                 | 37.3 |
| 35       | "         | "              | "                     | 20-70       | 11      | 4800         | 4.46                 | 33.7 |
| 39       | "         | "              | "                     | "           | 18      | 4860         | 4.81                 | 31.0 |
| 29       | "         | 2000A          | "                     | "           | 4.5     | 4250         | 6.66                 | 50   |
| 34       | "         | "              | "                     | "           | 10      | 4850         | 5.32                 | 50   |
| 37       | "         | 2000B          | "                     | "           | 15      | 4100         | 7.24                 | 60   |
| 41       | 2.5 l. Fe | 1000           | 100                   | 50-70       | -       | 2650         | 5.23                 | 36   |
| 43       | "         | "              | "                     | "           | 21      | 2380         | 2.57                 | 25   |
| 47       | "         | 1000A          | "                     | "           | 18      | 2200         | 2.52                 | 48   |

The solvent was a 180/250° hydrogenated cracked wax. In the column headed "solvent" in Table 8 "A" refers to fresh solvent and "B" to fresh anhydrous solvent. In the other experiments solvent which had been used before and which contained some polymerization products was used. Evidently the fresh solvent is superior. Comparing Experiments 24 and 41 with 39 and 43 it is seen that high pressure lowers viscosity and decreases VI. The nature of the autoclave material apparently does not influence the VI of propylene polymer. Effect of adding other substances to the solvent was investigated and summarized in Table 9. (All experiments using 300 g. solvent and 30 g.  $\text{AlCl}_3$ .)

Table 9

| Exp. No. | Additive to Solvent   |            | Duration<br>hrs. | Polymer<br>g. | Viscosity of >170° Prod. |      |      |
|----------|---|------------|------------------|---------------|--------------------------|------|------|
|          | Kind  | Amount, g. |                  |               | 38°                      | 99°  | VI   |
| 82       | Stearic Acid  | 3          | 6                | 315           | 303                      | 7.40 | 55   |
| 95       | CH <sub>3</sub> OH  | 2          | 6                | 260           | 85.3                     | 3.43 | 40.4 |
| 107      | C <sub>4</sub> H <sub>9</sub> OH                              | 8          | 6                | 75            | 26.4                     | 2.06 | 24.8 |
| 118      | Conc. HCl   | 2          | 6                | 321           | 102                      | 3.76 | 37.1 |
| 162      | Gaseous HCl   |            | 5-1/4            | 237           | 92.8                     | 3.68 | 44.9 |
| 156      | n-C <sub>4</sub> H <sub>9</sub> Cl                            |            |                  |               | 80                       | 3.32 | 35.9 |
| 153      | CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> | 2          | 5                | 128           | 87.5                     | 3.56 | 43.6 |
| 154      | CH <sub>3</sub> CHO   | 2          | 5                | 156           | 119                      | 4.04 | 36.4 |
| 159      | CS <sub>2</sub>   | 1          | 4                | 189           | 117                      | 4.11 | 42.8 |

None of the substances added was of benefit. However, the VI was improved by adding higher M.W. olefins from wax cracking, as shown by Table 10:

Table 10

| Exp. No. | Solvent<br>g. | AlCl <sub>3</sub><br>g. | Liq. Olef.<br>g. | C <sub>3</sub> H <sub>6</sub><br>g. | Temp.<br>°C | Visc. of >170° Prod. |      |      |
|----------|---------------|-------------------------|------------------|-------------------------------------|-------------|----------------------|------|------|
|          |               |                         |                  |                                     |             | 38°                  | 99°  | VI   |
| 18       | 300           | 30                      | 0                | 240                                 | 60          | 30.9                 | 2.28 | 45.8 |
| 98       | 0             | 15                      | 80               | 240***                              | 100         | 44.4                 | 2.97 | 78   |
| 103      | 0             | 30                      | 100*             | 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**            | 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   |

\* Prepolymerized.

\*\* Added after the C<sub>3</sub>H<sub>6</sub>.

\*\*\* Added as polymer from Run 18.

In Experiment 103 the wax-cracked olefins were polymerized without solvent while in Experiment 104 a solvent was employed. From Experiments 100, 105 and 108 it appears immaterial whether the wax cracked olefin or C<sub>3</sub>H<sub>6</sub> are polymerized initially or whether the two are copolymerized simultaneously. A wax-cracked olefin-C<sub>3</sub>H<sub>6</sub> ratio of 1:3 appears to be better than a 1:4 ratio.

Properties of C<sub>3</sub>H<sub>6</sub> polymer are compared with those of higher olefin polymers in Table 11. In this case the polymer is that boiling >150°C at 1 mm.

This table demonstrates the superiority of straight chain,  $\alpha$  olefins over branched or  $\beta$  olefins. It also shows that VI increases with the length of the C chain.

λ-

Table 11

| Exp. No. | Olefin                           | AlCl <sub>3</sub> g. | Temp. °C | Duration Hrs. | Viscosity *E |      |      | Sp.Gr. 20°C | Mol. Wt. | C Resid. | Flash Point |
|----------|----------------------------------|----------------------|----------|---------------|--------------|------|------|-------------|----------|----------|-------------|
|          |                                  |                      |          |               | 38°          | 99°  | VI   |             |          |          |             |
| 86       | C <sub>3</sub> H <sub>6</sub>    | 30                   | 60       | 5.7           | 126          | 4.34 | 44   | .851        | 649      | .12      | 244         |
| 78       | nC <sub>4</sub> H <sub>8</sub>   | "                    | "        | 5             | 74.6         | 3.34 | 43.2 | .857        | 654      | .11      |             |
| 5        | βC <sub>4</sub> H <sub>8</sub>   | "                    | "        | "             | 23.4         | 1.76 | -83  | .865        | 426      | .24      | 173         |
| 4        | isoC <sub>4</sub> H <sub>8</sub> | "                    | "        | "             | 25.6         | 1.77 | -107 | .876        | 406      | .35      | 175         |
| 164      | nC <sub>5</sub> H <sub>10</sub>  | "                    | "        | 4             | 43.3         | 2.84 | 73.4 | .868        | 527      | .12      | 215         |
| 1        | nC <sub>8</sub> H <sub>16</sub>  | "                    | "        | 5             | 38.7         | 3.56 | 114  | .851        |          |          |             |
| 3        | nC <sub>18</sub> H <sub>36</sub> | "                    | "        | 5             | 10.8         | 1.94 | 125  | .848        |          |          |             |

Oppanol (an isoC<sub>4</sub>H<sub>8</sub> polymer) was added to a C<sub>3</sub>H<sub>6</sub> polymer, in which it is quite soluble. The Oppanol increases its viscosity but not its VI:

|   | E°38 | E°99 | VI   |
|---|------|------|------|
| C <sub>3</sub> H <sub>6</sub> polymer         | 18.9 | 2.14 | 88.8 |
| C <sub>3</sub> H <sub>6</sub> plus 1% Oppanol | 48.5 | 3.27 | 88.0 |

Apparently Oppanol is dissolved molecularly, not colloiddally, in the polymer.



POLYMERIZATION OF ETHYLENE

Balson (Bull. Soc. Chim. 2, 31, 539, (1879)) first recorded the polymerization of  $C_2H_4$  to a viscous oil by means of  $AlCl_3$ . Gustafson (ibid 34, 322, (1880)) reported a similar reaction using  $AlBr_3$  and extended his investigation to other olefins. Aschan (Ann. 324, 23, (1902)) and Ipatiev (Ber. 44, 2978, (1911), 46 1748, (1913)) also investigated this phenomenon. Ipatiev first studied the thermal polymerization at  $325^\circ C$ , later observed that the reaction occurred at  $230^\circ C$  in the presence of  $ZnCl_2$  and at  $180^\circ C$  with  $AlCl_3$ . The product contained paraffins, naphthenes and olefins. DeMontmollin (Bull. Soc. Chem. Bd 19, 242, (1916)) produced a similar mixture of hydrocarbons from  $C_2H_4$  by dehydrating  $C_2H_5OH$  with  $P_2O_5$ . Damiens (Bull. Soc. Chim. Bd 33, 71, (1923)) found that  $C_2H_4$  could be polymerized by concentrated  $H_2SO_4$  containing  $CuO$  or  $HgSO_4$ . Hoffmann and Otto (QRP. 505265, 512959) claim that  $BF_3$ , especially in the presence of  $Ni$ , is a good polym. catalyst for  $C_2H_4$ . Azomethane also catalyzes  $C_2H_4$  polymerization (J. Am. Chem. Soc. 57, 1384 (1935)) (this is a  $CH_3$  catalyzed process). A more complete bibliography on  $C_2H_4$  polymerization is available in Ber. for May 1, 1939 and for April 20, 1940.

Nash et al. first undertook the production of lube oils from  $C_2H_4$  (J. Inst. Pet. Techn. 16, 830 (1930)). To a 2 liter steel autoclave containing 100 g.  $AlCl_3$  in 100 g. pet. ether they added  $C_2H_4$  to a pressure of 35-55 atm. at  $5-10^\circ C$ . After 1 day the pressure had fallen to 15 atmospheres and after several days to 10 atmospheres. After 23 days the autoclave was opened and 219 g. of "free oil" and 68 g. of "bound oil" were obtained. The free oil is not combined with  $AlCl_3$ , while the bound oil is that obtained by decomposition of the  $AlCl_3$ -hydrocarbon complex. The properties of the fractions of these oils boiling  $225/250^\circ C$  at 100 mm. are as follows:

Table 12

|                                  | <u>Free Oil</u> | <u>Bound Oil</u> |
|----------------------------------|-----------------|------------------|
| Sp. Gr. at $20^\circ C$          | .8332           | .8636            |
| $n_D$                            | 1.4622          | 1.4863           |
| M.W.                             | 384             | 380              |
| g. H per g. C                    | 17.04           | 15.58            |
| Visc. $^\circ E$ at $38^\circ C$ | 13.8            | 34.5             |
| at $99^\circ C$                  | 1.55            | 1.79             |
| V.I.                             | -104            | -199             |
| $I_2$ number                     |                 | 32               |

From this table it is evident that the "bound oil" is less saturated and has poorer V.I. It is also darker in color and is less resistant to  $KMnO_4$  oxidation. When the polymerization was carried out at higher temperatures, the oils obtained were less viscous and had poorer V.I.'s. Nash concluded that the oil obtained from  $C_2H_4$  polymerization could not compare with natural lube oils, in particular because of its poor resistance to oxidation. Nash proposed the following mechanism for the polymerization: the first step is the formation of higher olefins  $nC_2H_4 \longrightarrow (C_2H_4)_n$  which isomerized under the influence of  $AlCl_3$  to cycloparaffins. The isomerization step is thermodynamically possible at temperatures below  $400^\circ C$ . The cyclic compound, being saturated, is not able to form a complex with  $AlCl_3$ , and hence becomes a constituent of the "free oil", while the  $AlCl_3$  molecule is free to polymerize additional  $C_2H_4$ . The  $AlCl_3$  can also split the olefin combined with it into a paraffin hydrocarbon and polynuclear aromatics. In this way Nash envisages the formation of the "bound oil", which accounts for the loss in activity of the  $AlCl_3$ .

Waterman and Tulleners (Chim. et Ind., June 1933, p. 496) confirmed Nash's results. They used an iron autoclave and prepared  $C_2H_4$  from  $C_2H_5OH$ . Their results agreed almost exactly with Nash's, and they concluded that in addition to isomerization and polymerization, hydrogenation and dehydrogenation as well were occurring. The V.I.'s of their highest boiling products were from -56 to 2, somewhat better than the values obtained by Nash, all of which were below -100.

To us the fact that Waterman had obtained a V.I. of +2 seemed especially noteworthy, and we believed that by a careful study of the  $AlCl_3$ -catalyzed  $C_2H_4$  polymerization the V.I. of the product might be increased. In particular we felt that the use of especially pure reagents might be promising. Experiments were begun on September 26, 1934. The  $C_2H_4$  was an especially pure product obtained from Holten. During the course of the work it was found that the odor test was one of the safest criteria of the purity of the  $C_2H_4$ .

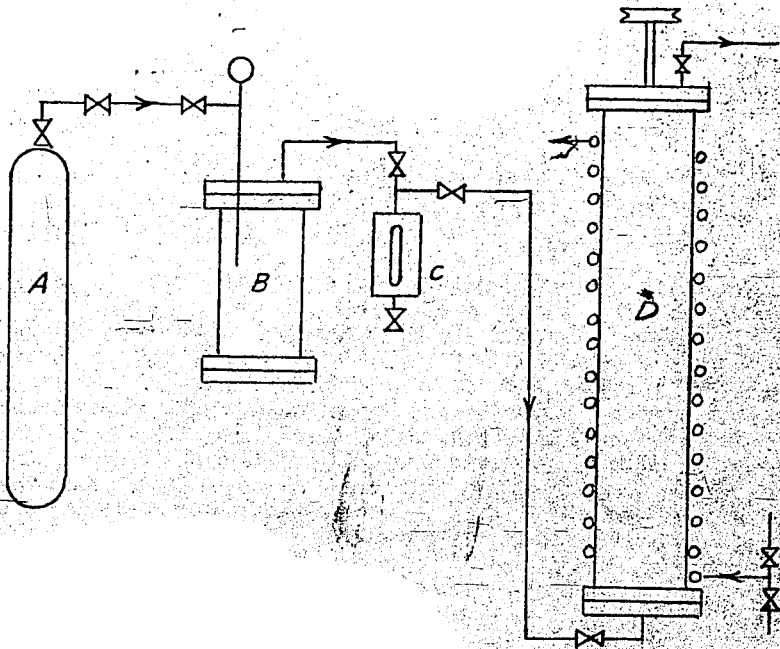
Exp. No. 1 (See Figure A.P.-1)

A 5 l. V2A autoclave with V2A stirrer was filled with 2 l. of a 225/305 fraction obtained by hydrogenating cracked wax, and 300 g.  $AlCl_3$  were added.  $C_2H_4$  flowed from cylinder A into a paraffin vessel (Paraffin gefass) B through a sight glass C filled with paraffin oil into the bottom of the autoclave D. The temperature within the autoclave rose from 24° to 38°. Ethylene was added without exterior heating until after 10 hours no further absorption could be observed. The pressure within the autoclave was 16 atm. at this time. After releasing the pressure, 2340 cc. of a dark brown product was withdrawn and a very viscous residue remained. Both the liquid product and the viscous residue were hydrolyzed with water. The liquid product was stripped of the solvent by means of steam at 260°, and the remaining oil was distilled to produce a residue boiling above 170° at 1 mm. The residue, 254 g., was treated with 2% clay (Tonsil) and yielded a bright yellow oil of 11.57°E viscosity at 38° and 1.82° at 99°, giving a V.I. of 90.8. The viscous residue from the autoclave was treated in the same way, yielding 209 g. of oil ( $E_{38}^o = 51.3$ ,  $E_{99}^o = 2.99$ , V.I. = 64.3). Thus for the first time was produced a  $C_2H_4$  polymer of high V.I. Upon repeating the experiment the temperature within the autoclave rose to 57°, and the oils boiling above 170°C at 1 mm. had these properties:

|                    | Liquid Product | Product from $AlCl_3$ Complex |
|--------------------|----------------|-------------------------------|
| Sp. Gr. at 20°     | 844            | .867                          |
| Visc. $E^o$ at 38° | 16.95          | 30.90                         |
| at 99°             | 1.93           | 2.32                          |
| V.I.               | 62.3           | 53.2                          |
| Carbon Residue     | 0.01           | 0.89                          |
| Molecular Weight   | 557            | 508                           |

In a third experiment only 200 g.  $AlCl_3$  were used. A steam coil was installed in the autoclave to permit higher temperatures and more rapid reaction whereas 20 l. of  $C_2H_4$  were absorbed in 45 minutes at 40°C, by raising the temperature to 70°C the time to absorb 20 l. was cut to 15 minutes. At 70°C the autoclave pressure fell from 58 atmospheres to 30 atmospheres and stayed at 30 in spite of rapid  $C_2H_4$  addition. From this experiment came 2540 cc. of liquid product and 518 g. of residue. The liquid product yielded 496 g. of oil upon vacuum distillation having  $E_{99}^o = 216$  and V.I. = 78.9 (Brit. Oxidation Test 0,

A.P-1



3

no asphalt formation). The oil from the residue had  $E_{99}^{\circ} = 8.05$  and V.I. = 61. An additional 20 experiments were run with hydrogenated wax-cracking products or pet. ether as solvents, varying  $AlCl_3$  concentration, experimental procedures, temperature and pressure. As much as 1400 g. of lube oil was obtained, and viscosities were as high as  $E_{99}^{\circ}$ . V.I. value varied between 65 and 95.

On October 10, 1934, a new supply of  $C_2H_4$  was obtained from Ludwigs-Hafan. Expt. 24 was begun, but after 4 hours was discontinued because no further reaction was occurring. The experiment was repeated with the same result. In both cases the addition compound floated in a voluminous mass upon the clear, nearly unchanged solvent. The complex was not adhesive and one could squeeze solvent from it as from a sponge. Specially dried petroleum ether was tried as solvent but with no improvement in results. A very poor yield of product boiling  $> 170^{\circ}C$  at 1 mm. had viscosities of 2 and  $2.5^{\circ}E$  at  $99^{\circ}C$  and V.I.'s of -17.6 and -70.4.

The  $C_2H_4$  was found to be contaminated with considerable quantities of liquid consisting of  $C_2H_5OH$ ,  $CH_3CHO$ , and  $CH_3CO_2C_2H_5$ . Several other cylinders from this shipment were similarly contaminated.

Removal of these impurities by various gas-washing techniques was investigated and it was found that a simple alkali wash was most effective. Accordingly a soda wash tower containing Rashig rings was installed. In spite of the fact that no impurities could be detected in the soda washed ethylene, a product of only 40 V.I. was obtained, and the high values of 80 or 90 could not be reproduced with this  $C_2H_4$  produced from alcohol. Accordingly, ethylene was again obtained from Holten, where it is recovered from coke oven gases by means of a Linde plant. This  $C_2H_4$  also gave varying V.I. values, but among them were many above 90. Accurate analytical study of the different supplies of  $C_2H_4$  showed that these variations in V.I. must be attributed to such impurities as  $CO$ ,  $CO_2$ ,  $H_2S$  and  $O_2$ . In Table 13 the effect of these impurities is illustrated.

Table 13

| Added Gas | % in $C_2H_4$ | Yield, l.   | $E_{99}^{\circ}$ | V.I.  |
|-----------|---------------|-------------|------------------|-------|
| None      | -             | 4.00        | 7.02             | 88.8  |
| CO        | 0.05          | 4.0         | 5.45             | 82.0  |
|           | 0.14          | 3.5         | 3.67             | 69.0  |
|           | 1.0           | 2.8         | 2.04             | 38.4  |
|           | 2.1           | 2.25        | 2.18             | 22.4  |
|           | 10.0          | 2.00        | 1.75             | -10.5 |
| $H_2S$    | 0.2           | no reaction |                  |       |
| $CO_2$    | 0.1           | " "         |                  |       |
|           | 0.4           | " "         |                  |       |
|           | 3.0           | " "         |                  |       |
| $O_2$     | 0.8           | " "         |                  |       |

All experiments in Table 13 were carried out under identical conditions using the  $C_2H_4$  and  $AlCl_3$  from the same source, a 5 l. V2A autoclave, and 2 l. pet. ether and 125 g.  $AlCl_3$ . While  $CO$  in small amounts does not decrease the yields, as little as 0.05% has a deleterious effect on product quality.

After the effect of impurities was recognized and taken care of by treating the gas, better V.I. values could be obtained, although they still showed variations. The reproducibility of the experiments was still unsatisfactory. The  $AlCl_3$  was accordingly subjected to careful scrutiny. The use of different samples of  $AlCl_3$  demonstrated a direct effect upon oil yield and quality of the iron content and content of involatile material of the  $AlCl_3$ , as shown in Tables 14 and 15.

Table 14 (5 l. V2A autoclave)

| <u>% Fe</u> | <u>Exp. No.</u> | <u>t °C</u> | <u>Yield, g.</u> | <u>Prod. b. &gt;170° at 1 mm.</u> |             |
|-------------|-----------------|-------------|------------------|-----------------------------------|-------------|
|             |                 |             |                  | <u>°E<sub>99</sub></u>            | <u>V.I.</u> |
| 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        |
| "           | 134             | 90          | 3820             | 2.57                              | 62.1        |
| 1.77        | 180             | 110         | 2975             | 3.76                              | 53.9        |
| "           | 176             | 90          | 2680             | 2.63                              | 59.5        |

Table 14 indicates that V.I. and viscosity of product decreases as the content of  $FeCl_3$  increases, and at high  $FeCl_3$  content the yield too decreases. The content of unsublimeable material in the  $AlCl_3$  also has an effect as shown in Table 15.

Table 15 (45 l. N6 autoclave)

| <u>% Resid. in <math>AlCl_3</math> *</u> | <u>Exp. No.</u> | <u>Yield, kg.</u> | <u>°E<sub>99</sub></u> | <u>V.I.</u> |
|--|-----------------|-------------------|------------------------|-------------|
| 1.56                                     | 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        |

\* Material which does not sublime in  $N_2$  stream at 250°C for 2-4 hours.

The  $\text{AlCl}_3$  used in these experiments was practically iron free, and was obtained at Ludwigshafen by treating iron-containing  $\text{AlCl}_3$  with metallic Al. Table 15 shows that these unsublimed impurities play a part similar to  $\text{FeCl}_3$ , lowering both the yield and V.I. The effect of adding other substances to  $\text{AlCl}_3$  is shown in Table 16, in which a series of experiments employing 125 g. iron-free  $\text{AlCl}_3$  and 2 liters of petroleum ether in a 5 l. V2A autoclave is summarized:

Table 16

| Exp. No. | Substance Added                 | Temp. °C | Yield, l. | °E <sub>99</sub> | 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. $\text{FeCl}_3$            | 120      | 2.60      | 1.82             | 28.3 |
| 301      | 5 g. $\text{TiCl}_4$            | 120      | 3.90      | 6.45             | 75.0 |
| 288      | 5 g. $\text{TiCl}_4$            | 130      | 3.80      | 2.76             | 58.1 |
| 264      | 5 g. $\text{SiCl}_4$            | 120      | 3.80      | 4.41             | 86.9 |
| 286      | 5 g. $\text{HgCl}_2$            | 120      | 4.00      | 3.81             | 80.0 |
| 278      | 2.5 g. $\text{NO}_2\text{Cl}_2$ | 120      | 4.20      | 3.19             | 75.1 |
| 277      | 1 g. $\text{I}_2$               | 120      | 4.20      | 4.81             | 76.0 |
| 275      | 5 g. $\text{LiCl}_2$            | 120      | 4.20      | 3.61             | 83.3 |
| 276      | 5 g. $\text{SbCl}_5$            | 120      | 3.20      | 2.18             | 58.6 |
| 330a     | 5 g. $\text{SnCl}_4$            | 120      | 3.38      | 2.70             | 51.6 |
| 289      | 125 g. $\text{BF}_3^*$          | 120      | 4.25      | 5.01             | 78.0 |

\* No  $\text{AlCl}_3$  added.

The results show that none of the above substances acts as a promoter. When  $\text{BF}_3$  is substituted for  $\text{AlCl}_3$  as catalyst, the product is obtained in essentially the same yield and has the same viscosity but is somewhat lower in V.I.

In connection with these experiments the behavior of the aluminum chloride aluminum trimethyl complex, an especially interesting product, was studied. It is a solid melting at  $48^\circ\text{C}$  which kindles spontaneously in air, reacts explosively with water and alcohol, but is easily soluble in  $\text{CCl}_4$  and saturated hydrocarbons. It was prepared by the I G. Hochst process by passing  $\text{CH}_3\text{Cl}$  over Al chips or grit etched with  $\text{I}_2$  or Hg. A quartz tube sealed to a receiver was filled with Al chips which were activated with  $\text{I}_2$  (Figure 1a). A slow stream of  $\text{CH}_3\text{Cl}$  was passed through the tube while the Al chips were being heated gently at one point to initiate the reaction. Often several hours are required to start the reaction; addition of HCl gas may shorten this period. After onset of the reaction the gas stream must be throttled to keep it under control. Depending on the feed rate and consequent reaction temperature, one of 2 products is formed; at low temperature a liquid, at high temperature a solid. Both are colored brown by impurities in the Al.

The chief difficulty in this process is dissipating the heat of reaction. Accordingly the apparatus was arranged to carry out the reaction in liquid Al-methyl chloride cooled externally by wet steam. Figure 1b shows the reaction tube

which is filled about one-half full with Al chips. Aluminum methylchloride is added to the tube, which is heated to 80-90° and CH<sub>3</sub>Cl is added slowly through the delivery tube. The reaction occurs readily and the product can be handled as a liquid. As it is unstable in air and spontaneously inflammable, it is led into a Claisen flask from which air is excluded, and is then distilled under normal pressure. The products are still liquid at 40-50°C. Dissolved in high-boiling hydrogenated cracked distillate, (20% conc.) it fumes strongly in air but no longer kindles so easily.

Table 17. Addition of Aluminum Alkyl to Solvent

5 l. V2A Autoclave

The aluminum alkyl was added in an atmosphere of N<sub>2</sub> to 2 l. of pet. ether and 125 g. AlCl<sub>3</sub>.

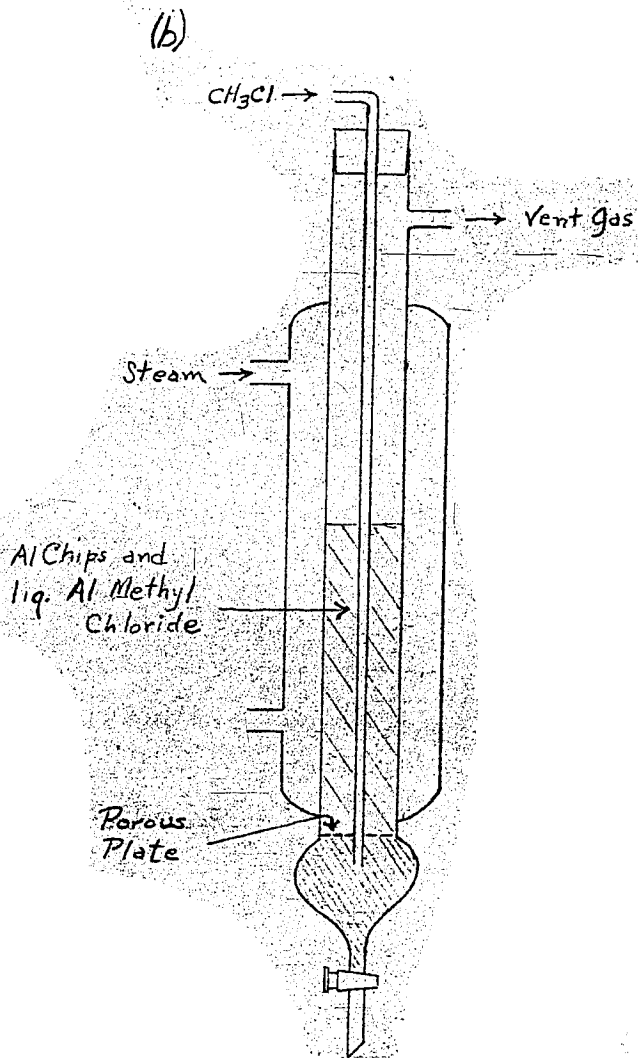
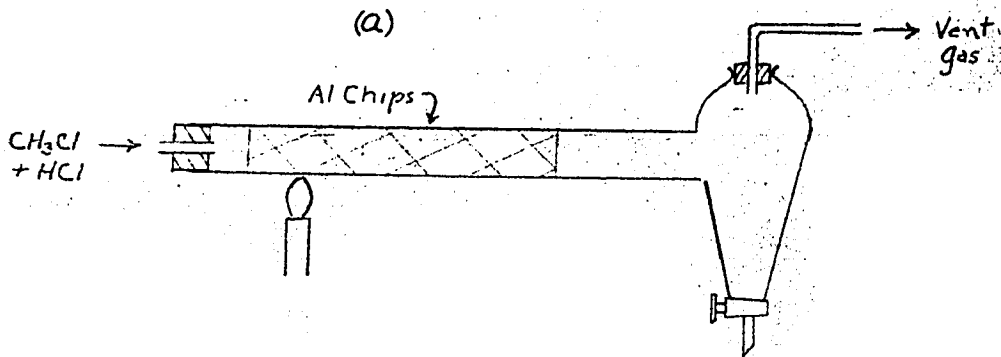
| Exp. No. | Al Alkyl Added,<br>g. | Temp.,<br>°C | Yield,<br>l. | Product |       |
|----------|-----------------------|--------------|--------------|---------|-------|
|          |                       |              |              | °E99    | V.I.  |
| 214      | -                     | 80           | 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                     | 120          | 4.00         | 4.99    | 95.0  |
| 321      | 2.5                   | 120          | 3.80         | 4.41    | 95.0  |
| 311      | 2.5                   | 130          | 4.20         | 4.26    | 89.4  |
| 316      | 5                     | 80           | 4.00         | 6.53    | 100.0 |
| 365      | 5                     | 90           | 3.85         | 6.25    | 103.0 |
| 315      | 5                     | 100          | 3.85         | 5.70    | 92.0  |
| 299      | 5                     | 120          | 3.70         | 5.53    | 98.0  |
| 272      | 5                     | 130          | 4.00         | 4.88    | 95.0  |
| 265      | 8.3                   | 120          | 3.40         | 5.94    | 91.0  |
| 284      | 8.3                   | 130          | 3.70         | 4.93    | 85.0  |
| 266      | 15                    | 120          | 3.20         | 6.08    | 90.0  |
| 355*     | 125 (solid)           | 120          | 2.65         | 2.23    | 47.7  |
| 349*     | 125 (liquid)          | no reaction  |              |         |       |

\* AlCl<sub>3</sub> absent.

In the experiments cited in Table 17, 125 g. of AlCl<sub>3</sub> (iron free) and 1-liter of pet. ether were first added to the autoclave after which the alkyl compound dissolved in 1 l. of pet. ether was introduced in a N<sub>2</sub> atmosphere. It is seen that 1-5 g. of the alkyl compound promote a small increase in V.I. of the product; for example, compare Expts. 507 and 324, 321. Larger quantities of the alkyl compound bring about no further increase in V.I. The liquid compound AlCl<sub>3</sub>·Al(CH<sub>3</sub>)<sub>3</sub> alone caused only a feeble reaction (Exp. 355). In this compound both free valence electrons of the AlCl<sub>3</sub>, which are active catalytically, are saturated; i.e. bound to the molecule Al(CH<sub>3</sub>)<sub>3</sub> which in turn possesses 2 free valence electrons. The product Al(CH<sub>3</sub>)<sub>3</sub>·2AlCl<sub>3</sub> is probably a solution of AlCl<sub>3</sub> in Al(CH<sub>3</sub>)<sub>3</sub>·AlCl<sub>3</sub>, for this product has catalytic activity.

+ ("In der Verbindung Al(CH<sub>3</sub>)<sub>3</sub>·AlCl<sub>3</sub> sind die beiden freien Valenz-elektronen des Aluminiumchlorids, welche seine katalytische Aktivität bedingen abgesättigt bzw. gebunden an das Molekül Al(CH<sub>3</sub>)<sub>3</sub>, welches je ebenfalls zwei freie Valenz-elektronen besitzt.")

Fig. 1





Also of interest were experiments in which Al powder was added. These were undertaken as a result of experiments carried out in an autoclave lined with sheet aluminum in which turbid oils were obtained. This turbidity was followed by precipitation of paraffin. In other experiments in a 5 l. autoclave containing 2 l. pet. ether and 125 g.  $AlCl_3$ , 1.20 g. of Al bronze were added. It was shown that the increased amounts of Al decreased the yield of polymer. With 20 g. of Al bronze present, the yield of polymer was but 1 kg. which contained 20% of a rubber-like product with a molecular weight of 900-1800 and a melting point of  $115^\circ$ . The product also was turbid when smaller amounts of Al bronze were used and its pour point,  $0^\circ C$ , was inferior. These experiments were not pursued further.

Having investigated the catalytic action of the  $AlCl_3$ , the catalytic influence of the autoclave material was studied. A 2 1/2 l. iron autoclave was first employed.

Table 18 (2.5 l. iron autoclave)

| 1000 cc. Pet. Ether + 100 g. $AlCl_3$ |              | Reaction time 18 hrs. |                                   |      |
|---------------------------------------|--------------|-----------------------|-----------------------------------|------|
| Exp. No.                              | t $^\circ C$ | Crude Product, g.     | Product b. > $170^\circ$ at 1 mm. |      |
|                                       |              |                       | E <sup>o</sup> <sub>99</sub>      | V.I. |
| 130                                   | 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 autoclave was charged with 1000 cc. pet. ether and 100 g.  $AlCl_3$ , ethylene was introduced under pressure, and the reactor was heated. In contrast to the experiments conducted in the V2A autoclaves, a strongly exothermic reaction was never observed in the iron vessel. Moreover, the pressure decrease occurred more slowly in the iron vessel; thus the experiments in Table 18 were terminated only after 18 hours, at which time the reactor was in no case full. With the V2A autoclave which was twice as large, reaction product completely filled the vessel in 3-4 hours. These experiments show that the polymer produced in the iron autoclave is less viscous and has a lower V.I. than polymer made under corresponding conditions in a V2A autoclave, as shown in Table 19. In Table 19 are presented results obtained using a V2A autoclave equipped with stirrers of different materials. For accurate comparison experiments in which the same  $C_2H_4$  and  $AlCl_3$  were used are grouped together. It is seen that a Cu agitator is less suitable than one of V2A (Exp. 491 gives an unexplained result). Fe is also less satisfactory as regards yield, V.I. and fluidity of the product. Experiments with an iron autoclave and iron agitator are included for comparison. Ni influences the V.I. of the product unfavorably, but not the yield. These results prompted us to undertake experiments in reactors containing no Ni, but only chrome as an alloying material. These materials are N<sub>5</sub>, N<sub>6</sub> and N<sub>8</sub> steel, having the following compositions:

Table 19. Influence of Agitator Material

5 liter V2A Autoclave

| C <sub>2</sub> H <sub>4</sub><br>Bomb | 8454     |           |       | 8400     |           |       | 7718     |           |       | 2918     |           |       |
|---------------------------------------|----------|-----------|-------|----------|-----------|-------|----------|-----------|-------|----------|-----------|-------|
|                                       | Exp. No. | Yield, l. | E° 99 | Exp. No. | Yield, l. | E° 99 | Exp. No. | Yield, l. | E° 99 | Exp. No. | Yield, l. | E° 99 |
| V2A                                   | 498      | 3.80      | 4.92  | 454      | 3.73      | 8.19  | 485      | 3.50      | 6.07  | 482      | 4.00      | 6.89  |
|                                       | 500      | 3.30      | 4.03  |          |           | 103.0 |          |           | 99.0  |          | 4.00      | 7.74  |
| Qu                                    | 496      | 3.45      | 3.00  | 449      | 3.70      | 4.04  |          |           |       | 491      | 4.00      | 5.90  |
| Fe                                    | 499      | 3.00      | 3.05  |          |           | 82.5  | 483      | 2.00      | 6.52  | 487      | 3.50      | 4.74  |
| Ni                                    | 497      | 3.80      | 4.65  | 450      | 3.75      | 4.74  |          |           |       |          |           | 78.7  |
|                                       |          |           |       | 450a     | 4.10      | 6.26  |          |           |       |          |           | 481   |
| Fe auto-clave with Fe agitator        |          |           |       |          |           |       | 488      | 1.70      | 2.38  | 486      | 2.10      | 2.44  |
|                                       |          |           |       |          |           |       |          |           |       |          |           | 68.4  |
|                                       |          |           |       |          |           |       |          |           |       |          |           | 479   |
|                                       |          |           |       |          |           |       |          |           |       |          |           | 1.75  |
|                                       |          |           |       |          |           |       |          |           |       |          |           | 2.22  |
|                                       |          |           |       |          |           |       |          |           |       |          |           | 30.5  |

1.5

|    | <u>N<sub>5</sub></u> | <u>N<sub>6</sub></u> | <u>N<sub>8</sub></u> | <u>V2A</u> |
|----|----------------------|----------------------|----------------------|------------|
| 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                  | -          |

The results using these materials are summarized in Table 20.

Table 20. Comparative Experiments with V2A and N-Metals

5 liter autoclave

| <u>V2A</u>     |             |                        |      |      | <u>N<sub>6</sub></u> |             |                        |      |       | <u>N58</u>     |             |                        |      |       |
|----------------|-------------|------------------------|------|------|----------------------|-------------|------------------------|------|-------|----------------|-------------|------------------------|------|-------|
| Exp. t,<br>No. | Yield<br>°C | E° <sub>99</sub><br>l. | V.I. |      | Exp. t,<br>No.       | Yield<br>°C | E° <sub>99</sub><br>l. | V.I. |       | Exp. t,<br>No. | Yield<br>°C | E° <sub>99</sub><br>l. | V.I. |       |
| 598            | 150         | 4.00                   | 3.71 | 75.2 |                      |             |                        |      |       |                |             |                        |      |       |
| 601            | 140         | 4.15                   | 4.34 | 89.2 | 600                  | 140         | 4.10                   | 5.80 | 97.0  |                |             |                        |      |       |
|                |             |                        |      |      | 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 | 130.0 | 626            | 120         | 3.6                    | 4.38 | 90.8  |
|                |             |                        |      |      | 611                  | 110         | 4.00                   | 6.41 | 94.0  | 618            | 110         | 3.7                    | 5.48 | 98.0  |
|                |             |                        |      |      |                      |             |                        |      |       |                |             |                        |      |       |
| 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 |

Comparing the results obtained in V2A with those obtained in N<sub>5</sub>, N<sub>6</sub> and N<sub>8</sub> metals under comparable conditions, it is seen that the exclusion of Ni, with its unfavorable effect, has led to polymer of increased V.I. for each of the 3N metals. Of the 3N metals N<sub>6</sub> appears the best because of the higher yields obtained.

The next variable to be investigated, C<sub>2</sub>H<sub>4</sub> concentration, was studied by adding to the pure C<sub>2</sub>H<sub>4</sub> feed varying amounts of the following catalytically indifferent gases: (1) H<sub>2</sub> (2) N<sub>2</sub> (3) CH<sub>4</sub> (4) C<sub>2</sub>H<sub>6</sub>. Table 21, a-c, summarizes these experiments.

Table 21a. Hydrogen

5 l. V2A Autoclave

| V%    | Exp. No. | Yield, l.   | Product E° <sub>99</sub> | V.I.    | V% CH <sub>4</sub> |      |
|-------|----------|-------------|--------------------------|---------|--------------------|------|
| 2.8   | 338      | 4.07        | 8.46                     | 97.0(?) | 4.1                |      |
| 5.0   | 350      | 4.00        | 5.27                     | 83.0    | 7.9                |      |
| 7.5   | 298      | 3.80        | 6.45                     | 80.0    | 8.7                |      |
| 10    | 304      | 3.70        | 2.78                     | 66.9    | 11.7               |      |
| ca.20 | 340      | 2.80        | 2.07                     | 36.3    | 14.0               |      |
| ca.50 | 379      | no reaction |                          |         |                    | 20.0 |

Table 21b. CH<sub>4</sub>

5 l. V2A Autoclave

| Exp. No. | Yield, l. | Product E° <sub>99</sub> | V.I. |
|----------|-----------|--------------------------|------|
| 359      | 4.40      | 3.15                     | 81.0 |
| 322      | 4.00      | 3.58                     | 71.6 |
| 287      | 3.00      | 2.28                     | 70.6 |
| 290      | 2.70      | 2.32                     | 66.4 |
| 357      | 2.10      | 3.13                     | 57.7 |
| 306      | 2.30      | 2.30                     | 43.1 |

Table 21c. Nitrogen

5 l. V2A Autoclave

| Wt %<br>N <sub>2</sub> | Exp.<br>No. | t,<br>°C | Yield,<br>l. | Product          |      |
|------------------------|-------------|----------|--------------|------------------|------|
|                        |             |          |              | E° <sub>99</sub> | 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  |                  |      |

Table 21 d and e

| 2.0 l. Solvent<br>125 g. AlCl <sub>3</sub> |             |                |       |                  |      | 12 kg. Solvent<br>1.4 kg. AlCl <sub>3</sub> |                |       |                  |       |
|--|-------------|----------------|-------|------------------|------|---|----------------|-------|------------------|-------|
| 21d  |             |                |       |                  |      | 21e   |                |       |                  |       |
| %<br>C <sub>2</sub> H <sub>4</sub>         | Exp.<br>No. | Press.<br>Atm. | Yield | E° <sub>99</sub> | V.I. | Exp.<br>No.                                 | Press.<br>Atm. | Yield | E° <sub>99</sub> | 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 |
| 20%  | 535a        | 80             | 3.60  | 5.47             | 97.2 | 82  | 30             | 33.5  | 4.61             | 110.7 |
|  | 536         | 60             | 3.85  | 6.56             | 90.0 | 96  | 65             | 32.0  | 3.89             | 106.4 |
|  | 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  |

Increasing dilution with each of these four gases results in a lower yield of polymer of lower viscosity and V.I. In the series summarized in Table 21d and e, both the C<sub>2</sub>H<sub>4</sub> partial pressure and the total pressure were varied. At 80% C<sub>2</sub>H<sub>4</sub>, increasing the total pressure increased the V.I. This effect was less marked at 70% concentration. In neither of these cases is the yield as good as with 95% C<sub>2</sub>H<sub>4</sub>, nor is the yield improved by raising total pressure. These results were confirmed in a 45 l. V2A autoclave (Table 21e) using 11.9 kg. solvent (pet. ether) and 1.4 kg. AlCl<sub>3</sub>. Comparing Experiments 108 and 82, it is seen that with 60% C<sub>2</sub>H<sub>4</sub> the total yield was only 2 kg. polymer (the remaining 13.3 kg. being solvent and AlCl<sub>3</sub>) while in Experiment 82 at 95% C<sub>2</sub>H<sub>4</sub> concentration, a yield of 20.2 kg. of actual polymer was obtained. Moreover, the 20.2 kg. yield in Exp. 82 was obtained in 4 hours, while 21 hours were required to produce the 2 kg. yield in Exp. 108. Thus, dilution of the C<sub>2</sub>H<sub>4</sub> has a deleterious effect on yield and quality of polymer, and if it is desired to obtain a high quality polymer, C<sub>2</sub>H<sub>4</sub> of at least 95% purity and preferably higher purity still should be employed.

The effect of the quantity and kind of solvent was next investigated.

Table 22. Various Quantities of Solvents

The experiments were carried out in the 5 liter V2A autoclave. The charge consisted of the indicated amounts of petroleum ether and 125 g. of the same  $AlCl_3$ . Ethylene from various shipments had to be used.

| Exp. No. | t, °C | Grude Prod. cc. | Product b. >170 in Vac. |      |            |
|----------|-------|-----------------|-------------------------|------|------------|
|          |       |                 | °E <sub>99</sub>        | V.I. |            |
| 192      | 120   | 3600            | 3.68                    | 83.7 |            |
| 193      | 110   | 3600            | 3.61                    | 81.5 |            |
| 194      | 100   | 3500            | 4.31                    | 85.6 | 3 liters   |
| 168      | 90    | 4080            | 5.39                    | 89.0 | pet. ether |
| 185      | 120   | 3850            | 5.37                    | 92.0 |            |
| 174      | 110   | 3200            | 4.88                    | 92.0 | 2 liters   |
| 173      | 110   | 3270            | 7.21                    | 94.0 | pet. ether |
| 164      | 90    | 3700            | 6.69                    | 94.0 |            |
| 196      | 120   | 4500            | 7.15                    | 97.5 |            |
| 197      | 110   | 4400            | 7.75                    | 94.0 | 1 liter    |
| 178      | 100   | 4400            | 7.76                    | 92.0 | pet. ether |
| 177      | 90    | 4600            | 8.70                    | 96.0 |            |

The above table shows the effect of quantity of solvent. In all experiments the same  $AlCl_3$  in the amount of 125 g. was employed. The less solvent employed the more viscous was the resulting polymer and the better was the V.I. As had been previously observed, with higher temperatures the polymer was more liquid. The same was evident also with hydrogenated cracked paraffin products in the following Table 23.

Table 23

| Exp. No. | Nature of Solvent                              | Amount of Solvent, cc. | Temp. | Yield | Viscosity |                          |
|----------|--|------------------------|-------|-------|-----------|--------------------------|
|          |  |                        |       |       | Product   | 170°/mm. Hg<br>°Egg V.I. |
| 411      | Petroleum ether                                | 2000                   | 80°   | 4.30  | 6.69      | 91.0                     |
| 400      | Hydrogenated cracked paraffins 20-180°         | 2000                   | 80    | 4.25  | 6.52      | 92.0                     |
| 397      | " 180-250                                      | 2000                   | 80    | 4.60  | 7.90      | 92.0                     |
| 191      | " 180-250                                      | 2000                   | 100   | 4.45  | 13.9      | 102                      |
| 190      | " 180-250                                      | 2000                   | 110   | 3.9   | 11.5      | 98                       |
| 187      | " 180-250                                      | 2000                   | 120   | 4.7   | 11.7      | 102                      |
| 201      | " 180-250                                      | 2000                   | 130   | 4.2   | 5.1       | 82                       |
| 206      | " 180-250                                      | 2000                   | 140   | 4.1   | 3.0       | 67                       |
| 144      | Isooctane                                      | 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      | Isododecane                                    | 2000                   | 120   | 4.7   | 12.9      | 102                      |
| 169      | "  | 3000                   | 120   | 4.5   | 13.1      | 101                      |
| 385      | Pet. ether + fl. olefin <sup>1)</sup>          | 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                       |
| 394x)    | Pet. ether + fl. olefin with AlCl <sub>3</sub> | 1900+100               | 80    | 4.2   | 8.0       | 93                       |
| 428x)    | " " "  | 1900+100               | 120   | 4.1   | 6.0       | 93                       |
| 444x)    | Pet. ether + propylene with AlCl <sub>3</sub>  | 2000                   | 80    | 3.9   | 7.4       | 94                       |
| 445x)    | " " "  | 2000                   | 120   | 4.0   | 4.2       | 96                       |
| 325      | Pet. ether + 15 g. Oppanol                     | 2000                   | 80    | 4.1   | 8.8       | 96                       |
| 312      | " " "  | 2000                   | 120   | 4.2   | 4.5       | 77                       |

- 1) Liquid Olefins = liquid cracked paraffins boiling from 20-260°.  
 x) The red-brown addition product of AlCl<sub>3</sub> with cracked wax olefins or C<sub>3</sub>H<sub>6</sub> was first made, and C<sub>2</sub>H<sub>4</sub> added subsequently.

The above experiments were again carried out in a 5 l. V2A autoclave with 125 g. AlCl<sub>3</sub>, with the exception of Experiment No. 142, which was run in an iron autoclave with 100 g. AlCl<sub>3</sub>. Of special interest are the experiments carried out with isooctane and isododecane. They confirm the finding made with propylene that isododecane produces a polymer of higher V.I. than isooctane. In contrast to the propylene experiment, the high viscosity of the ethylene polymer produced with isododecane is remarkable.

In Experiment No. 142, carried out with isooctane in an iron autoclave, the unfavorable catalytic effect of iron on the yield and on the V.I. is very clearly shown.

Through experiments 385, 386, 389a and 390 in which petroleum ether<sup>2</sup> was mixed with varying amounts of 20/260° liquid olefin derived from cracked paraffin, it is shown that these liquid olefins, which of themselves produce polymerized lube oils with very high V.I. (110-120°) in small amounts as adulterant or even in larger amounts in experiment 390 have an unfavorable influence on the yield. When employed in larger amounts, they apparently disturb the course of polymerization of ethylene.

The experiments 394, 428, 444 and 445 had the aim of facilitating the introduction of the  $AlCl_3$  into the autoclave in liquid form. For this purpose  $AlCl_3$ -cracked wax addition product was prepared, (Experiments 394 and 428) and another time  $AlCl_3-C_3H_6$  addition product (Experiments 444 and 445). In both cases both yield and V.I. were normal.

Experiments 325 and 312 are of interest because petroleum ether containing a small amount of Oppanol was used as solvent. At  $80^\circ C$  the added Oppanol has no appreciable influence, while if the temperature is raised to  $120^\circ C$ , Oppanol has a deleterious effect on the polymer, as shown in Exp. 312. The isobutylene polymer reacts with the  $AlCl_3$  at the higher temperature.

Table 24

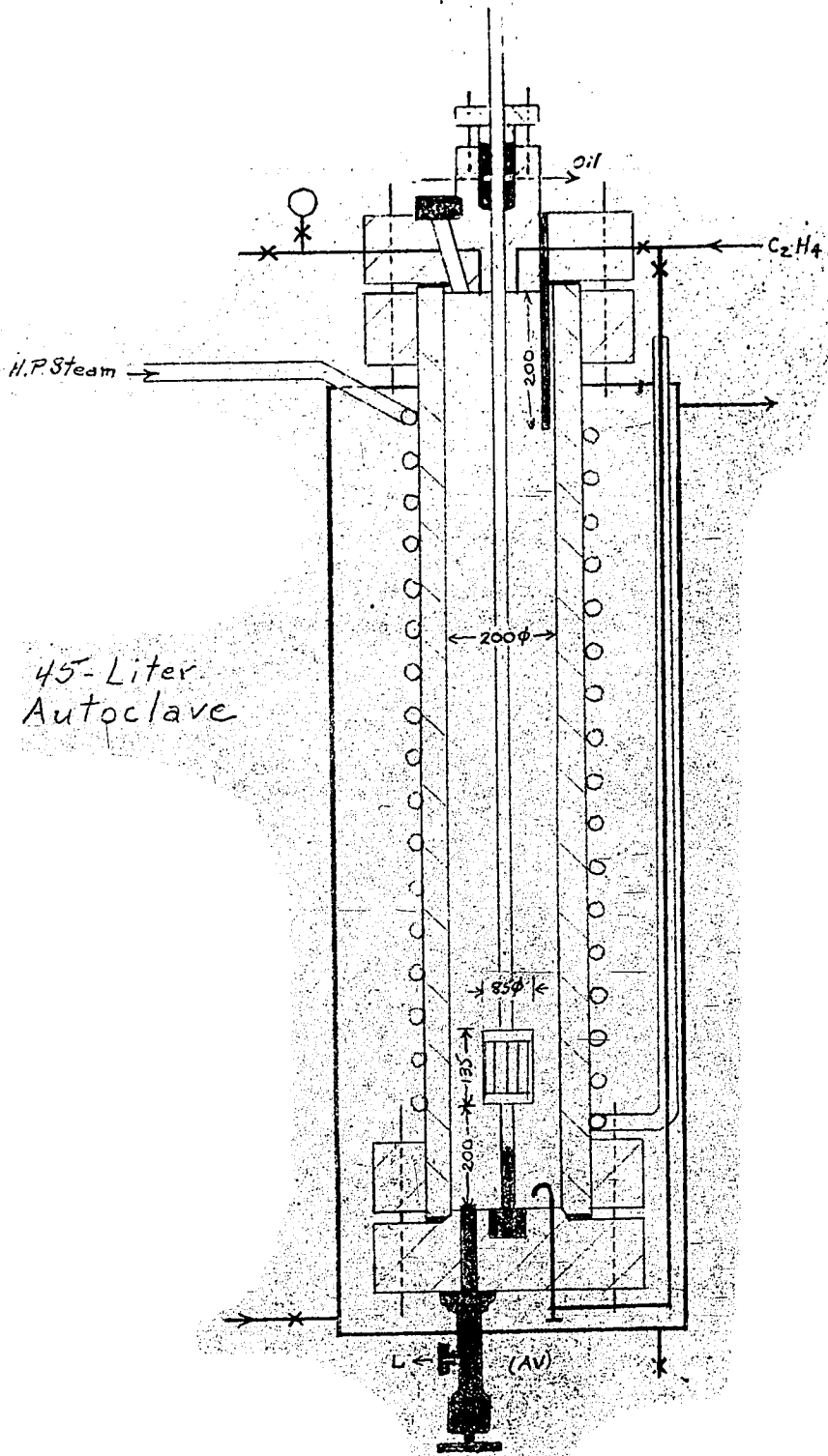
125 g.  $AlCl_3$  and 2 liters solvent

| Exp. No. | Solvent                  | Yield, l. | Lube Oil       |       |
|----------|--------------------------|-----------|----------------|-------|
|          |                          |           | $E_{99}^\circ$ | V.I.  |
|          | Crude prod. from G.V. 10 | -         | 4.88           | 96.0  |
| 415      | " " " "                  | 4.40      | 7.95           | 93.0  |
| 415a     | " " " Exp. 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 |

In Table 24 are presented the results of experiments designed to test the feasibility of continuous operation. Instead of using fresh solvent for each experiment, a portion of the crude product from the previous run was used as solvent. This crude reaction product still contained the  $AlCl_3$ -hydrocarbon complex, to which was added 125 g. of fresh  $AlCl_3$ . To begin the series, 2 liters of crude product from G.V. 10 which yielded a lube oil having  $E_{99}^\circ$  of 4.88 and a V.I. of 96.0 was used as solvent, and 4.4 l. of product were obtained in Exp. 415. Two liters of this crude product were used as solvent in Exp. 415a, and so on. The remainder of the crude product was decanted from the  $AlCl_3$  sludge and worked up in the customary way. The lube oils whose properties are given in Table 24 b. >  $150^\circ$  at 1 mm. The results of this series show that the yield and V.I. remain essentially constant while the viscosity of the product increases.

Following the experiments in a 5 l. reactor, a 45 l. autoclave was constructed from V2A. V2A was chosen instead of  $N_6$  because the latter was not available in plates. The accompanying sketch shows its construction. Gas inlets are provided both in the gas phase and under the liquid. In the bottom flange of this reactor is a special cut off valve AV. This globe-type valve communicates with the exterior through a stuffing box and its purpose is to prevent the intrusion of  $AlCl_3$  complex into the product draw-off line (L) and high pressure valve contained therein during charging or processing. This construction has proved suitable for the plant-scale reactors.

FIG. 13





The autoclave was first equipped with a simple, 300 rpm. blade type stirrer. The charge for the autoclave was 1.4 kg.  $AlCl_3$  and 11-12 kg. solvent. It was heated to ca.  $40^\circ C$ , and  $C_2H_4$  was introduced at 40 atm. Heating was continued to  $70-80^\circ C$ , at which time an exothermic reaction set in and the temperature rose to  $150-180^\circ C$ . The pressure falls to about 20 atm. after the attainment of this maximum temperature. By cooling with water of  $70-80^\circ C$  (cold water stops the reaction too completely) the autoclave contents are cooled to  $90-100^\circ C$ , and this temperature is maintained by regulating the  $C_2H_4$  feed rate. The reaction is stopped when the autoclave becomes full of liquid, as indicated by a sudden pressure rise. When using a blade-type stirrer, ethylene absorption ceased after 7-11 hours, and the crude product amounted to 31 l., i.e., the autoclave was not completely full.

We surmised that improper agitation was responsible for the incomplete reaction, as it seemed probable that the stirrer was unable to keep the heavy  $AlCl_3$  properly suspended. We then investigated an Hoesch-type stirrer, which was shown in model experiments employing glass vessels to give a much better agitation of sand and water than a blade-type stirrer at the same r.p.m. Accordingly, an Hoesch type stirrer was constructed from V2A metal, using dimensions and form suggested by the model experiments. As a result of installing this stirrer, the reaction rate increased so that the 45 l. vessel was completely filled in 4-5 hours with 31-33 kg. of product. In Table 25 is shown the dependence of reaction time on stirrer velocity.

Table 25. Influence of Stirring Speed for Hoesch-Type Stirrer

| Exp. No. | Stirring Speed,<br>rpm. | Duration,<br>hours | Yield,<br>kg. | Lube Oil         |       |
|----------|-------------------------|--------------------|---------------|------------------|-------|
|          |                         |                    |               | $^{\circ}E_{99}$ | 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              | 31.5          | 5.47             | 101.0 |
| 49       | 560                     | 2-3/4              | 29.5          | 6.11             | 105.0 |

A stirring speed of 440 rpm. appears optimum, and higher speeds are unnecessary. Reaction times for the 5 liter and 45 liter autoclaves are then about equal. In Table 26 are summarized experiments designed to determine the optimum quantity of  $AlCl_3$  required in the 45 l. autoclave.

Table 26. Influence of  $AlCl_3$  Concentration

| $AlCl_3$ Used,<br>g. | Exp. No. | Yield,<br>kg. | Lube Oil         |      | % $AlCl_3$ Relative<br>to Lube Oil |
|----------------------|----------|---------------|------------------|------|------------------------------------|
|                      |          |               | $^{\circ}E_{99}$ | V.I. |                                    |
| 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                               |

These experiments show that 1400 g. of  $\text{AlCl}_3$ , or about 8% of product, is the optimum amount; larger quantities of  $\text{AlCl}_3$  cannot increase the yield as with 33 kg. the reactor is full, nor can they increase the quality. Yield and quality both decrease if smaller amounts of  $\text{AlCl}_3$  are used. In these and subsequent experiments the  $\text{AlCl}_3$  used had the following composition: Al, 20.10%; Fe, 0.04%; Ti, 0.002%; Si, 0.02%; Cl, 79.50%; non-volatile residue, 1.4%. Table 27 shows the  $\text{C}_2\text{H}_4$  should be added beneath the surface of the liquid rather than in the gas space:

Table 27

| Exp. No. | Stirring Speed, rpm. | Location of Gas Inlet | Solvent, kg. | $\text{AlCl}_3$ , g. | Duration, hrs. | Yield, kg. |
|----------|----------------------|-----------------------|--------------|----------------------|----------------|------------|
| 31       | 440                  | gas phase             | 14           | 1400                 | 12             | 23.5       |
| 32       | 440                  | liquid "              | 14           | 1400                 | 4              | 32.0       |

Graph No. 28 illustrates the course of a polymerization in the 45 liter vessel. The  $\text{C}_2\text{H}_4$  feed rate was adjusted so that the reaction would be complete in about 6 hours. The Roman numerals on the temperature curve refer to the samples withdrawn from the reactor at the specified times. It is seen that before the maximum temperature ( $154^\circ\text{C}$ ) is attained, the pressure decrease has set in. The zig-zag character of the subsequent pressure curve is caused by irregularities in the  $\text{C}_2\text{H}_4$  additions which are adjusted to keep the temperature constant. The properties of the individual oil samples shown on Graph 28 indicate that the maximum V.I. is attained in about 4 hours; thereafter the polymer continues to become more viscous but V.I. does not increase.

The significance of the rapid temperature rise at the onset of the reaction was now investigated. In previous experiments the solvent was heated to  $40^\circ\text{C}$  and ethylene introduced under pressure. With this technique a maximum temperature of  $150$ - $180^\circ\text{C}$  was attained. In the experiments described in Table 29 ethylene was added at various pressures before the solvent was heated. All experiments used  $\text{C}_2\text{H}_4$  and  $\text{AlCl}_3$  from the same sources.

Table 28 Various Experimental Procedures

| Type of Procedure                                      | Exp. No. | Yield, kg. | Lube Oil $^{\circ}\text{Egg}$ V.I. | Max. Temp., $^{\circ}\text{C}$ |
|--|----------|------------|------------------------------------|--------------------------------|
| $\text{C}_2\text{H}_4$ added with simultaneous heating | 207      | 33.3       | 6.18 104.5                         | 160-180°                       |
|  | 213      | 33.0       | 5.33 104.6                         |                                |
| 10 atm. $\text{C}_2\text{H}_4$ added at room temp.     | 206      | 30.0       | 5.72 108.0                         | 180-190                        |
|  | 207      | 33.0       | 6.11 105.3                         |                                |
|  | 209      | 31.8       | 5.71 104.7                         |                                |
| 20 atm. $\text{C}_2\text{H}_4$ added at room temp.     | 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                         |                                |

(Table 28 continued on next page.)

| Type of Procedure   | Exp. No. | Yield, kg. | Lube Oil |       | Max. Temp. °C |
|---|----------|------------|----------|-------|---------------|
|   |          |            | °Eg9     | V.I.  |               |
| 30 atm. C <sub>2</sub> H <sub>4</sub> added at room temp. | 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 atm. C <sub>2</sub> H <sub>4</sub> added at room temp. | 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 |               |

The maximum temperature reached as a result of the initial exothermal reaction increases with increasing C<sub>2</sub>H<sub>4</sub> pressure, and at the same time the V.I. of the product increased and the viscosity decreased. The V.I. appears to pass through a maximum at 30 atm. C<sub>2</sub>H<sub>4</sub> pressure, corresponding to a maximum temperature of ca. 200°C. Higher C<sub>2</sub>H<sub>4</sub> pressures lead to a higher maximum temperature, but decrease the V.I. of the product; in addition the yield of product is poorer and its color, which is ordinarily golden yellow or greenish yellow, becomes a dark red-brown or brown-black. Table 29 shows the effect of the maximum temperature on the yield in the polymerization process.

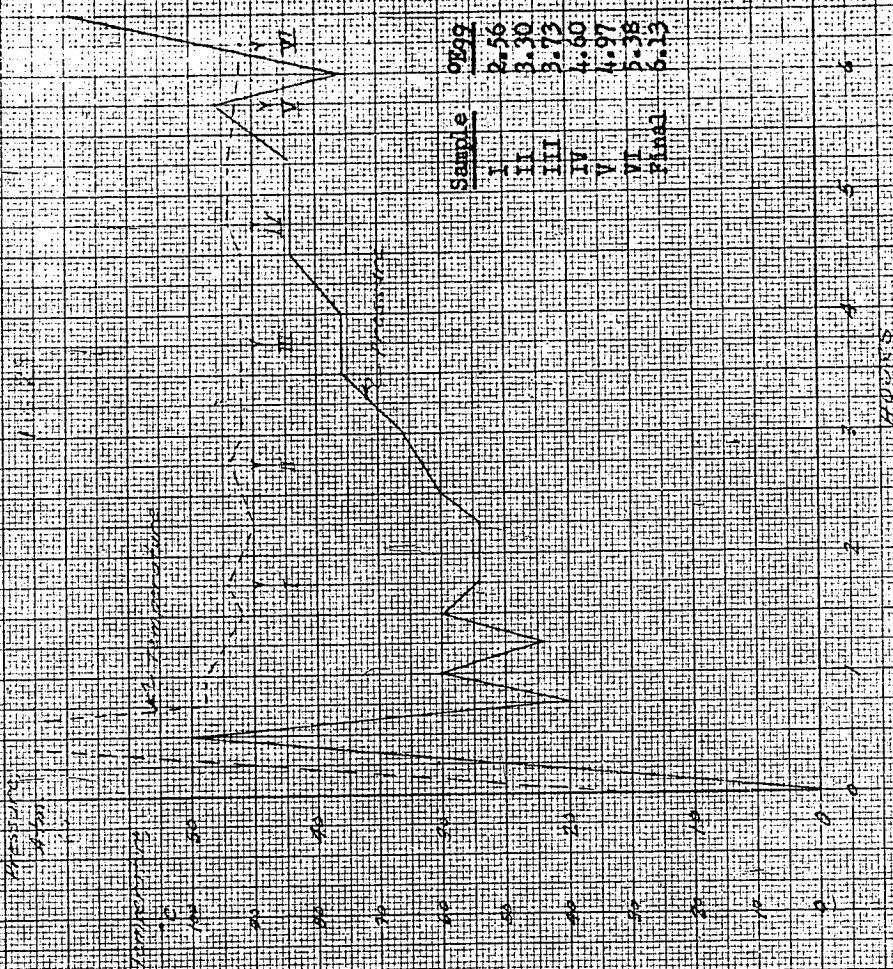
Table 29

| Max. Reactor Temp. °C | Polymer Contents kg. | Polymer Produced, kg. | Lube Oil |      | Fore-runnings* |      | Quantities per 100 kg. Lube Oil |                       |              | °Eg9 | V.I. |
|-----------------------|----------------------|-----------------------|----------|------|----------------|------|---------------------------------|-----------------------|--------------|------|------|
|                       |                      |                       | kg.      | wt.% | kg.            | wt.% | Fore-runnings                   | AlCl <sub>3</sub> kg. | Solvent, kg. |      |      |
| 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 | 29.5                            | 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  |

\* Including loss.

The above results are mean values of experiments in the 5 liter and 45 liter autoclaves, using identical specimens of C<sub>2</sub>H<sub>4</sub> and AlCl<sub>3</sub> (1.4% residue). As the maximum temperature attained increases, the content of lube oil in the polymer (fraction b. > 150°C at 1 mm.) decreases steadily, as does the viscosity of the oil. The V.I., however, increases, so as the maximum temperature increases one obtains smaller yields of a thinner oil with higher V.I. To illustrate the reproducibility of the process, a series of runs were made under identical conditions, as summarized in Table 30.

| Sample | Wt%  | V.I.  |
|--------|------|-------|
| I      | 2.56 | 100.2 |
| II     | 3.30 | 102.3 |
| III    | 3.73 | 107.0 |
| IV     | 4.60 | 111.5 |
| V      | 4.97 | 111.0 |
| VI     | 5.38 | 110.0 |
| Final  | 6.13 | 110.0 |



Wt%

V.I.

Table 30. Experiments in 45 l. Autoclave

|                        |                             |
|------------------------|-----------------------------|
| Solvent                | 15 l. = 12 kg. forerunnings |
| AlCl <sub>3</sub>      | 1.4 kg. (1.3% residue)      |
| Max. Temperature       | 225-235°                    |
| Duration of Experiment | 4 hours                     |

| Exp. No. | Reactor Contents,<br>kg. | Lube Oil Properties |       |
|----------|--------------------------|---------------------|-------|
|          |                          | °Egg                | 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 solvent used in these experiments was the forerunnings from distillation of previous products. The table shows that both the yield and product quality are readily reproducible. This fact was further confirmed by experiments in a 100 liter Ni-metal autoclave 0.2 m. in diameter and 4 m. long, equipped with a Hoesch type stirrer operating from the bottoms. It is possible to obtain oils of lower viscosity by thermal depolymerization of the highly viscous C<sub>2</sub>H<sub>4</sub> polymer, as illustrated in Table 31.

Table 31. Depolymerization

An oil with °Egg of 7.23 and a V.I. of 106.2 was subjected to gentle depolymerization for 15 hours by heating at 330°. The temperature was raised slowly, taking 5 hours to reach 330°C.

| Fractions b. at 1 mm. | %                   |                    |                     |                     |
|-----------------------|---------------------|--------------------|---------------------|---------------------|
|                       | On reaching<br>330° | 5 hours<br>at 330° | 10 hours<br>at 330° | 15 hours<br>at 330° |
| <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 160°   | 17.2                | 20.0               | 20.8                | 21.2                |
| Lube Oil:             |                     |                    |                     |                     |
| °Egg                  | 7.23                | 5.52               | 4.44                | 3.64                |
| V.I.                  | 107.0               | 107.5              | 107.6               | 107.2               |

The depolymerization was carried out in the absence of air, and a small amount of decomposition to lower boiling products occurred. The desired result of

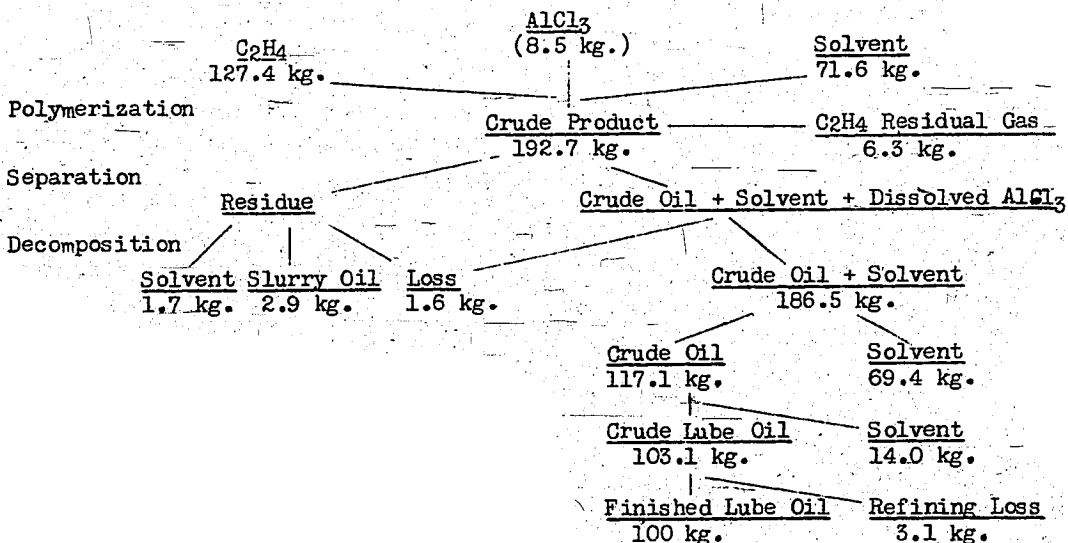
lowering the viscosity without decreasing V.I. was achieved. Graph 33, p. 42a, shows the course of the depolymerization for C<sub>2</sub>H<sub>4</sub> polymer as compared with other oils. (Note: page 42a is missing.) As the temperature was held below 330°C, the time for depolymerization was correspondingly longer (120 hours). Oils produced in the 45 and 100 l. autoclave were subjected to motor tests in cooperation with RLM. In these tests the ethylene lube oils showed a superiority over the mineral oils previously used. The synthetic oil, which was assigned the code number SS900 by RLM, had significantly longer life in a single cylinder motor, gave less carbon deposition, and had a favorable viscosity-temperature property, thereby making possible the actual planning of higher output aircraft motors.

On June 10, 1936 it was decided to construct a 700 T/yr. plant at Leuna. Ethylene requirements were to be obtained from waste gas ethane by means of the cracking process developed by Dr. Klein. Recovery and purification from the cracked gas was to be accomplished in a Linde plant. RLM first asked that this plant produce a lube oil of 3.0° Engler viscosity at 99°C. Since, as is evident from Table 30, there are always small variations in the viscosity of the product and furthermore since RLM asked for a flash point higher than 200°C, which implies a viscosity above 3°E<sub>99</sub>, their specifications could be attained in practice by a subsequent depolymerization.

A material balance for the ethylene polymerization process is given in Table 32. The figures represent mean values for a series of experiments carried out in the 45 liter autoclave. This balance was used as a basis for the design of the 700 T/yr. semi-commercial plant at Leuna.

Table 32. C<sub>2</sub>H<sub>4</sub> Balance

45 liter Autoclave



From 127.4 kg.  $C_2H_4$  are obtained:

|                    | <u>kg.</u>   | <u>wt. %</u> |
|--------------------|--------------|--------------|
| Lube Oil           | 100.0        | 78.4         |
| Solvent            | 13.5         | 10.6         |
| Slurry Oil         | 2.9          | 5.0          |
| Unreacted $C_2H_4$ | 6.3          | 2.3          |
| Loss               | 4.7          | 3.7          |
|                    | <u>127.4</u> | <u>100.0</u> |

Part II

Development of the Commercial Ethylene Polymerization Plants at Leuna

A) The 700 T./yr. SS 903 Plant

The flow diagram No. 34 shows the operating principles of the 700 T./yr. SS 903 plant whose construction was decided upon in June, 1936, and begun in August, 1937.

A cracked gas containing 30%  $C_2H_4$  was obtained by cracking  $C_2H_6$  in hydrogenation off-gas by the oxygen-vacuum process-(Dr. Klein, Dr. Haubach) in Me 125. This dilute ethylene was concentrated to a pure product in Me 125a by a Linde plant consisting of 3 distilling columns. The  $C_2H_4$  then was furnished to Me 126 at a pressure of 60-200 atm. for polymerization.

After clearing up a few difficulties with the hairpin bundle preheater - originally of FF-30, later of Si-chromal - the cracking plant went on-stream in June 1937 and proved unobjectionable.

Because of an ethane shortage early in 1937 the cracking plant had to be converted to process propane. This conversion resulted in a considerably greater quantity of liquid product in the cracked gas so that the scrubbing section of the Linde plant had to be expanded. To free the cracked gas of the accompanying liquid hydrocarbons required an increase in the absorbing facilities, whose efficiency could be significantly improved by the substitution of a benzol absorbing oil in place of middle-oil B. This enlargement of the absorber made necessary the installation of an absorbing oil regenerator. An Alkazid plant was installed for the removal of  $CO_2$  from the cracked gas. Since this plant showed a tendency to foam excessively, a carbon tower was installed ahead of it to remove the last traces of oil.

Carryover of lubricating oil from the circulating compressor with high pressure  $C_2H_4$  caused further disruptions in the operation of the Linde plant, since in this way the perforated plates (Siebboden) of the last two distilling columns of this apparatus were obstructed, leading to impaired fractionation and finally to complete plugging. The installation of separators did away with these upsets. Only after the installation of these safeguards was satisfactory operation of the Linde plant possible. On the average, the Linde plant then furnished 98-99%  $C_2H_4$  containing 0.5-1.0%  $C_2H_2$  and practically free of  $O_2$ , CO and  $CO_2$ .

The polymerization plant consisted of two autoclaves of 1000 liter content (500  $\phi$  x 5000) of  $N_6$ -metal, corresponding to previous experience in 5, 50 and 100 liter scale. For agitation an Hoesch stirrer was used, which was inserted into the reactor from below and was driven by a V-rubber belt (Gummikeilriemen). As in the small scale experiments, the process was batchwise, with ports for adding solvent and catalyst in the top flange while the gas inlet and the polymer drawoff were in the bottom flange. Heating and cooling were provided by a water jacket connected to a water circulating system and reservoir.



After charging 150-250 l. of forerunnings (solvent) and 20-25 kg.  $AlCl_3$  (Kontakt) to the autoclave, ethylene was introduced at a pressure of 20-45 atmospheres, depending on the end product desired, and the reaction between  $C_2H_4$  and  $AlCl_3$  initiated by heating the water jacket to ca.  $120^\circ C$ . Without further heating or cooling from the exterior, the interior temperature was allowed to rise to the requisite maximum value, feeding in  $C_2H_4$  if necessary. After the maximum temperature ( $160-220^\circ$ ) was attained, the autoclave was cooled and upon reaching  $120^\circ C_2H_4$  was introduced. In this way the reaction temperature was held at  $110^\circ-120^\circ$  by regulation of the hot water circulating system (at  $50-100^\circ$ ).

After the autoclave was completely full, (requiring 8-9 hours) the entire contents were released into a 10 cu.m. settling vessel. This was an insulated vessel and had a conical bottom to aid in the separation of the residue. At least 24 hours was required for complete separation, so that of the 3 separators installed, one was always filling, one separating and the third emptying.

After separation of the  $AlCl_3$  slurry consisting of the addition compound of  $AlCl_3$  and oil, the oil of the upper layer was neutralized batchwise in a 2 cu.m. hydrolyzing kettle by addition of hydrated lime, which was filtered out in a press. The clear filtrate, the crude product, was separated into a low-boiling top product and a residue by an atmospheric still consisting of a heat exchanger, pipe still, and a bubble plate column. The top product was returned again to polymerization and the raw SS oil is processed further. Since its viscosity ( $E^{99} = 4.0 - 4.5$ ) was too high, it was subjected to thermal depolymerization in the absence of air until the viscosity of the fraction b.  $> 150^\circ C$  at 1 mm. dropped to  $3^\circ E_{99}$ .

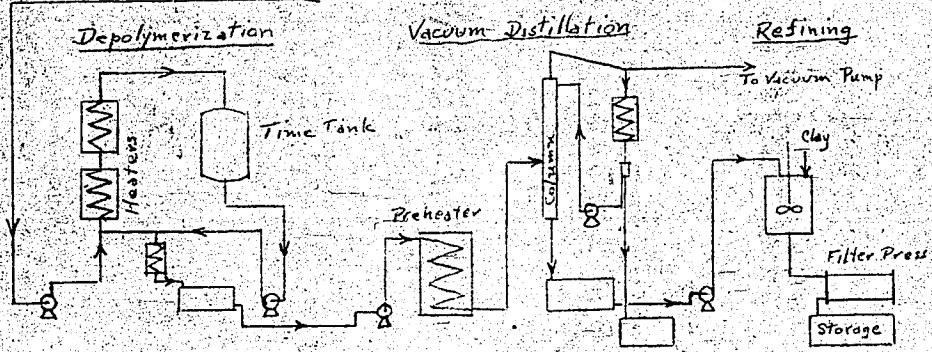
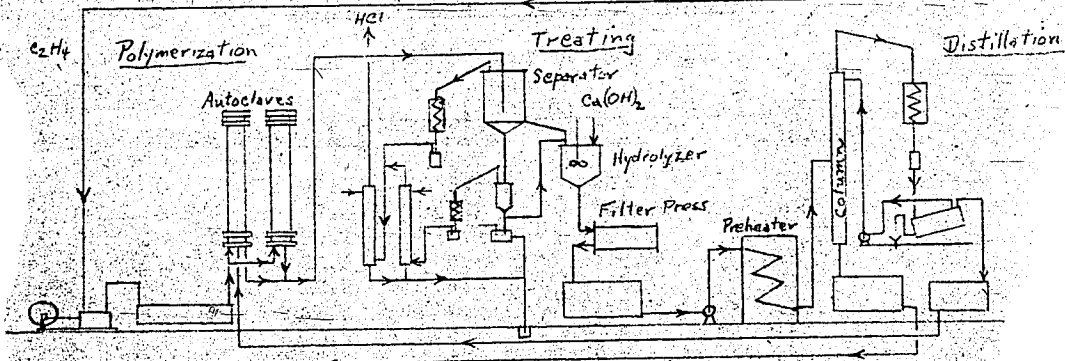
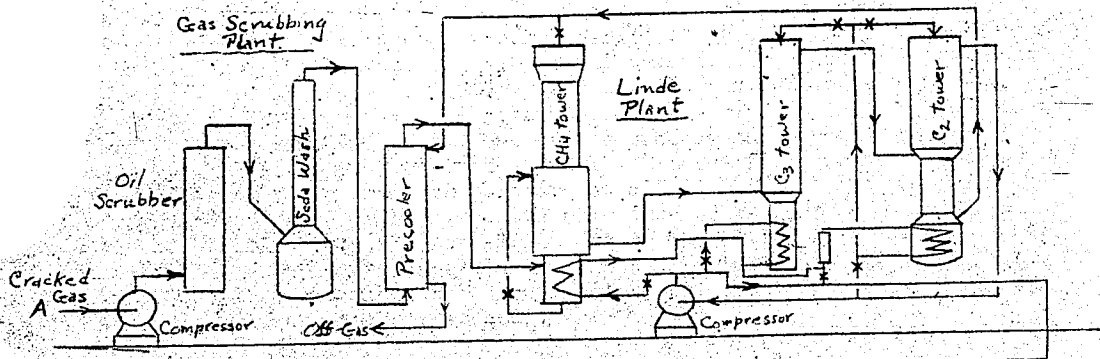
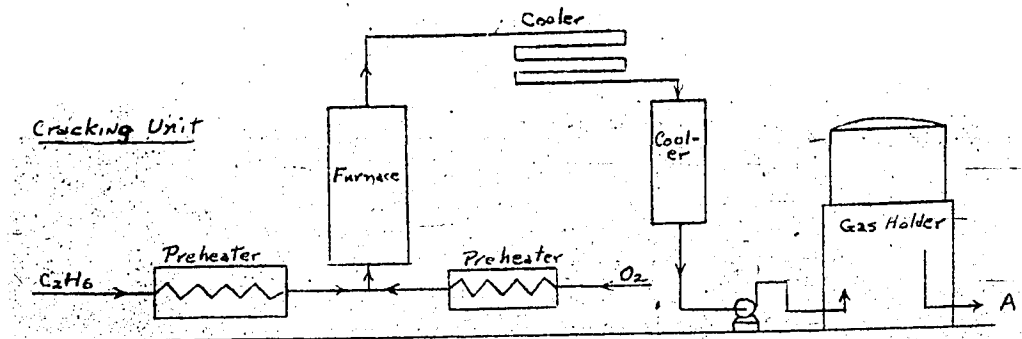
The crude oil was then freed of the low boiling cracked products formed in the thermal treatment by vacuum distillation. The distillation residue was then refined by treatment with 5% bleaching earth at  $80^\circ C$  and subsequent filtration. The refined SS oil was adjusted to the exact desired viscosity in a mixing kettle, centrifuged for final purification and filled into drums.

By the end of 1937 the first SS oil was produced. It conformed to the specification then in effect for SS 903: V.I. of over 115 at  $3^\circ E_{99}$ .

In 1938 the testing of the oil produced in this process began at the Oppau proving station and by RLM. During 1938 production was increased to ca. 60 T/month and thus the design production figure for the plant was attained. The yield of SS oil, calculated on  $C_2H_4$  consumed, was raised during the year from 56 to 70%. In September 1938 delivery to the Luftwaffe was begun.

Meanwhile, experiments had shown that a valuable aircraft engine oil with almost the same performance properties as SS 903 oils could be produced by making a very viscous ethylene oil of  $6^\circ E_{99}$  (SS 906) and mixing this with a highly refined low viscosity mineral oil of  $1.8^\circ E_{99}$ . Therefore production was shifted from SS 903 to SS 906 by the RLM and at the same time the ratio of mineral oil to synthetic oil was established at 1:1.

FIG. 34



Because of the shift in production from SS 903 to the thicker SS 906, the depolymerization process and consequently the vacuum distillation step could be omitted. An atmospheric distillation sufficed to remove the forerunnings from the lube oil provided about 10% steam was added at the bottom of the column. The vacuum distillation of the entire crude polymer was out of the question because of the high per cent of tops (40-50).

Depolymerization

The depolymerization process was in operation only for a short time. The plant in Me 1266 consisted of a 10 cu.m. N<sub>6</sub>-metal vessel which was insulated and opened at the top through a condenser. The product to be depolymerized was withdrawn from the bottom of the N<sub>6</sub>-metal vessel, and circulated continually by a pump through an electric heater. Circulation was continued until the desired degree of depolymerization was attained, as determined by means of samples withdrawn from the system. At the end of the process the product was cooled to about 60°. The process required about 12-16 hours for a charge of 4000 l. of distillation residue and a temperature of 375°. While these conditions produced the desired change in viscosity, the oil darkened markedly and the pour point was raised from -30 or -35° to -16 to -22°. The latter effect could be avoided by operating at a lower temperature. Table 33 illustrates the course of the depolymerization reaction when 4 cu.m. of SS oil of 5.6°E99 were depolymerized under very mild conditions, at 360°.

Table 33. Depolymerization of SS Oil

Charge: 4000 l. of 5.6°E99 Oil

| Sample Number | Hours  | SS Oil b. > 150° at 1 mm. |      |       |           |          |
|---------------|--------|---------------------------|------|-------|-----------|----------|
|               |        | %                         | °E99 | V.I.  | Flash Pt. | Pour 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      |

It required 6 hours to bring the oil up to 360°, and 8-3/4 hours thereafter sample No. 2 was withdrawn. It is seen that a rapid fall in viscosity, from 5.6° to 3.4°Egg, occurred during the first half of the run, but thereafter the viscosity remained essentially unchanged, even though additional thermal decomposition is occurring as shown by the decrease in yield of lube oil from 80% to 68.8%. Thus the depolymerization is essentially complete in 24 hours at 360°. The advantage of this carefully conducted thermal treatment is seen in the flash and pour points of the samples; whereas the flash point remains higher than 230° the pour point drops from -34 to -41 in the first 17 hours. It is evident that the space-time yield of the depolymerization process is poor. However, because the shift to the production of SS 906 led to the abandonment of the process projected experiments on depolymerization under pressure were never carried out.

#### Vacuum Distillation

Plant 2, originally designed for vacuum distillation has in the meantime been converted to atmospheric pressure operation, but in case of necessity can be restored to its original service by altering the design of the stillhead according to Sketch No. 80.

#### Operating Conditions:

|                |                |
|----------------|----------------|
| Vacuum         | 20 mm.         |
| Oil Exit Temp. | 330°           |
| Throughput     | 450-500 l./hr. |
| Top Product    | 75-100 l./hr.  |
| Bottoms        | 200-250 l./hr. |

#### B. The 3000 T/yr. SS 906 Plant

After conversion of the original plant to SS 906 oil and attainment of the designed production rate, its expansion from 700 to 3000 T/yr. was undertaken in the fall of 1938. For this purpose a switch from 1000 l. to 4500 l. autoclaves (800  $\phi$  x 9000) was made (see drawing No. 35). Four 800 mm. N<sub>6</sub>-metal autoclaves were installed and corresponding expansion of the settling and distillation facilities was accomplished. The first 2 of the large autoclaves went in operation in May, 1939, and the transition from the 1000 l. to the 4500 l. autoclaves was made without difficulty. The third and fourth autoclaves started up in the autumn, and operated normally. By the end of the year the yield of SS 906 oil was 75% and design production was attained (3000 T/yr.). By expansion of the AlCl<sub>3</sub>-hydrolyzing facilities and improvement in general operation the production in 1940 was raised to 4000 T/yr.

In 1940 the construction of a larger plant, of 10,000 T/yr. capacity, was undertaken. This expansion required an increased number of units. Frection of 6 additional autoclaves (800  $\phi$  x 9000), as well as other parts of the plant, was to have been completed by the middle of 1941. Because of difficulties in obtaining materials, only two of the 6 N<sub>6</sub>-metal autoclaves were in operation by the end of the year, and plant output was limited to 500 T/month. The last 4 autoclaves went into operation during 1942. These 4 autoclaves could not be made from N<sub>6</sub>-metal as Krupp had ceased to produce it, but instead were made from normal high-pressure steel. These vessels operated poorly at first but in the course of time the quality of the polymer improved. SS oil production rose during 1942 to 700-750 T/month.

FIG. 80

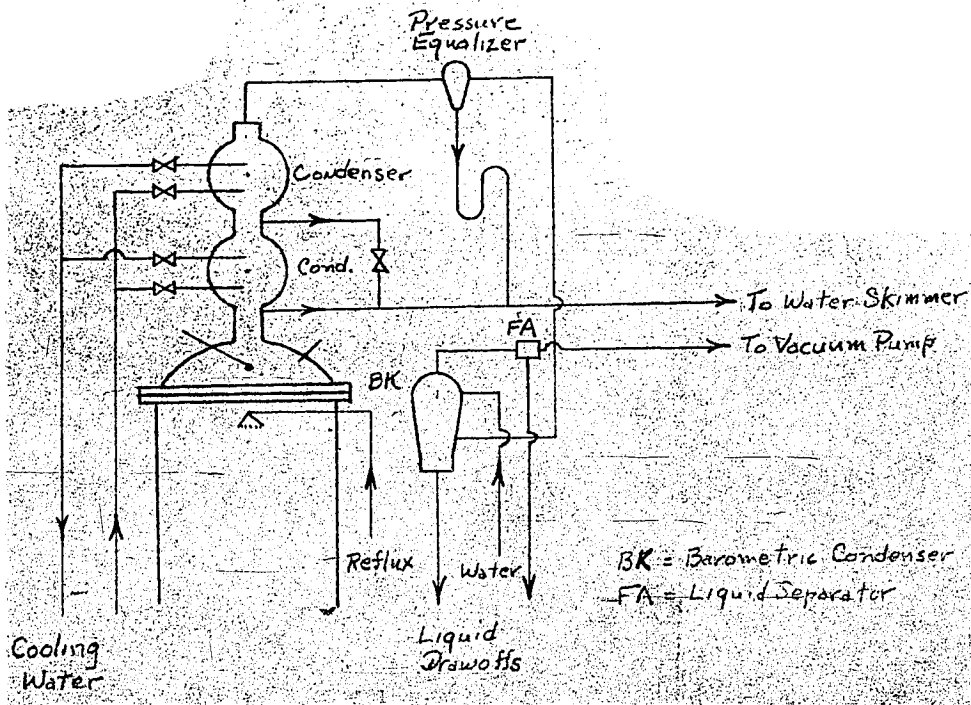
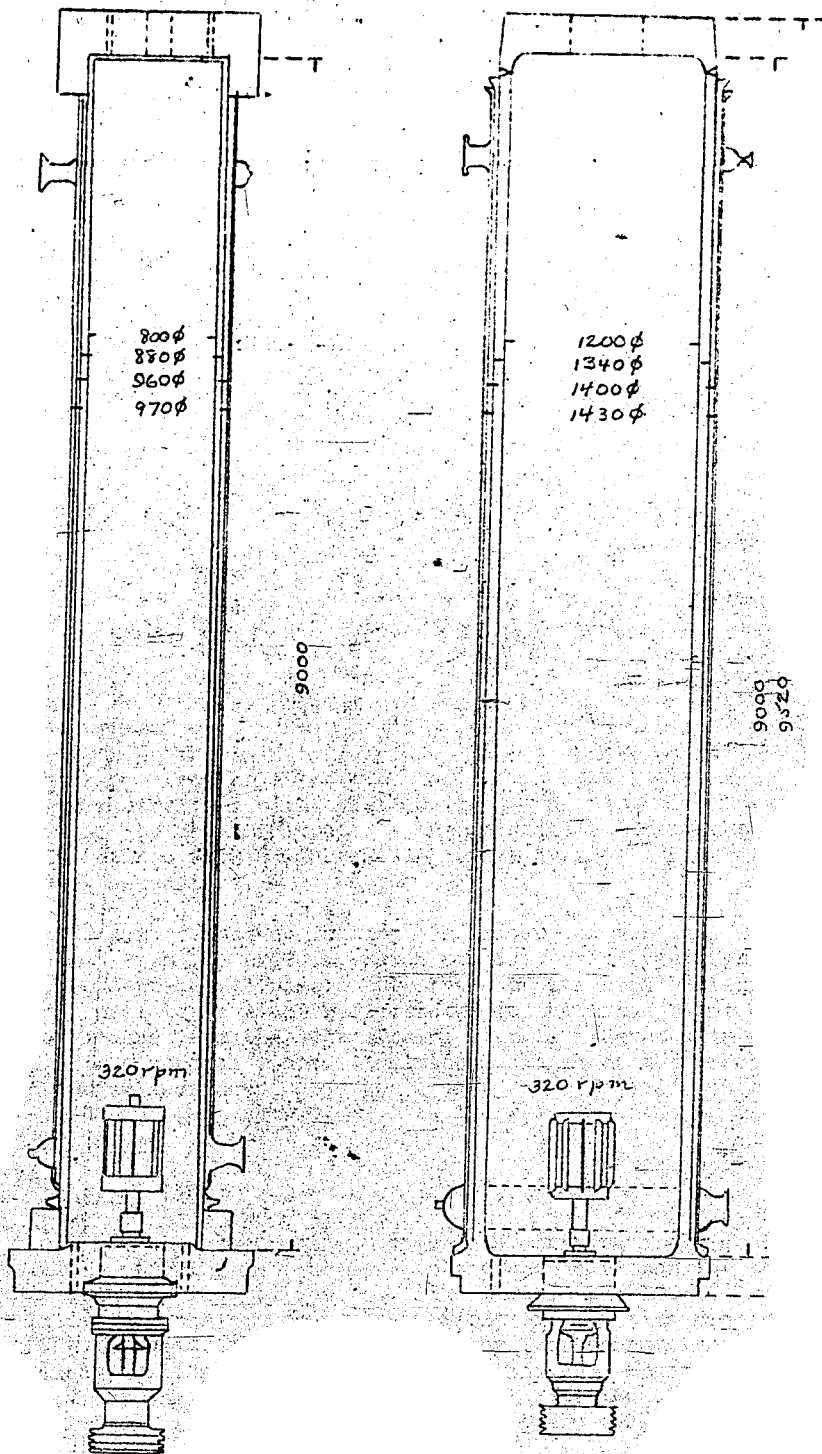


Fig. 35



For the new SS oil plants at Moosbierbaum, Schkopau and Heydebreck even larger autoclaves (10,000 l.) of 1200 mm. diameter were built.

### General Description of the Process

Charging of an 800  $\phi$  autoclave (4500 l.) is accomplished as follows: From 1200 to 1500 l. of forerunnings (solvent) together with 125 kg. of  $AlCl_3$  are added with stirring. After the vessel is closed,  $C_2H_4$  is introduced in the cold for about 30 minutes. If SS 906 is desired, the initial  $C_2H_4$  pressure is 20 atm. and the maximum temperature attained is 150-160°; if SS 903 is being made, the pressure is 35 atm. and the maximum temperature 200-220°. The autoclave is heated to an exterior temperature of 130-140° by 5 atm. steam and reaction begins within 1/2 hour. When the reaction temperature exceeds that of the water jacket, the heating system is shut off so that it will not act as a coolant. Upon attainment of the desired maximum temperature (which may require further addition of  $C_2H_4$ ) the water circulating system is again opened up and runs continuously as a cooling system for the remainder of the run. When the reaction temperature drops to 140° addition of  $C_2H_4$  is begun. Now the circulating cooling medium is gradually cooled down from 130° to 50-60° and  $C_2H_4$  is added in increasing quantities (from 100 to 300 cu.m./hr.) to maintain a constant reaction temperature; namely, 110-115° for SS 906 oil and 120-130° for SS 903. After approximately 8 hours of ethylene input, the autoclave is full, as is evidenced by the rising of elements attached to the interior of the top flange and by an increase in pressure to 60 atm. The autoclave contents are now drained into the first hydrolyzer, to which acid methanol is added continuously, then to the centrifuges. The partially purified product leaving the second centrifuge goes to the main hydrolyzer. When the main hydrolyzer is filled with the entire charge from an autoclave, the oil is hydrolyzed at 80° with fresh methanol and neutralized with hydrated lime. The lime is removed in a frame filter press. The clear filtrate is then distilled and the column bottoms (SS oil) is refined with 0.7% bleaching earth at 120°. Finally it is clarified in Alfa Laval separators.

The hydrocarbon-containing gas arising as vent gas from the reactor and as off-gas from the process, which consists chiefly of  $C_2H_4$  and  $C_2H_6$ , is water- and soda-washed to remove HCl, freed of its high boiling (40/140°) fractions in charcoal tower A and recirculated to the Linde plant or burned as fuel. The residue from the centrifuging step is treated with water and worked up as R oil in a special plant. Individual stages of the process are discussed in the following sections.

## I. Polymerization

### a. Stirring

It has already been mentioned in describing small-scale experiments that efficient stirring is necessary to promote heat transfer and polymerization. The agitator in the 1000 l. reactor, like that in the 100 l., was a Hoesch-stirrer built into the bottom flange. Early difficulties due to severe corrosion of the shaft of the stirrer were overcome by improvements in the stuffing box design, namely, oiling the lip packing by means of a Bosch pump and providing a means of introducing a small amount of SS' oil into the autoclave so that the penetration of  $AlCl_3$  sludge into the packing gland was prevented.

Early difficulties due to severe corrosion of the shaft of the stirrer were overcome by improving stuffing box design and by sealing the stuffing box by injection of a small amount of SS oil so that back-flow of  $AlCl_3$  sludge into the packing gland was prevented.

On going over from the 1000 l. to the 4500 l. autoclave, construction of the stuffing box was improved in several ways, in particular by constructing it in two parts so that the packing could be changed without dismantling the whole stirrer. Furthermore the stirrer assembly was flanged to the lower lid of the autoclave so that it was easier to get into the reactor. Better cooling of the packing was also provided (see drawing 38). This type of stirrer construction has proven itself during 4 years operation. With careful assembling and regular lubrication, only one packing change (4 hours work) was required in several months' time. All stirrers had to be replaced after 8-10 months, requiring 8-10 hours of work. In the best case a stirrer lasted over a year. Table 34 shows the life of the stirrers in autoclaves 1-4 during 1940:

Table 34

| Stirrer           | <u>Autoclave I</u> | <u>II</u> | <u>III</u> | <u>IV</u> |
|-------------------|--------------------|-----------|------------|-----------|
| Installed (date)  | 2/26/40            | 3/14/40   | 7/26/39    | 2/24/40   |
| Repacked          | 3/15               | 8/6       | 12/5       |           |
| Repacked          | 9/8                |           | 8/1/40     |           |
| Repacked          | 2/12/41            |           |            |           |
| Repacked          | 6/8                | 10/16     | 10/28      | 10/22     |
| Service in Months | 15                 | 6-1/2     | 13         | 8         |

SS 903 or R oil was used as lubricant.

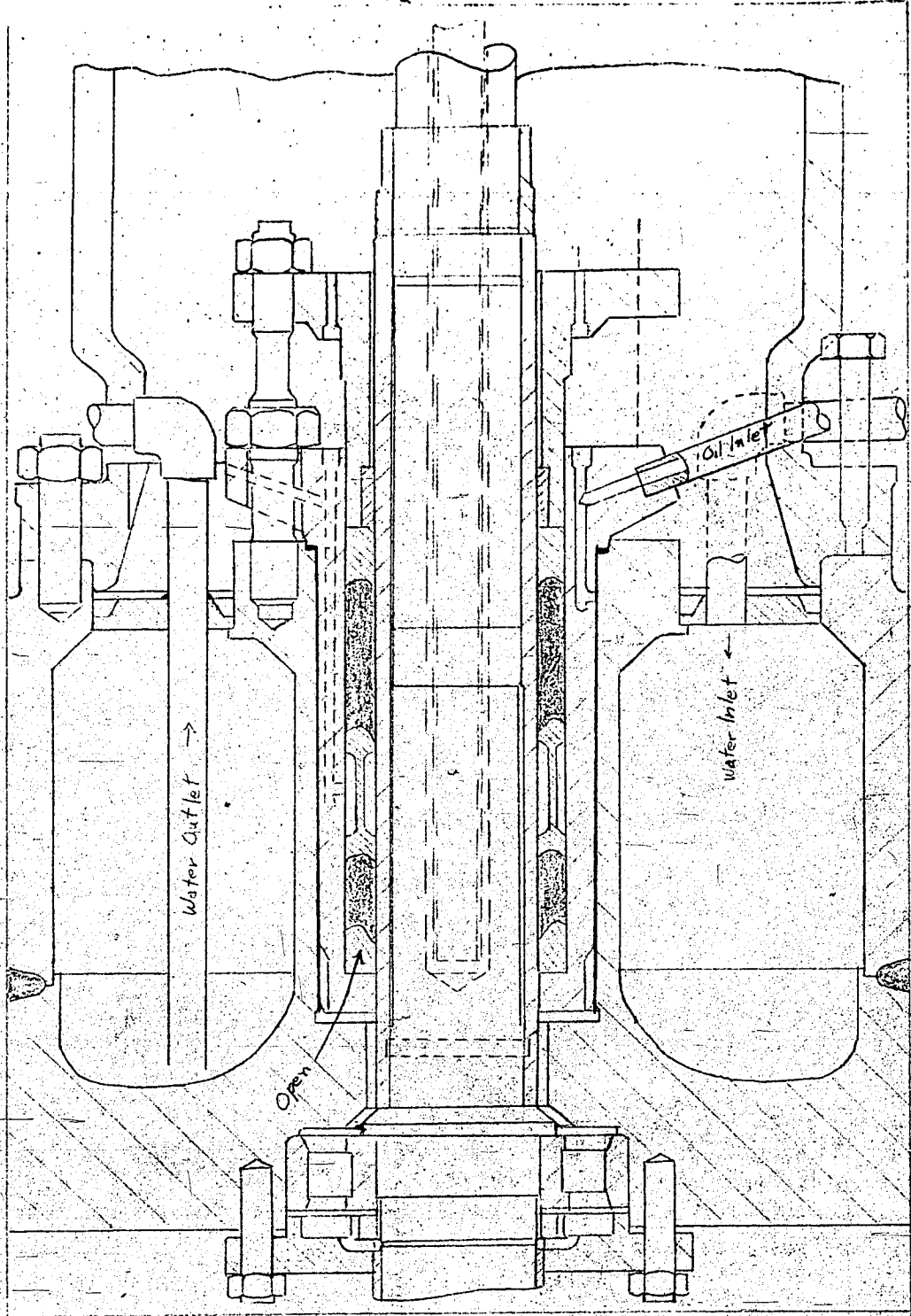
It was established that the optimum stirring speed in the 800  $\phi$  autoclaves was 250/300 rpm. Velocities above this had no further effect and velocities of 120 rpm. caused a marked decrease in the rate of absorption of  $C_2H_4$ , doubling the reaction time. The autoclave operator should be impressed with the importance of the lubrication routine as well as the cooling of the interior and exterior of the stirrer. Too great pressure in the lead to the stuffing box lantern-gland is to be avoided at all times as this could crush the lip packing and cause the stirrer to overheat or even seize completely. It has been found expedient for the life of the packing to keep the stirrer running continually, even if the autoclave is temporarily out of service.

b. Autoclave Material.

It was shown in small scale experiments that the reactor material can have a great influence on the polymerization process. For this reason both the 1000 l. and the first six 4500 l. autoclaves were constructed of  $N_6$  metal. Operation of these reactors was unobjectionable from the first, as Table 35 will show. (Table 35 missing.) Difficulties were first encountered when no more  $N_6$  metal could be procured for making reactors VII - X. This is discussed under section I.g.



FIG 38



c. Gas

It was previously noted in small scale experiments that the purity of the  $C_2H_4$  had a profound effect on the polymerization, and the same effects were noted in the 1000 l. autoclave. Carryover of small quantities of CO and  $CO_2$ , which occurred in the early work before the operation of the gas-scrubbing and Linde plants was under thorough control, depreciated the quality of the oil as well as the yield or even stopped the reaction if the content of oxygen containing gases rose above 0.1%.

Presence of up to 3%  $C_2H_2$  had no deleterious effects on the reaction. The polymerization process could be carried out with only 92%  $C_2H_4$  provided the gas was free from oxygen containing compounds and the diluent was  $C_2H_6$  as could occur, for example, by contamination with bottoms from the third distilling column in the Linde plant, too high an operating temperature in the reboilers, or other variations in the operation of the distilling columns.

On the basis of experience obtained with the 500 and 800 mm. diameter autoclaves, the feed gas should have the following purity requirements: The  $C_2H_4$  should be at least 95% pure, and more if possible; a higher content than 5% of inert gases such as  $N_2$ ,  $CH_4$  or  $C_2H_6$  is undesirable. The quality of the oil is not influenced by these inerts.

|   |  |
|---|--|
| <u>Acetylene</u>                          | Up to 3% not harmful.  |
| <u>Butylene &amp; higher monoolefins</u>  | Less than 0.5%   |
| <u>Butadiene &amp; higher diolefins</u>   | Without effect up to 0.1%  |
| <u>Carbon dioxide</u>                     | Very harmful. Barium hydroxide solution should not become cloudy even upon tests of long duration.                                   |
| <u>Carbon monoxide</u>                    | Tolerable up to 0.005%, but a CO content below 0.001% is desirable. (According to Linde the hemoglobin test is sensitive to 0.004%.) |
| <u>Carbonyl sulfide</u>                   | Up to 5 mg./cu.m. is tolerable.  |
| <u>Phosgene</u>                           | Undesirable, but upper tolerable limit has not been determined.  |
| <u>Molecular Oxygen</u>                   | Over 0.01% is harmful.   |
| <u>Oxygen containing organic products</u> | Alcohols, aldehydes, ketones, ethers, etc. are very harmful but order of magnitude not known.  |
| <u>Ammonia and amines</u>                 | Undesirable, but tolerable limit unknown.  |
| <u>Hydrogen sulfide</u>                   | Harmful, but limiting concentration unknown.   |

|   |  |
|---|--|
| <u>Methyl- and higher mercaptans</u>      | Less harmful. Concentration should not exceed 15 mg./cu.m.                         |
| <u>Chlorinated hydrocarbons</u>           | Have no significant influence on the reaction.                                     |
| <u>Phosphorus &amp; arsenic compounds</u> | Not yet investigated.  |
| <u>Water vapor</u>                        | Over 300 mg./cu.m. gives polymers of low viscosity. Up to 250 mg./cu.m. tolerable. |

All of the above figures in mg./cu.m. or volume per cent refer to 15°C and 735 mm. pressure.

#### The Water Absorptivity and Drying of Ethylene

The water content of  $C_2H_4$  used for the manufacture of SS oil is important because too high a water content can affect the polymerization adversely. It has been shown previously that ethylene can have a higher water content that would be predicted from the gas laws. It is also known that ethylene, like propane, ethane and similar gases can form stable hydrates at these temperatures. These facts show that water and ethylene interact at these high pressures more strongly than would be inferred by analogy to other compounds. According to publications of the Linde Company, gases with strong associative power for water, such as  $CO_2$ , can absorb from 4 to 5 times as much water vapor at 50° and 87 atm. than the perfect gas laws predict.

In recent processes for the concentration of ethylene, as for example, the copper-alkali scrubbing process of Dr. Hauber or in the chemical removal of impurities from a concentrated ethylene stream, the ethylene comes in contact with aqueous solutions and can become saturated. Consequently it was necessary to investigate the water absorptivity of ethylene and to study means of removing it.

#### Determination of Water

Various methods were used for the determination of small concentrations (10-50 mg./cu.m.) of water in ethylene. Direct freezing out of water from the gas at -80° is uncertain in practice. Use of  $Mg_3N_2$  also leads to uncertainties at these low concentrations because of the presence in the nitride of small amounts of adsorbed  $NH_3$ ; thus, even carefully dried nitrogen gave a blank value of 20 mg./cu.m.

Since the ethylene available for this investigation was free of higher olefins which are known to polymerize in the presence of  $P_2O_5$ , it was possible to use this reagent by spreading it on glass wool in a U-tube and absorbing water from the gas with it. Check experiments with  $Mg(ClO_4)_2$  gave comparable results.

#### Water Absorptivity

The theoretical water content of 1 cu.m. of saturated gas at 20°C is 17.35 g. In agreement with this calculation, the water content of  $C_2H_4$  at 20°

and 1 atm. was found by the above method to be 19.8 g./cu.m. According to the gas laws, the water content should decline in inverse proportion to the pressure. Since ethylene is highly compressible; that is, in a unit volume of compressed gas there are more normal cubic meters than in the case of an ideal gas, the water content per normal cubic meter must be less than that determined by calculation. These values are compared with the experimentally determined values in Table 35a.

Table 35a. Results in g./cu.m.

| 20°        | Experimental value | Value calculated from gas laws | Compressibility factor | Calculated value corrected for compressibility |
|------------|--------------------|--------------------------------|------------------------|--|
| 1 atm.     | 19.8*              | 19.0                           | 1.05                   | 18.9   |
| 10 "       | 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  |
| <u>40°</u> |                    |                                |                        |  |
| 1 atm.     | 71.0               | 63.0                           | 1.0                    | 63.0   |
| 10 "       | 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   |

\* 19.5 with N<sub>2</sub>.

The experimental water contents vary by ± 5-10% in a series of experiments and it was not possible to obtain better agreement despite careful work. The experimental procedure was as follows: Dry ethylene from a Linde plant was led through a reducing and regulating valve into the apparatus, which was held at the desired temperature in a water bath. The apparatus consisted of a coiled tube in which the C<sub>2</sub>H<sub>4</sub> was brought to temperature and 2 450 cc. vessels in series which were filled with wet filter paper. It later developed that 1 vessel would have been sufficient to saturate the ethylene at a rate of 40 l./hour. From the saturating chamber the ethylene was vented into another coiled tube to return it to the desired temperature, conducted into the water absorption train and finally vented through a gas meter.

It is seen in Table 35a that the observed values far exceed the calculated, and lie in a range in which water had a bad effect on the polymerization. Accordingly, experiments on the drying of C<sub>2</sub>H<sub>4</sub> were initiated, using the apparatus described above to which was added a drying tower. The following conclusions resulted: -

Silica gel B (30 cc.) at first dried gas of 0.75 g./cu.m. water content to 0.3-0.4 g./cu.m. at 20°C and 100 atm. but after 2 liters of gas had been put through the water content rose to over 0.5% at 4 liters. The small water content of the silica gel, 10%, was confirmed by regeneration.

Silica gel A was much more absorbent. With 30 cc. of gel at 100 atm. and 20°C, the water content of the gas after 40 l. had been passed was between 0 and 60 mg./cu.m.; after 4300 l. the water content was still between 0 and 60; after 6000 l. over 100 and after 7500 l. over 200 mg. Similar results were obtained when, after regeneration, the flow rate was increased to 200 l./hr. Apparently the silica gel A is saturated at about 25% water. The quantity of water held by the silica gel at saturation is the same at atmospheric pressure as at 100 atm. and on this basis it was expected to obtain a dry gas of 0.5 mg./cu.m. water content whereas the actual value was about 50. This also indicates the powerful water absorbing property of compressed C<sub>2</sub>H<sub>4</sub>.

Calcium carbide proved outstandingly reactive. With 30 cc. of CaC<sub>2</sub>, throughput rate of 200 l./hr. and temperatures of 20 and 40°, water contents varied from 20-50 mg./cu.m. After passage of 10 cu.m. of gas through the 30 cc. of CaC<sub>2</sub>, of the 34.5 g. of CaC<sub>2</sub> only 10.8 g. was still in the form of granules, the remaining 23 g. having been decomposed and powdered.

Use of CaCl<sub>2</sub> and NaOH was not technically feasible so experiments with them were given up.

In order to test the ethylene dried by calcium carbide in the polymerization process, experiments were carried out on a semi-plant scale. Ethylene with a water content of 600-800 mg./cu.m. was passed at a rate of 15 N cu.m./hr. through 30 l. of granulated carbide contained in a tower 200 mm. in diameter at 100 atm. pressure and was dried to a water content of 40-60 mg./cu.m. While the wet gas polymerized very poorly, with the reaction ceasing prematurely, and produced an oil of only 90-95 V.I. at 4-4.5°Egg the ethylene dried with carbide gave a normal polymerization run and produced an SS 906 oil of normal properties. By drying a gas containing 800 mg./cu.m. of water is produced a dry gas containing 0.1% acetylene, but this is not harmful to the polymerization. As these experiments and larger scale tests at Schkopau have shown, there is no danger that this drying process will produce H<sub>2</sub>S, PH<sub>3</sub> and the like in sufficient amounts to be harmful. Hydrogen sulfide cannot be detected in the dry gas when C<sub>2</sub>H<sub>4</sub> containing 20 g./cu.m. of water is dried with carbide.

#### d. Aluminum chloride.

Another point investigated was the quality of the aluminum chloride which can have a very important effect on the polymerization process. The content of residue plays an important part in small scale runs. It is obvious that as the equipment becomes larger this effect will decrease since only the upper layer, which can come in contact with the atmosphere, will form the unsublimable residues of aluminum oxychloride, aluminum hydroxide and oxide which are injurious to the polymerization. The residue analysis of an old and a fresh shipment gives results as follows.

|  |                         |       |         |
|--|-------------------------|-------|---------|
| 3-month-old shipment:                      | Sample from upper layer | 19.9% | Residue |
|  | Deep sample - powder    | 3.7%  | "       |
|  | Deep sample - granular  | 0.9%  | "       |
| Fresh shipment:                            | Original sample, top    | 1.8%  | "       |
|  | Sieved - coarse         | 0.7%  | "       |
|  | Sieved - fine           | 4.3%  | "       |
| Original sample after 3 minutes in the air |                         | 5.9%  | "       |

Even in the case of larger charges (30 kg. for the 1000 l. reactor, 125 kg. for the 4500 l. reactor) the filling procedure should be carried out carefully in order to prevent unnecessary air or moisture to enter. For this purpose a simple device was constructed to eliminate manual charging. This device has various advantages. Before charging the oven the lid of the catalyst vessel is exchanged for a special lid (conical with shut-off). This exchange can be made very quickly so that air is excluded. Around the catalyst vessel is a ring which enables it to be drawn up by a pulley and tipped over the charging hole. Meanwhile the autoclave is charged with forerunnings with stirring. In this manner the catalyst charging is easily and quickly carried out without damage to the catalyst and without dust and odor troubles.

By going to the 1000 l. autoclaves with charges corresponding to the small experiments (250-300 l. forerun and 25-30 kg. catalyst at a maximum temperature of 200°) the course of the reaction appeared the same. Also the appearance of the oil, the viscosity and V.I. were good; however, a large deterioration of the pour point was observed. In a longer series of experiments it was determined that the pour point increase was caused by the lower iron content of the AlCl<sub>3</sub> used which came from a new plant in Ludwigshafen. After this, alumina with a higher iron content was used which caused the pour point to return to -30° again. The following table shows experiments with iron-poor and iron-containing catalyst.

Table 36

| AlCl <sub>3</sub> Iron-poor (0.6% Fe) |              |            |             |                      | AlCl <sub>3</sub> Iron-containing (2% Fe) |              |            |             |                      |
|---------------------------------------|--------------|------------|-------------|----------------------|---|--------------|------------|-------------|----------------------|
| No.                                   | Max.T.<br>°C | SS<br>°Egg | Oil<br>V.I. | 150°<br>i.V.<br>P.P. | No.                                       | Max.T.<br>°C | SS<br>°Egg | Oil<br>V.I. | 150°<br>i.V.<br>P.P. |
| 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 at various temperatures from 200-225° and varying rate of gas feeding they all show the strong effect of the iron content; iron-poor catalyst yields pour points of -20 to -14° while iron-containing catalysts give -32 to -35°. When the conversion to the production of SS 906

occurred in 1939 by lowering the maximum temperature to 160-170°, the iron content of the AlCl<sub>3</sub> was no longer important for with this product good pour points are easily obtained.

Table 37

| No.  | Max. Temp., °C | SS Oil b. >150° in Vacuum |       |            |             |
|------|----------------|---------------------------|-------|------------|-------------|
|      |                | °Egg                      | V.I.  | Pour Point | Flash Point |
| S299 | 173            | 6.38                      | 113.3 | -37        | 208         |
| N306 | 170            | 6.58                      | 110.1 | -35        | 220         |
| S300 | 175            | 7.01                      | 114.5 | -35        | 212         |
| N307 | 180            | 6.19                      | 113.4 | -36        | 220         |
| S301 | 170            | 6.42                      | 113.8 | -37        | 218         |
| N308 | 170            | 6.23                      | 113.7 | -36        | 218         |
| S302 | 173            | 6.14                      | 112.2 | -35        | 216         |

Table 37 shows the properties of the first high viscosity oils obtained in the 1000 l. autoclave. The optimum amount of AlCl<sub>3</sub> is the same as for the production of SS 903, namely 7-7.5% based on finished lube oil. At the end of 1941 we were faced with the problem of producing light oil for the manufacture of cold-starting oil for panzers and airplanes, said oil to have the highest possible V.I. and lowest possible pour point at a viscosity of 3°Egg. Since we had in the meantime switched to 4500 l. autoclaves and were obtaining AlCl<sub>3</sub> from the Schkopau plant, the polymerization experiments were carried out at temperatures above 200°. The runs listed in Table 38 were made in the N-6 autoclaves I-VI (4500 l. capacity) using 1200-1400 l. of forerunnings and 125 Kg. AlCl<sub>3</sub>, maximum temperature of 220° and reaction temperature of 110-120°.

Table 38

| Types of Aluminum Chloride                              | No.                   | E° <sub>99</sub> | V.I.  | Pour Point | Flash Point |
|---|-----------------------|------------------|-------|------------|-------------|
| (a) AlCl <sub>3</sub> I; Fe-containing;<br>0.1% Fe      | III 1453              | 2.96             | 124.2 | -19        | 194         |
|   | IV 1397               | 3.67             | 122.7 | -22        | 210         |
| (b) AlCl <sub>3</sub> II; Fe-containing;<br>2.5-3.5% Fe | IV 248                | 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 <sub>3</sub> I and II mixed<br>50% I + 50% 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 )<br>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 )<br>VI 358 ) | 2.24             | 120.4 | -21        | 201         |

It is again evident that an iron-free  $AlCl_3$  (a) at a high maximum temperature gives a product with a high V.I. but a poor pour point. With an  $AlCl_3$  containing more than 2.5% Fe (b), on the other hand, at this high maximum temperature an SS oil is produced which has a viscosity of 3°E99, a good pour point of -35 to -40° and a flash point of over 200°. It is important to note that the requisite iron content cannot be obtained by mixing samples of  $AlCl_3$  with different iron contents but must be obtained through sublimation to a homogeneous product (b), as the extremely variable results of the experiments in series c and d indicate.

The disadvantage of this method of preparing thinner SS oil was that the filtration of the  $AlCl_3$ -lime sludge from the main hydrolyzer was made much more difficult. The filter cloth became plugged and as a result operation of the filter was very variable, resulting in additional work, loss of oil, and interrupted production. The crude oil obtained when using larger amounts of lime than in the SS 906 process or when employing filter aids such as bleaching clay, were easily filterable only when the clean filter press was precoated with lime cake from a charge of SS 906.

In March, 1942, large quantities of SS 903 oil (50 cu.m.) were produced by this method for the first time together with the normal production of SS 906. The SS 903 oil had the following properties:

|           |            |                 |                  |
|-----------|------------|-----------------|------------------|
| 3.72 E°99 | 117.9 V.I. | -32° pour point | 213° flash point |
| 2.86 E°99 | 113.8 V.I. | -39° pour point | 193° flash point |

As the last half of this batch had a low V.I., it was redistilled, whereupon its viscosity and pour point were improved.

Repetition in the autumn of 1942 under the same flow conditions (max. temperature 220° and operating temperature 120°) gave a product with such extremely variable properties that SS 903 could not be made from it, as the following samples listed in Table 39 show:

Table 39

| Date    | Number       | First Runnings<br>liters | SS Oil 150° i.V. |       |            |             |
|---------|--------------|--------------------------|------------------|-------|------------|-------------|
|         |              |                          | E°99             | V.I.  | Pour Point | Flash Point |
| 9-16-42 | I 2150       | 1500                     | 3.87             | 113.7 | -39        | 210         |
|         | VI 966       | 1200                     | 4.27             | 116.0 | -36        | 214         |
| 9-18-42 | 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         |
| 9-19-42 | 4 Autoclaves | 1200                     | 2.61             | 125.6 | -34        | 194         |
| 9-21-42 | 7 Autoclaves | 1200                     | 2.40             | 124.1 | -36        | 222         |

In all cases the working up of the crude oil involved great difficulty. Since the quality of gas and forerun was in order, the difficulty could only be due to the  $AlCl_3$ . There was no indication of irregularities in its analysis, however.



A re-examination of the source of bauxite used at Schkopau for  $AlCl_3$  production during the preceding month revealed that the  $AlCl_3$  was first produced from French Bauxite, but that later, however, mixtures of French and Hungarian Bauxite were used.

French Bauxite gave  $AlCl_3$  which contained less than 0.5%  $TiCl_4$ . The use of mixtures of Hungarian Bauxite gave instead a titanium content of about 3%. The polymer produced with this  $AlCl_3$  caused the operating difficulties described above to a somewhat greater extent. (According to word from Dr. Paetsch of Schkopau these titanium containing aluminum chlorides have caused emulsion formation in other cases.)

For the preparation of SS 903, Schkopau now furnish an aluminum chloride with uniform Fe content (K-type  $AlCl_3$ ) made from French Bauxite. The following table lists a series of experiments which were carried out in the new 4500 liter autoclaves, which under the same conditions produce a less viscous oil.

Autoclave X (V2A) and autoclave VII (chromium plated) were charged with iron-free and K-type  $AlCl_3$  and operated under various maximum temperatures.

Table 40a

Iron-containing  $AlCl_3$  (K-type) Autoclave X  
4500 liters, V2A coated  
Ingredients: 1200 l. foreruns, 125 kg.  $AlCl_3$ .

| <u>Max. Temp.</u> | <u>No.</u> | <u>E°<sub>99</sub></u> | <u>V.I.</u> | <u>Pour Point</u> | <u>Flash Point</u> |
|-------------------|------------|------------------------|-------------|-------------------|--------------------|
| 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 40b

Iron-containing  $\text{AlCl}_3$  (K-type) Autoclave VII  
 4500 liters chromium plated  
 Ingredients: 1200 l. foreruns, 125 liters  $\text{AlCl}_3$

| <u>Max. Temp.</u> | <u>No.</u> | <u>E°99</u> | <u>V.I.</u> | <u>Pour Point</u> | <u>Flash Point</u> |
|-------------------|------------|-------------|-------------|-------------------|--------------------|
| 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 of the normal autoclave (I - VI) on this day the V.I. values were only 108.

Table 40c

Iron-free  $\text{AlCl}_3$ , Autoclave VII, 4500 liter chrome plated  
 Ingredients: 1200 liters forerun, 125 kg.  $\text{AlCl}_3$

| <u>Max. Temp.</u> | <u>No.</u> | <u>E°99</u> | <u>V.I.</u> | <u>Pour Point</u> | <u>Flash Point</u> |
|-------------------|------------|-------------|-------------|-------------------|--------------------|
| 150               | 190        | 4.77        | 107.8       | -38               | 216                |
|                   | 202        | 4.67        | 113.4       | -33               | 228                |
|                   | 223        | 5.82        | 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                |

It is seen that by use of the autoclave, thinner polymers are produced than in the case of the N<sub>6</sub> autoclave. The maximum temperature must be raised to 200° to produce SS oil with viscosities of 3 to 3.5°E<sub>99</sub>. However, with iron-free  $\text{AlCl}_3$  a product having a pour point of no more than -15° to -20° is produced. With K-type catalyst this pour point trouble only occurred at temperatures over 210°.

In the preparation of SS 903 in an autoclave not made of N<sub>6</sub> material the purity of the gases is of still greater importance. The polymerization of ethylene with high maximum temperature to SS 903 is not possible at all in a N<sub>6</sub> autoclave if the gas is polymerized only with difficulty to an SS 906 oil. This is still more difficult in the 800 mm. autoclaves VII - X, which in operations at low maximum temperature are very sensitive to gas impurities. Concerning the working up of the crude SS 903 product made with K-type  $\text{AlCl}_3$ , the difficulties formerly experienced in the settling and subsequent processing of the  $\text{AlCl}_3$ -slurry

(for example, severe contamination of the centrifuge and plugging of the residue draw-off line) can be eliminated, if the raw product is forced into the primary hydrolyzer at 125-130°C and if the decomposition with methanol is carried only far enough to give a product from the primary hydrolyzer of 8-12 mg. KOH/g. acid number. In the case of the SS 906 oil, if decomposition is carried out to an acid number only half this great the addition compound separates in gritty form, which causes damage to the centrifuge. Since the addition compound from the product made at higher maximum temperatures is more difficult to decompose than that made at lower temperature, the treatment of the slurry must be carried out at a higher temperature. In this case it is advantageous to concentrate the AlCl<sub>3</sub>-liquor only to 25% instead of to 40% in order to minimize decomposition of the slurry. In using K type AlCl<sub>3</sub> it has also proven possible to filter the lime slurry directly. Temperature should be maintained at 75-80°C.

e) Initial Charge

Small scale experiments have shown that the amount of solvent in the original charge affects the viscosity of the final product. This effect also is apparent in the 1000 l. and 4500 l. autoclaves as shown in Tables 41 and 42.

Table 41

1000 l. N<sub>6</sub> Autoclave; 30 kg. AlCl<sub>3</sub>  
Max. Temp. 200°  
Working Temp. 130°

| a) 250 l. Forerun |              |             |           |           | b) 200 l. Forerun |              |             |           |           |
|-------------------|--------------|-------------|-----------|-----------|-------------------|--------------|-------------|-----------|-----------|
|                   | <u>E°/99</u> | <u>V.I.</u> | <u>PP</u> | <u>FP</u> |                   | <u>E°/99</u> | <u>V.I.</u> | <u>PP</u> | <u>FP</u> |
| N 221             | 4.27         | 110.8       | -37       | 214       | N 227             | 5.04         | 116.4       | -30       | 195       |
| S 215             | 4.04         | 114.3       | -38       | 195       | S 221             | 5.33         | 109.4       | -30       | 221       |
| N 222             | 4.35         | 110.6       | -36       | 216       | N 228             | 5.39         | 113.1       | -37       | 200       |
| S 216             | 3.98         | 108.1       | -36       | 220       | S 222             | 5.00         | 113.8       | -36       | 203       |
| N 223             | 4.39         | 110.5       | -40       | 205       | N 229             | 5.26         | 113.8       | -33       | 226       |
| S 217             | 4.00         | 112.5       | -37       | 198       | S 223             | 5.31         | 109.4       | -34       | 211       |
| N 224             | 4.38         | 112.3       | -34       | 205       | N 230             | 5.87         | 110.0       | -34       | 220       |

Table 42

4500 l. N<sub>6</sub> Autoclave I-IV; 125 kg. AlCl<sub>3</sub>  
Max. Temp. 160°  
Working Temp. 120°

| a) 1200 l. Forerun |              |             |           |           | b) 800 l. Forerun |              |             |           |           |      |     |
|--------------------|--------------|-------------|-----------|-----------|-------------------|--------------|-------------|-----------|-----------|------|-----|
| <u>13.10.40</u>    | <u>E°/99</u> | <u>V.I.</u> | <u>PP</u> | <u>FP</u> | <u>14.10.40</u>   | <u>E°/99</u> | <u>V.I.</u> | <u>PP</u> | <u>FP</u> |      |     |
| 13.40              | IV 711       | 5.58        | 110.7     | -34°      | 198               | 23.30        | IV 714      | 7.82      | 112.9     | -35° | 226 |
| 15.00              | II 768       | 6.06        | 109.3     | -34°      | 215               | 3.40         | II 771      | 7.98      | 114.1     | -35° | 220 |
| 17.00              | I 808        | 6.57        | 110.6     | -34°      | 220               | 8.30         | I 811       | 7.20      | 116.6     | -35° | 222 |
| 19.10              | III 760      | 5.80        | 113.1     | -34°      | 199               | 12.15        | III 763     | 7.89      | 114.8     | -35° | 215 |
| 23.10              | IV 712       | 6.21        | 112.6     | -34°      | 205               | 16.00        | II 772      | 7.75      | 113.4     | -35° | 226 |

One sees, especially in the 1000 l. autoclave, that at a maximum temperature of 200° a lowering of the initial charge by 20% raises the viscosity at 99° from 3.8-4.4 to 5.0-5.9. In the 4500 l. autoclave, which was used to produce SS 906, the effect is weaker. A decrease of 33% forerun raises the viscosity from 5.6-6.6 to 7.2-8.0.

f) Polymerization Course

The course of the polymerization, using the 4500 l. N<sub>6</sub> autoclave, shown by three records in Table 43, demonstrates the following:

- A. Good reaction rate with normal gas addition
- B. Good reaction rate with high gas addition
- C. Bad reaction rate

Table 43

| Autoclave No.         | II/1910          |  |  |  | VI/541          |  |  |  | VI/403          |  |  |  |
|-----------------------|------------------|--|--|--|-----------------|--|--|--|-----------------|--|--|--|
| Charge l.             | 1400             |  |  |  | 1200            |  |  |  | 1200            |  |  |  |
| AlCl <sub>3</sub> kg. | 120              |  |  |  | 120             |  |  |  | 120             |  |  |  |
| Gas introduction      | 13.20 h. 20 atm. |  |  |  | 4.30 h. 20 atm. |  |  |  | 18.5 h. 20 atm. |  |  |  |
| Heat applied          | 13.50            |  |  |  | 5.0             |  |  |  | 18.45           |  |  |  |
| Max. Pressure         | 14.15 19 atm.    |  |  |  | 5.15 32 atm.    |  |  |  | 19.00 30 atm.   |  |  |  |
| Max. Temperature      | 14.25 150°       |  |  |  | 5.20 160°       |  |  |  | 19.15 180°      |  |  |  |

| Time  | II/1910 |     |     | P atm. | C <sub>2</sub> H <sub>4</sub> m <sup>3</sup> /h | Time  | VI/541 |     |     | P atm. | C <sub>2</sub> H <sub>4</sub> m <sup>3</sup> /h |
|-------|---------|-----|-----|--------|---|-------|--------|-----|-----|--------|---|
|       | 1       | 2   | 3   |        |   |       | 1      | 2   | 3   |        |   |
| 14.30 | 98      | 139 | 77  | 12     |   | 5.45  | 78     | 140 | 70  | 13     |   |
| 45    | 80      | 120 | 61  | 10     |   | 6.00  | 72     | 139 | 52  | 12     | 350   |
| 15.00 | 74      | 112 | 53  | 10     | 230   | 15    | 72     | 123 | 60  | 13     |   |
| 15    | 72      | 111 | 53  | 10     |   | 30    | 78     | 121 | 52  | 17     |   |
| 30    | 71      | 111 | 52  | 10     |   | 45    | 80     | 125 | 53  | 20     |   |
| 45    | 70      | 110 | 52  | 12     |   | 7.00  | 80     | 128 | 52  | 20     | 350   |
| 16.00 | 75      | 110 | 52  | 15     | 300   | 15    | 82     | 122 | 51  | 22     |   |
| 15    | 87      | 112 | 52  | 16     |   | 30    | 82     | 125 | 51  | 23     |   |
| 30    | 88      | 112 | 52  | 16     |   | 45    | 82     | 125 | 51  | 26     |   |
| 45    | 85      | 111 | 52  | 17     |   | 8.00  | 85     | 128 | 51  | 27     | 430   |
| 17.00 | 83      | 110 | 54  | 17     | 320   | 15    | 85     | 127 | 51  | 28     |   |
| 15    | 85      | 110 | 65  | 18     |   | 30    | 85     | 122 | 50  | 29     |   |
| 30    | 90      | 115 | 60  | 19     |   | 45    | 87     | 122 | 50  | 30     |   |
| 45    | 87      | 112 | 58  | 20     |   | 9.00  | 92     | 123 | 50  | 33     | 480   |
| 18.00 | 87      | 110 | 62  | 21     | 350   | 15    | 102    | 128 | 50  | 36     |   |
| 15    | 88      | 110 | 64  | 21     |   | 30    | 123    | 127 | 70  | 39     |   |
| 30    | 90      | 110 | 66  | 22     |   | 45    | 135    | 135 | 100 | 60     |   |
| 45    | 95      | 110 | 68  | 24     |   | 10.00 | 130    | 130 | 115 | 60     | 430   |
| 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     |   |       |        |     |     |        |   |
| 15    | 110     | 110 | 110 | 60     | 350   |       |        |     |     |        |   |

| VI/403 Temp. °C |    |     |    |        | VI/403 Temp. °C                                 |      |     |     |     |        |   |
|-----------------|----|-----|----|--------|---|------|-----|-----|-----|--------|---|
| Time            | 1  | 2   | 3  | P atm. | C <sub>2</sub> H <sub>4</sub> m <sup>3</sup> /h | Time | 1   | 2   | 3   | P atm. | C <sub>2</sub> H <sub>4</sub> m <sup>3</sup> /h |
| 19.30           | 85 | 140 | 70 | 12     |   | 1.15 | 95  | 110 | 95  | 52     |   |
| 45              | 75 | 115 | 75 | 20     |   | 30   | 100 | 115 | 110 | 52     |   |
| 20.00           | 75 | 115 | 60 | 28     | 250   | 45   | 100 | 115 | 110 | 52     |   |
| 15              | 75 | 115 | 60 | 28     |   | 2.00 | 100 | 112 | 80  | 58     |   |
| 30              | 80 | 120 | 60 | 33     |   | 15   | 100 | 110 | 100 | 60     |   |
| 45              | 80 | 118 | 60 | 36     |   | 30   | 100 | 110 | 100 | 60     |   |
| 21.00           | 75 | 115 | 60 | 38     | 260   | 45   | 100 | 110 | 105 | 60     |   |
| 15              | 75 | 110 | 60 | 40     |   | 3.00 | 100 | 120 | 110 | 60     | -100  |
| 30              | 80 | 115 | 70 | 41     |   | 15   | 100 | 118 | 100 | 60     |   |
| 45              | 80 | 112 | 60 | 42     |   | 30   | 100 | 110 | 100 | 50     |   |
| 22.00           | 80 | 110 | 60 | 44     | 235   | 45   | 100 | 110 | 100 | 60     |   |
| 15              | 80 | 110 | 65 | 50     |   | 4.00 | 100 | 110 | 100 | 60     |   |
| 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   |      |     |     |     |        |   |

Analysis of the SS Oils Boiling at 150° in vacuo

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

For this type of autoclave the optimum gas velocity lies between 250-350 m<sup>3</sup>/h. At higher velocities up to 500 m<sup>3</sup>/h one obtains a deterioration of the product quality. Better quality oil is obtained if the ethylene is added at a gradually increasing rate.

T<sub>2</sub> in Table 43 is the most important temperature reading and is the lower part of the autoclave. T<sub>1</sub> is the temperature at the top of the autoclave and T<sub>3</sub> the temperature of the autoclave mantel which must be held lower during the strong exothermic reactions (A & B) than during the slower one (C) in order to hold the liquid polymer at the desired temperature.

A was produced at a normal reaction rate with a maximum temperature of 150° and a working temperature of 110°. The entire process from the first

introduction of  $C_2H_4$  at 20 atm. until the end takes 7 hours. One can see from the values of  $T_1$  and from the sudden increase from 28 to 60 atm. that at the end of the 6-1/2 hours the autoclave is full of liquid reaction product. During the last quarter hour the mantle temperature  $T_3$  must be raised in order to hold  $T_2$  as no more gas is introduced on account of the pressure increase.

Example B was initially brought up to a gas introduction of 350  $m^3/h$  and was gradually increased to 480  $m^3/h$ . With cooling water at 50° the exit stream is between 120° and 130°. The duration of the run is only 5-1/2 hours, but the V.I. of the oil falls to about 107.

Example C shows the course of an arrested reaction which is likewise the case when the purification of the gases is poor. While in A & B, in spite of the vigorous gas introduction, the autoclave pressure only rises to 60 atm. in the last half hour; this increase appears in C in the middle of the reaction and the desired inner temperature can only be kept by raising the outer temperature. Since in the case of C the autoclave does not become full one does not get agreement of  $T_1$  and  $T_2$ .

In order to follow the course of the reaction, samples were withdrawn from a 4500 l. autoclave run beginning at the moment of maximum temperature and at short intervals for a short time and then at 30 minute intervals.

IV 870 (Curve 50a) was run with hydrogenated high boiling forerun (250-340°); I 998 (Curve 50b) was run with hydrogenated low boiling forerun (130-250°). Besides the course of the inner temperature and autoclave pressure one sees after the first hour a gradual rise in the viscosity of the oil and the amount that distills over 150° in vacuo. The use of the high boiling oil yields a thicker end product.

Table 44 shows numerically the course of the reaction T998.

NEUFFEL & EBERT CO., N. Y. NO. 380-13  
 Milling Machine, Patent, for accepting, and, filing, survey.  
 Made in U. S. A.

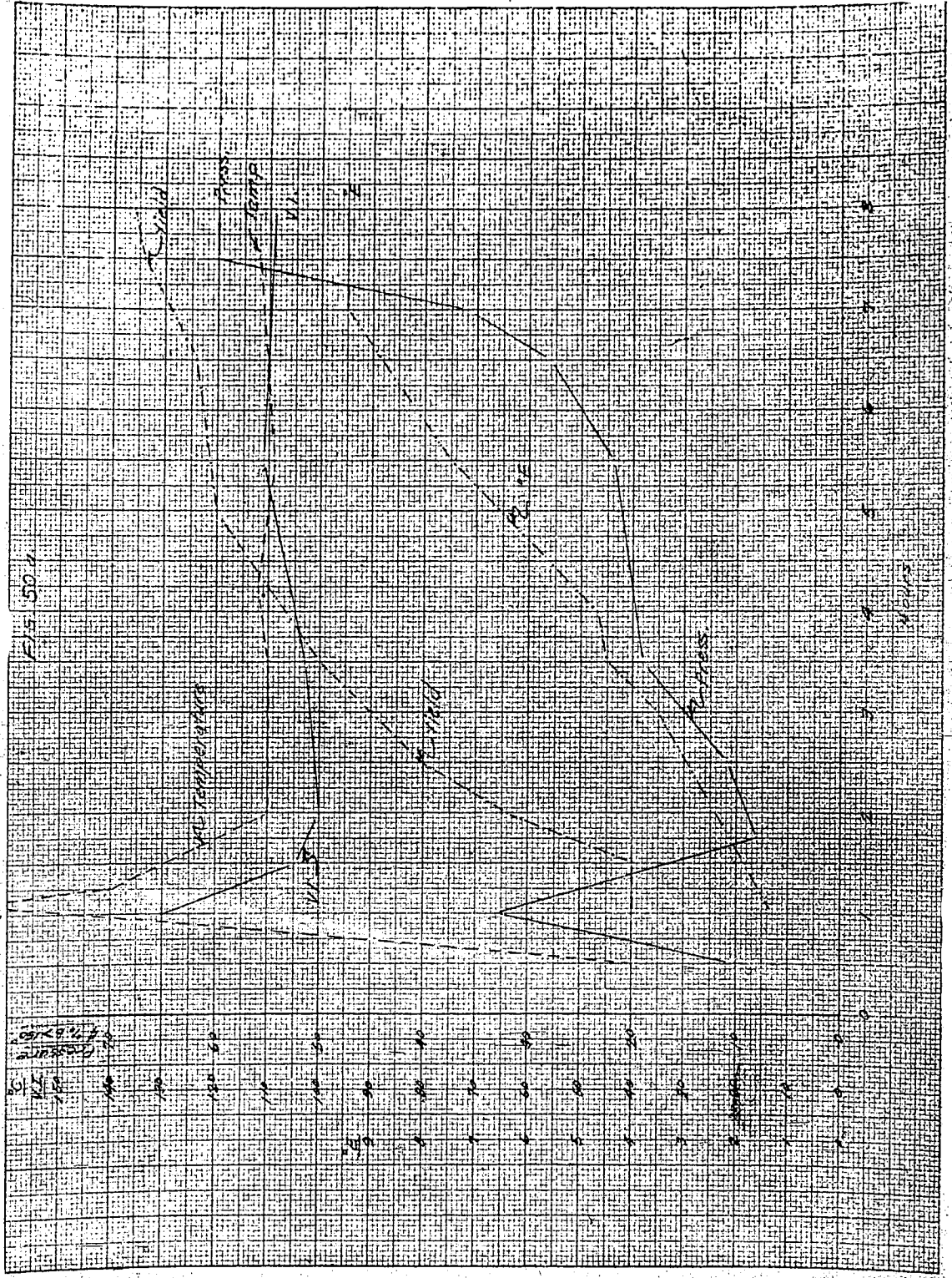






Table 44

| Test No. | Time Min. | Press. Atm. | Temp. |       | SS Oil 150°/0.4 mm. |                  |       |          | Iodine Number (Hanns) |               |             |         |      |
|----------|-----------|-------------|-------|-------|---------------------|------------------|-------|----------|-----------------------|---------------|-------------|---------|------|
|          |           |             | Inner | Outer | Wt. %               | E° <sub>99</sub> | V.I.  | Pour Pt. | Fl. Pt.               | Crude Product | Distil-late | 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          | 128   | 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                   |               | 10.9        | 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   | 63.6                |                  | 108.6 | -32      | 230                   |               | 5.7         | 1.6     | 7.3  |

Operating Experience in the Polymerization Process

The following are a collection of technical details and experiences which are important in the operation of the polymerization process:

Before the cover of the catalyst inlet nozzle is loosened all gas must be removed from the autoclave as described in the following:

1. After the raw oil is de-pressured the main amount of residual gas is removed by careful opening of the high pressure valve (next to the soda wash tower in the basement). The gas should not be expanded too quickly, as the adjoining residual gas meter may blow out.
2. The remaining gas is allowed to escape through the roof-vent and in no case into the filling room (explosion danger).
3. Of the 12 bolts of the vessel 10 are now removed and the other two only loosened. The blind flange is now lifted. Should there still be appreciable gas pressure the lid is bolted back until the last gas has been vented. The remaining screws are then removed. This procedure is very important to prevent accidents by explosion or fire.

If a fire occurs in removing the lid the hand extinguisher is used. Should there be a fire in the autoclave when still under pressure, the pressure

is to be released through the emergency release valve (in the basement) or the overhead vents in the filling-room and the autoclave filled with nitrogen.

The change-over from gas to  $N_2$  is made as follows:

1. Shut off gas, also regulating valve R and before everything block valve A.
2. Block off gas meter.
3. Close off intermediate expansion-valve Z and check that  $N_2$  pressure gauge shows 200 atm.
4. Open both  $N_2$  valves.
5. Admit  $N_2$  through regulating valve R.

The operators of the autoclaves should be thoroughly instructed that the intermediate expansion valve Z must be always kept open (no gas into the  $N_2$  line and reverse).

While charging catalyst care should be taken that the inter-exchange of the lid and the filling-cone be rapid (entry of the air). Also a small quantity of catalyst is to be poured in at first and after checking that the stirrer is in operation, the main charge can be poured in (adhesion of grainy catalyst to the bottom). While the autoclave is open, one should not use air to blow off catalyst-fines which settled during filling but should sweep them up.

Before closing the lid: Clean male-and-female joint well, if necessary put on new gasket. Do not use cotton-waste to clean filling nozzle. Before charging, inform the operator that the autoclave is "ready"; he must check that all valves at the head are closed and that the cooling water circulation system is filled, i.e. that the level can be seen in the lower gauge-glass of the expansion vessel. The operator, before admitting gas into the apparatus, must see that all valves at the bottom of the autoclave are properly set.

While operating the autoclave one should watch that while cooling down from the maximum temperature the temperature differential between the outer and inner wall does not exceed  $100^\circ\text{C}$  (cracking of the high pressure vessel). If operations are made at a maximum temperature of over  $200^\circ\text{C}$ , one should watch that, during cooling down from the maximum temperature and when admitting gas, the inner temperature does not go below  $120^\circ\text{C}$  (adversely affecting the reaction). The pressure in the autoclave should not exceed 60 atm. If the inner temperature of an autoclave, in which the process has been thus far completed, has dropped too low and therefore must be heated again before releasing pressure, one should observe the pressure before heating, as if one were to heat up at 60 atm., the pressure would quickly rise above allowable working pressure. In that case the pressure should be reduced by venting to approximately 40 atm, before starting the heating. With each increase in pressure over 60 atmospheres again cut off gas, turn off heat and if necessary open emergency release valve.

Influence of the Autoclave and Construction Material on the Polymerization Process

The original four autoclaves (400, 400, 800, 800 mm.  $\phi$ )-at Leuna were made of N6-material and the oil products from these were characterized by a viscosity of 6° Engler at 99° and a V.I. of more than 108. The next two (V & VI) were also constructed of N6 and gave similar results. Autoclaves VII and VIII could not be fabricated of N6 on account of a shortage of material, and it was necessary to use S2-steel with an inner lining of N6. The latter had, however, to be removed on account of cracking of the surface, so that the inner surfaces of autoclaves VII and VIII were essentially of S2 material which had been lathed down.

Although small scale experiments had shown the harmful effects of iron wall material, the units VII and VIII were used in the described process since in the meanwhile it had been determined that the influence of the wall material in the case of larger reaction vessels was greatly diminished. This observation was made when polymerization was carried out in a 4500 l. stirred autoclave (#IV) made of N6 material. The autoclave, for the purposes of these experiments, was fitted with an iron lining of M-1 material to a height of about 5 meters, which had only the normally rolled surface present. The results from the polymerization reaction of these experiments are shown in Table 45. They show that the iron surface of the guard can no longer be held responsible for the degradation of oil quality. These results justified the decision to use normal steel in going from 800 to 1200 mm. inside diameter autoclaves, since on account of the supply situation it was no longer possible to construct autoclaves on the S.P. plants out of high chrome content steel.

Table 46 shows the effect of the iron surfaces in autoclaves VII and VIII. The viscosities and V.I. values of the oil products lie considerably below those to be expected. It appeared likely that this was due to the freshly turned surfaces of the iron autoclave, whereas the harmless iron liner used earlier in autoclave IV had been annealed.

Therefore, a series of experiments was carried out with variously treated Fe packing in a 50 l. N6 autoclave---

1. Iron lining tube. The results (Table 47) are better than those from the iron autoclave VII (Table 46) and are similar to those from the addition of iron to the autoclave of N6 (Table 45).

Table 45. Iron Lining Tube in the 800 mm. diam. N6 Autoclave (IV)

| <u>No.</u> | <u>Temp.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|--------------|-------------|--------------------|-------------------|
| IV/208     | 160          | 5.16         | 110.4       | 205                | -31               |
| 209/10     | 160          | 5.33         | 112.8       | 198                | -30               |
| 211/12     | 160          | 5.54         | 111.2       | 203                | -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               |
| 223        | 220          | 3.08         | 121.7       | 210                | -19               |
| 229        | 220          | 3.44         | 123.3       | 224                | -25               |

Table 46. 800 mm. diam. Iron Autoclave  
(VII), Untreated

| <u>No.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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 47. Iron Lining Tube in the 50 l.  
N<sub>6</sub>-Experimental Autoclave

| <u>Date</u> | <u>No.</u> | <u>Temp.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|-------------|------------|--------------|--------------|-------------|--------------------|-------------------|
| 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                |

2. Iron lining tube, radiated. The results (Table 48) are poorer than expected.

Table 48. Iron Lining Tube, Radiated,  
in 50 l. N<sub>6</sub> Autoclave

| <u>Date</u> | <u>No.</u> | <u>Temp.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|-------------|------------|--------------|--------------|-------------|--------------------|-------------------|
| 4/10/42     | 693        | 205          | 4.17         | 115.7       | 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. Iron lining annealed for a N<sub>2</sub> autoclave. The results are like those in Table 47. (See Table 49.)

Table 49. Ignited Iron Lining Tube,  
for N<sub>2</sub> Autoclave

| <u>Date</u> | <u>No.</u> | <u>Temp.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|-------------|------------|--------------|--------------|-------------|--------------------|-------------------|
| 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. Iron lining, annealed and turned down (Table 50). Half of the experiments were interrupted, the remainder gave no clear picture.

Table 50. Lathed Iron Lining Tube  
for N<sub>2</sub> Autoclave

| <u>Date</u> | <u>No.</u> | <u>Temp.</u> | <u>°E/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|-------------|------------|--------------|--------------|-------------|--------------------|-------------------|
| 5/16/42     | 716)       | broken off   |              |             |                    |                   |
| 5/16/42     | 717)       |              |              |             |                    |                   |
| 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)       | broken off   |              |             |                    |                   |
| 5/26/42     | 727)       |              |              |             |                    |                   |
| 5/27/42     | 728        | 180          | 2.87         | 93.4        | 209                | 37                |
| 6/1/42      | 729)       |              |              |             |                    |                   |
|             | -732)      |              |              |             |                    |                   |

These experiments were now transferred to the 800 mm. diam. iron autoclave VII:

1. Iron lining tube, still heavily covered with mill scale (Table 51) - no effect beyond that of the rough autoclave.

Table 51. Sheet Iron Annealed and Covered  
with Scale 800 mm. diam. Iron Autoclave (VII)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                |

2. Iron lining turned down (Table 52). Results are clearly better (especially V.I.) than these from the rough autoclave, not good enough, however.

Table 52. Lathed Sheet Iron in 800 mm.  
diam. Iron Autoclave (VII)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 76         | 5.51         | 110.6       | 227                | -37               |
| 77         | 3.74         | 108.4       | 197                | 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. Iron lining copper treated (Table 53). Results about like those from raw surface.

Table 53. Sheet Iron, Copper Plated in  
800 mm. diam. Iron Autoclave (VII)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                | 36                |
| 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                |

4. Iron lining, treated with aqueous chromic acid (Table 54).  
Results better than raw surface, not enough though.

Table 54. Iron Lining Treated with Chromic Acid  
in 800 mm. diam. Autoclave (VII)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 126        | 3.77         | 108.5       | 212                | -38               |
| 127        | 3.26         | 127.0       | 217                | 31                |
| 128        | 4.42         | 107.7       | 225                | 37                |
| 129        | 4.17         | 102.6       | 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         | 113.0       | 209                | 37                |
| 134        | 3.88         | 112.8       | 233                | 38                |
| 135        | 4.86         | 110.1       | 217                | 38                |
| 136        | 3.90         | 106.1       | 207                | 36                |
| 137        | 3.18         | 103.8       | 210                | 40                |
| 138        | 4.52         | 110.9       | 208                | 38                |
| 139        | 4.37         | 110.0       | 206                | 35                |
| 140        | 4.24         | 107.8       | 208                | 37                |
| 142        | 4.65         | 112.8       | 208                | 36                |
| 143        | 4.07         | 108.2       | 199                | 33                |

5. Iron lining, polished and electrolytically chromic plated.  
Chromic coating soon eroded (Table 55). Results as above.

Table 55. Iron Lining Tube, Electrolytically Chrome  
Plated in 800 mm. Diameter Autoclave (VII)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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         | 115.1       | 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                |

6. V<sub>2</sub>A-lining in 800 mm. diameter iron autoclave VIII (Table 56).  
The Engler and especially the V.I. values are the best of all experiments.

Table 56. Autoclave VIII with V<sub>2</sub>A Lining Tube.  
800 mm. diam. Same as Iron Autoclave VII

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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         | 118.3       | 215                | 38                |
| 287        | 5.14         | 109.2       | 208                | 32                |
| 286        | 2.00         | 112.8       | 204                | 29                |
| 289        | 3.66         | 116.4       | 228                | 31                |
| 290        | 3.16         | 119.7       | 215                | 21                |
| 291        | 3.66         | 112.2       | 215                | 38                |
| 292        | 4.67         | 115.4       | 229                | 36                |
| 293        | 4.49         | 110.8       | 228                | 36                |
| 215)       |              |             |                    |                   |
| 296)       | 5.81         | 109.6       | 250                | 32                |
| 297        | 4.30         | 112.0       | 214                | 34                |
| 298        | 5.30         | 111.3       | 208                | 33                |

7. A copper lining was totally destroyed after a few experiments (no exact data).

8. An aluminum lining was destroyed in the first experiment.

Table 57. Autoclave X, 800 mm. diameter  
without the V<sub>2</sub>A Lining

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                |



Table 57. (cont'd)

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                |

Therefore it appeared that the construction of a V<sub>2</sub>A lining in the large 1200 mm. diam. iron autoclave should be undertaken, in case the oils from it should have the same poor properties as those from the 800 mm. diameter iron autoclave. The correctness of this intention was substantiated when the results from autoclave X (800 mm. diameter iron vessel without V<sub>2</sub>A lining) were available (Table 57).

In the meanwhile another 800 mm. diameter autoclave from N<sub>6</sub> material gave results (Table 58), which did not agree with those from the older N<sub>6</sub> autoclaves (1-4) although the analysis of the Shell material agreed with the normal composition of a N<sub>6</sub> steel - 6% Cr, 0.3% Mo, and 0.15% v. It was concluded that the differences in the oil properties were due to unrecognizable variations in the composition of the construction material, as had been seen in the case of the iron autoclaves.

Table 58. Autoclave IX,  
800 mm. diam., N<sub>6</sub> Metal

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                |

Finally when the first of the large 1200 mm. diam. iron autoclaves (III) arrived the correct results (Table 59) were obtained similar to those from the two smaller autoclaves of N<sub>6</sub> material, which had been made by another firm (Table 60).

Table 59. Iron Autoclave III, 1200 mm. Diameter

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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                |

Table 60. Iron Autoclave II, 1200 mm. Diameter

| <u>No.</u> | <u>E°/99</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|------------|--------------|-------------|--------------------|-------------------|
| 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 autoclaves could therefore produce oils with correct properties without any surface treatment (activation or passivation) or installation of extra liners. Some doubt had now arisen in regard to the correct construction of the small iron autoclaves, after a more or less extended breaking in period. The properties of the oil product from these had indeed slowly improved somewhat, but were still considerably below requirements. Since the large iron autoclave immediately gave correct results, regardless of which manufacture they were and what quality of gas they employed (the 4 autoclaves in Schkopau gave the same performance), it was concluded that the different behavior of the two small iron autoclaves did not lie in the accidental composition of the metal used in the various autoclaves. (When the autoclaves at Heydebrech and Moosbierbaum are in operation, there will be autoclaves from four different firms for comparison). The true reason for the abnormal behavior of the two iron 800 mm. diameter autoclaves VII and VIII are probably due to variations in the manufacturing procedures followed by the various supplying firms and it may not be possible to recognize and control them.

Those autoclaves that give poor oil products appear to be very little influenced by changes in process conditions. The hope to produce SS 903 successfully with the small iron autoclaves, could not be attained on a long term basis any better than with the other vessels. Also the color of the abnormal oils (SS 906 and SS 903) was very dark (opaque blue-green to dark brown) with slightly increased Conrad values.

## II. Finishing the Crude Polymer

### a) Old Method

The disadvantages of the old finishing methods previously described, the settling of the addition compound insoluble in the hot oil, and the removal of the heavy sludge were as follows: There was insufficient disengaging space and the sludge draw-off pipe plugged easily. Moreover the method of adding lime to the hydrolyzer for the neutralization of dissolved sludge was technically unsound. If lime was added to the open kettle, there was troublesome evolution of solvent or HCl vapor, and if a screw conveyor was used for the addition, caking of the lime occurred due to the vapors evolved from the vessel. Furthermore the sludge precipitated in this way was difficult to filter and high oil losses were suffered to the filter cake.

In order to overcome these disadvantages, a gas-tight dish type centrifuge with a wide outlet was developed in cooperation with Alfa-Laval. This made possible continuous separation immediately after polymerization of that part of the  $AlCl_3$  sludge which was solid at these temperatures. However, in continuous operation this method was unsatisfactory; low throughputs were experienced because of frequent repairs and low product purity. Installation of a Haubold cup type centrifuge (Schalzentrifuge) to make a rough preliminary separation permitted smoother operation of the Laval centrifuge, but it was not a satisfactory solution because cleaning and maintenance of the Laval machine was costly and time-consuming.

Therefore a further search for better finishing methods for the crude product was begun. Attempts to treat the oil by washing with water, alkali, or

salt solutions were unsuccessful, as the precipitated  $\text{Al}(\text{OH})_3$  caused the formation of emulsions which were difficult to centrifuge or filter. This method of wet finishing was therefore abandoned.

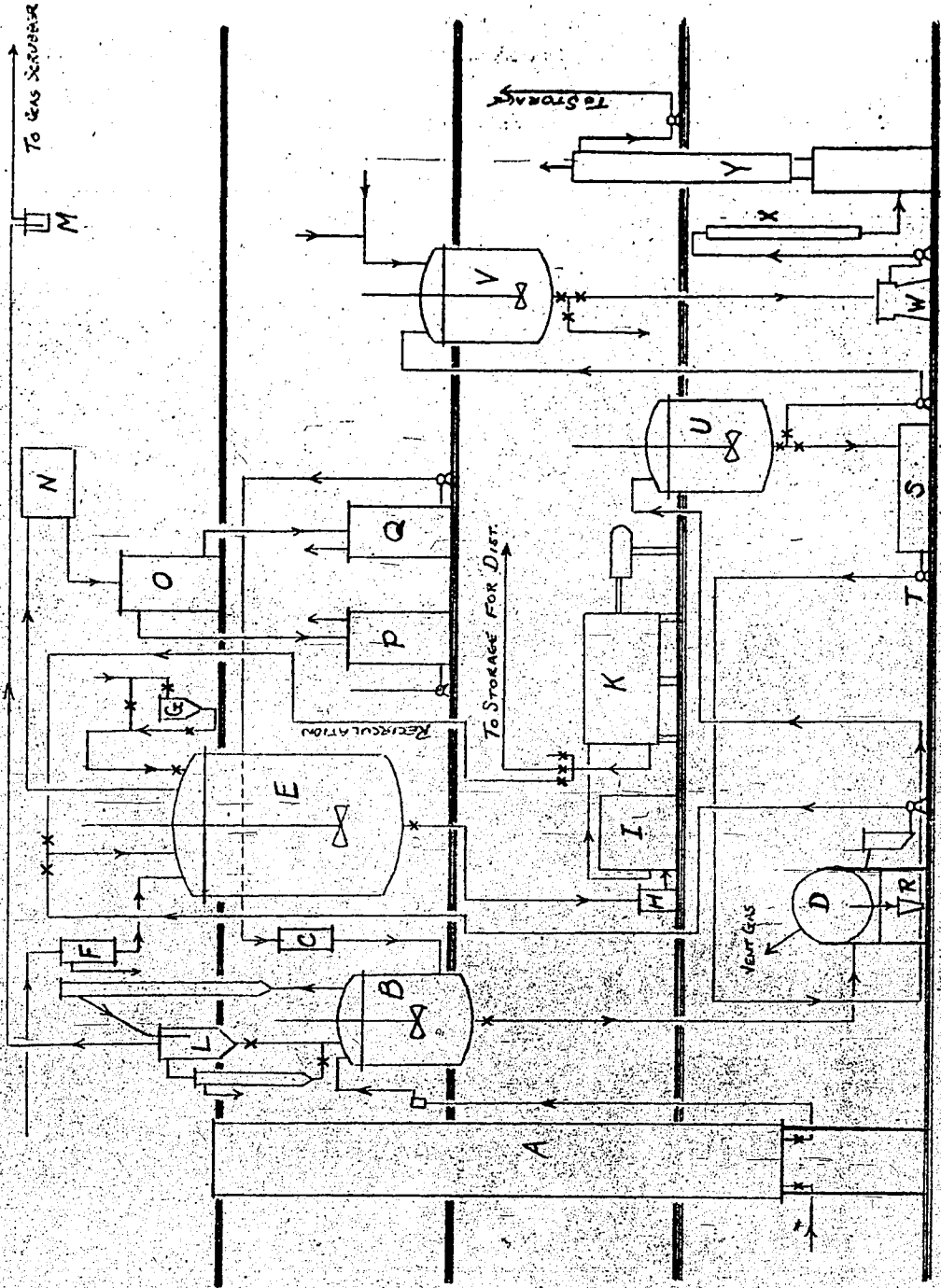
Methanol solutions of alkali and ammonia were next tested both on a laboratory and plant scale. However, precipitation of  $\text{NaCl}$  and sublimation of  $\text{NH}_4\text{Cl}$  causes plugging of the lines and filtration difficulties, and in addition the solubility of  $\text{NH}_4\text{Cl}$  in the oil interfered with the subsequent distillation step.

In these experiments it was observed that by using small amounts of methanol the oil-soluble part of the addition compound could be precipitated without hydrolyzing the  $\text{AlCl}_3$  to  $\text{Al}(\text{OH})_3$  and without contaminating the SS oil with the undesirable oil component of the sludge, phenomena which always occurred when water was employed. Since this procedure could be carried out in the presence of the oil-insoluble sludge, the following method was adopted.

b) The Present Method (see Diagram 53).

The crude polymer is run continuously from the autoclave A into the stirred kettle B at  $120^\circ$  while methanol is added from C. For this purpose  $\text{HCl}$ -containing methanol from the main hydrolyzer E is used. The quantity of methanol is adjusted so that the sludge precipitated is still liquid as it passes through the centrifuge D. Too much methanol causes the formation of a granular sludge which can cause difficulties in the centrifuge, while too little methanol leaves a residue of sludge in the oil which makes for difficult filtration of the lime slurry following the main hydrolysis step. It has proven advantageous in the slurry separation to operate the centrifuge as an overflow centrifuge (Uverlaufzentrifuge) rather than by the customary batch method (Chargenbetrieb). Therefore a second centrifuge was installed as security. Every 20 minutes the flow from B to D was interrupted, the oil (top phase) removed from the housing, and the sludge scraped out. The amount of residue obtained from one charge to an 800 mm. diameter autoclave amounted to 350 kg. It consists of equal parts of  $\text{AlCl}_3$  and hydrocarbon oil. This residue is decomposed by cold water, the reaction occurring at first very slowly but after some time so vigorously that the water boils. This decomposition is carried out in a Korting eductor with cast iron spray nozzles, using not fresh water but an  $\text{AlCl}_3$  solution obtained from a prior hydrolysis step. The  $\text{AlCl}_3$ -oil slurry separated from the centrifuge D is removed from the sludge tank R by means of the eductor fed with the aqueous  $\text{AlCl}_3$  solution. This solution is transferred from the vats by the ferro silicon pump T to the Korting eductor under the sludge tank, and the resulting mixture of sludge and  $\text{AlCl}_3$  solution is forced into the sludge hydrolyzer U. Here the complete hydrolysis of the sludge occurs upon 10-15 minutes stirring, after which the stirring is stopped and the oil and aqueous solution separate into two layers in 10-15 minutes. The oil is transferred to the stirred kettle V where it is washed several times with hot water to remove the remaining traces of  $\text{AlCl}_3$ . The major part of the water is removed by decanting and the remainder by centrifuging in the Laval centrifuge W. The oil, now containing 1-1.5% water and having 1-5 acid number, passes through the preheater X and alkali wash tower Y. This tower is filled initially with 50%  $\text{NaOH}$  and is renewed when its strength drops to 5%. The major part of the  $\text{Al}(\text{OH})_3$  formed in this neutralization step settles on the tower walls and can be rinsed off. The remainder is pumped with the oil, which still contains 0.5% water, to the storage tanks where the  $\text{Al}(\text{OH})_3$  and water settle and are drawn off occasionally. Accordingly, withdrawal of oil from the storage tank should be from somewhere above the bottom.

Fig. 53



The  $\text{AlCl}_3$  solution is recirculated to the eductor. When its density rises to 1.25-1.30 it is discarded, as at high concentrations the hydrolysis of the sludge is incomplete. Table 6l shows the variation of density and freezing point of the  $\text{AlCl}_3$ -solution upon  $\text{AlCl}_3$  content (this table missing).

Table 6lb. Corrosion of  $\text{M}_1$ -Iron by  $\text{AlCl}_3$ -Water Mixtures at 20°C

| $\text{H}_2\text{O}$         | 9    | 8    | 7    | 6    | 5    | 4    | 3    | 2    | 1    | 0        |
|------------------------------|------|------|------|------|------|------|------|------|------|----------|
| 40% Al Solution              | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | Solution |
| Wt. % Loss of $\text{M}_1$ : |      |      |      |      |      |      |      |      |      |          |
| in 785-hrs.                  | 0.69 | 1.50 | 1.52 | 1.0  | 0.91 | 0.76 | 0.41 | 0.2  | 0.1  | 0.08     |
| in 1459 hrs.                 | 1.45 | 2.78 | 3.28 | 2.18 | 2.12 | 1.67 | 0.98 | 0.49 | 0.62 | 0.42     |

Table 6lb, giving data on the corrosion of  $\text{M}_1$  iron by  $\text{AlCl}_3$  solutions, shows that most severe corrosion occurs with the 8-12% solutions, while higher concentrations are less corrosive. The solution with 1.25-1.30 density mentioned above is generally less corrosive. Formation of a white precipitate of Al oxy-chlorides and hydrates occurs by hydrolysis, but only after 3 or more months.

Further use is also made of the  $\text{AlCl}_3$  used for polymerization, the  $\text{AlCl}_3$  solution is employed in tannin manufacture at the Ludwigshafen plant.

Details of the nozzle construction of the eductor are shown in the Sketch 53a. (This drawing is missing.)

When operating with 2 centrifuges, the time required to work up one autoclave charge (4 cu.m.) is about 1-1/2 hours.

The centrifuged crude oil is now pumped directly to the main hydrolyzer E. The oil, which has an acid number of 2-3 is stirred with small quantities of methanol from the gauging tank F until all of the HCl is distilled off with the methanol. Last traces of acid are removed with lime, which also takes up small quantities of  $\text{Al}(\text{OH})_3$  which are present, thereby making the subsequent filtration easier. Pneumatic feeding of the powdered lime has proven convenient (described subsequently).

The oil-lime slurry is then fed through a pulverizer H (Steinabschneider) to the lantern pump (Drillingspumpe) (and is forced from this into the filter-press K. Until the filtrate becomes clear it is recirculated back to the main hydrolyzer. Upon complete clarification the oil is transferred to a storage tank from which it is withdrawn for distillation.

The gas vented from the prehydrolyzer B during the discharging of the crude polymer from the autoclave is passed through the receiver L and the oil scrubber M (see drawing 53). Gases vented from the main hydrolyzer E are condensed in the Iplet cooler N. Methanol and polymer forerunnings are separated into 2 phases in the separator O. The forerunnings are transferred to the receiver P and thence back to the process as solvent while the acidic methanol is stored in the receiver Q and used again in the hydrolysis.

The filter cake from K still contains about 50% of oil. By washing it with forerunnings (which are combined with the main product and sent to distillation) and blowing it with nitrogen while it is still hot, the cake can be removed

from the press easily. Although it appears entirely free of oil, it still contains considerable quantities, as shown by the following tests.

- 1) 40% is soluble in ether upon extraction.
- 2) By heating in vacuum 21.5% of oil distills off; an additional 15.5% water and 10% forerunnings are obtained by refrigerating.
- 3) After dissolving the lime in HCl, 27% oil was obtained from the CaCl<sub>2</sub> solution.

It was also observed that by treating the cake with water at 90°, a reaction occurred accompanied by much frothing; the water displaced the oil absorbed on the lime. The lime dissolved in the water and the oil floated on the solution. A completely dry, unpulverized sample of cake treated in this way gave 20% of oil which upon distillation gave 62.5% of residual oil having these properties.

|                  |       |
|------------------|-------|
| °E <sub>38</sub> | 68.5  |
| °E <sub>99</sub> | 5.01  |
| V.I.             | 112.2 |
| Pour Point       | -35.5 |
| Flash Point      | 223   |
| Conradson Carbon | .063  |

The oil remaining in the filter cake is thus of the same composition as the filtered crude product and upon distillation has the properties of an SS oil, except that the color is sometimes darker. The boiling range of the oil obtained from the filter cake is remarkable since in other experiments in which the filter cake was washed with forerunnings in the ordinary way, the washings contained only a little oil:

| <u>Washing time</u> | <u>% forerunnings in washings</u> |
|---------------------|-----------------------------------|
| 15 min.             | 64                                |
| 20                  | 77                                |
| 30                  | 83.3                              |
| 40                  | 95.5                              |
| 50                  | 94.4                              |
| 60                  | 97.2                              |

In spite of this, the lime contained more viscous oil and less rerunnings than the washings.

In practice, then the lime was treated with 3 times its amount of water at 90° in a kettle equipped with an anchor type stirrer which scraped the sides and bottom while turning slowly (20 rpm.). In this way the lime, which becomes hard (speckig) as the reaction proceeds, can be broken up without violent agitation and decomposed. After 1/2 to 1 hour water is forced into the aqueous layer through an annular horizontal pipe and the oil layer rises and is forced slowly out of the highest point of the conical cover of the kettle until water overflows. After further stirring, the lime slurry is pumped from the bottom of the kettle into the slurry line by means of a centrifugal pump. This method, besides increasing the yield of oil, is more convenient than the former method which involved manual handling of the cake.

The lime sludge reacts most rapidly with hot water if treated immediately after removal from the press. If it is allowed to stand it reacts more slowly, probably because the last traces of CuO (whose presence is necessary for the reaction to occur) disappear upon standing.

This method of handling the lime is also advantageous in case there are difficulties with the filtration step (as for example, in the production of SS 903), since the filter cake is then especially rich in oil. The amount of recoverable oil averages about 25% of the lime filter cake. Thus, for a lime consumption of 30T/month corresponding to 10,000 T/year of SS-906 the recovered oil amounts to about 10 T/month. From Sept. 11 to Oct. 13, 1943, 25,740 cu.m. of oil were produced in Me 125 and about 20 T/month were recovered. This was included in the SS filtrate, since repeated tests showed it to be of the same quality.

#### c) Treating Procedure

Several points must be observed in working up the crude product. Experienced and reliable attention is required in the preliminary hydrolysis step since the acid methanol is metered only by means of a sight glass in a measuring tank and since it has not been possible to solve the problem of metering the hot crude polymer, which contains sludge and is under a pressure which varies from 0-60 atm. In charging the centrifuge as steady a flow as possible should be maintained. This is especially true for the first of the two centrifuges, as the motor is easily overloaded. To have a constant feed rate to the centrifuge requires that the crude polymer be discharged at a constant rate into the prehydrolyzer, since a constant level must be held in that vessel.

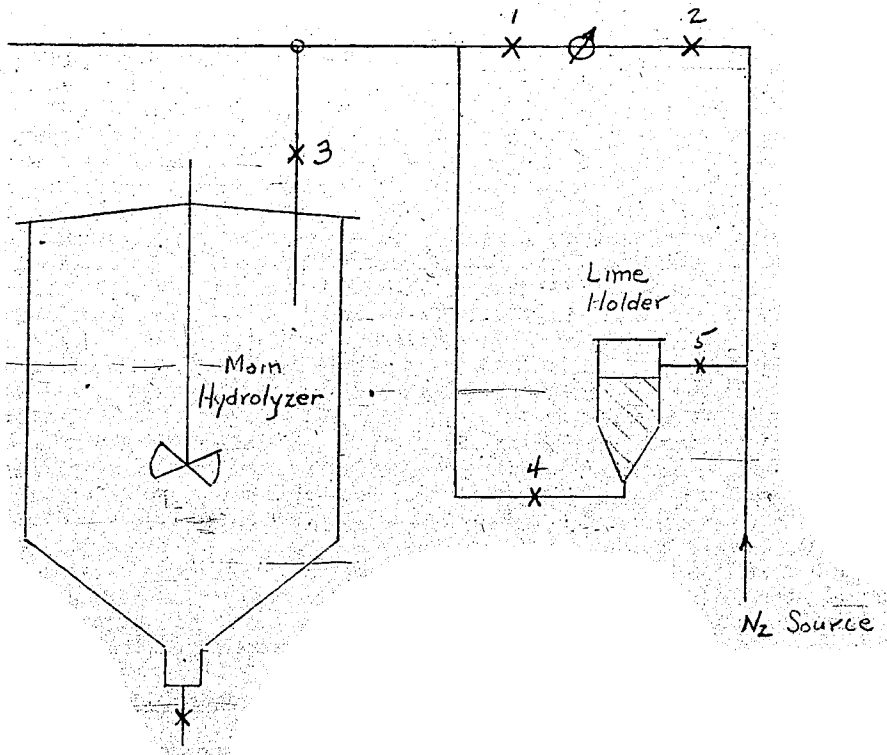
During the centrifuging operation the oil level in the sight glasses of both the oil collectors should be observed frequently. If the oil level should rise suddenly, indicating a failure of the product pump, the centrifuge motor should be turned off immediately and the valve between the prehydrolyzer and the centrifuge closed. This will prevent the oil rising into the centrifuge drum from acting as a fluid break and overloading or burning out the motor. Even though a nitrogen plunger (Stickstofftauchung) whose pressure increases when the oil level rises and thereby shuts off the centrifuge motor is provided in the product receiver, the centrifuge operator should be impressed with the importance of checking the oil level.

Removal of the oil phase from the housing and cups of the centrifuge must be done slowly to make a good separation of oil from sludge. In lubricating the centrifuge the oil pressure (which should be not over 0.1 atm.) and cooling water should be watched carefully.

Use the following procedure in introducing lime into the main hydrolyzer through the pneumatic system: (See drawing 54).



Fig. 54



- 1) Fill the lime container.
- 2) Open valve 1 and slowly open valve 2 until the pressure in the line rises to 0.1 atm.
- 3) Open valve 3, so that a small stream of  $N_2$  flows into the hydrolyzer, thereby preventing hydrocarbon vapors from backing up into the line.
- 4) Open valve 4 and by means of valve 5 impress 1 atm. of  $N_2$  on the lime container until the  $N_2$  flows through without resistance. Then close valves 5 and 4.
- 5) Close valves 3 and 2.

The filter press should be operated so that the compression furnished by the hydraulic pump does not exceed 250 atm. To avoid damage to the filter cloth, the pressure relief valve on the drilling pump should be set for 8 atm. When the press is cleaned especial attention should be paid to the surface of the packing, and before assembly it should be coated with oil and graphite. Originally 8 mm. strips of leather along with 3 mm. strips of pasteboard were used as packing. As the quality of these materials was poor and they gave very poor service, a change was made to 8 mm. strips of PQ material or Perbuna. For the filtration double Igelit filter cloths are used, one a very finely woven PC-cloth which lies against the perforated plate and the other a coarse PC-cloth which imparts to the cake the necessary smoothness. If filtration becomes slow or the filtrate becomes cloudy the cloths are removed and washed with HCl and  $CCl_4$  (tetra). Before further use the cloths are inspected for thin spots or rips and if necessary patched. In this way cloths will last for 30-50 washings. The following procedure is to be used for washing PC cloths: The dirty cloth from the press is immersed over night in water at  $60^\circ$ . Then it is smoothed out on a table and scrubbed (nachbursten) with water. Thereafter it is soaked for half a day in 3% HCl to dissolve the lime remaining in its pores, rinsed in water and dried. Any oil remaining in the cloth is washed out with  $CCl_4$  and the cloth is then hung up to dry. Before it is reinstalled in the press it is examined by drawing it over a glass plate illuminated from below and weak spots are touched up with an acetone-solution of PC.

#### d) Corrosion Control

Originally, corrosion due to HCl vapor was severe in the hydrolyzers especially in zones where condensation occurs, such as the top of the hydrolyzers and their gas vent lines. The normal precautions against HCl corrosion did not avail when dealing with HCl in methanol at  $90-120^\circ$  in the presence of low boiling hydrocarbons. The following linings for the 2 cum. hydrolyzing kettles were tested in actual operation:

- 1) Coating the walls first with Asplit and then with a coating of Hochster cement SW 20 did not work as under the varying temperature conditions in the kettles the protective coating soon cracked, especially at the welded joints and the edges.

- 2) Putting an elastic coat of Oppanol B200 between the Asplit and the Hochster cement caused even more rapid cracking of the protective coating because of swelling of the Oppanol.
- 3) A hard rubber coating of Para Hart 28 (natural rubber) began to dissolve off the surface within a day and at the end of 8 days was completely destroyed).
- 4) A 5 mm. layer of hard natural rubber containing 50% graphite (SPML-Hartgummischicht) has given 12 month's service. It has remained solid during this period and its surface did not seem to be altered by the acid hydrocarbon vapors.—The vapor lines to the kettles were similarly coated. As packing material a similar rubber which was not completely vulcanized was used.
- 5) As the above natural rubber was no longer available when the hydrolyzing section of the plant was enlarged, various kinds of Buna rubber had to be used. However, they have not been at all satisfactory, as they become brittle and crack.

The 5 and 10 cu.m. kettles are now lined in the liquid zone with acid resistant ceramic blocks. These blocks, which are fitted by means of grooves and projections, are used in two layers, with an intervening layer of rubber and are sealed with Hochster cement SWD 20. Other lining materials and their applications:

Prehydrolyzer cover: Baked-on lacquer (Neoresit) and Exterior insulation.

Shaft: Baked on lacquer (Einbrennlack)

Main Hydrolyzer cover: Ceramic coating

Cone: Enamel or asplit

Shaft: Unprotected

Dipping Basket: Rubberized

Condenser above main hydrolyzer: Igelit (Made by Dr. Henning and Dipl. Eng., Leuna)

Gas scrubber: Ceramic

All pipes and appurtenances which are subject to temperatures no higher than 80° can best be made of Igelit; for vessels subject to these temperatures, such as separators, dipping tanks, etc. a coating of Igelit suffices. Pumps for acidic methanol are of porcelain, and for acidic forerunnings stoneware was formerly used but has been replaced by ferrosilicon.

### III. Distillation

The distillation plant of Me 126 is illustrated in Figures 55 and 56 (photographs). The hydrolyzed crude oil is transferred from the storage tanks by pumps 8 or 9 through the heat exchanger 7 and pipe still 1 into column 3. The furnace is a pure convection type with horizontal tubes and is heated by a selfdraft burner (selbst ansaugenden Brenner). Local overheating of the tubes is minimized by means of the cylindrical gas blower 2 (Walzgasgeblase). The 1000 mm. column has 25 bubble plates above the feed inlet and, to facilitate cleaning, is equipped with Raschig rings below the feed inlet.

The bottom product (of the proper flash point) is drawn off through the heat exchanger 7, a cooler and is pumped by pump 10 to storage (see Fig. 57). An intermediate cut can be withdrawn from a plate higher up in the column and stripped with steam in a 500 mm. 2 plate stripper 3a. This stripper is used periodically when enough so-called V-oil is accumulated (about 20-30% of total forerunnings).

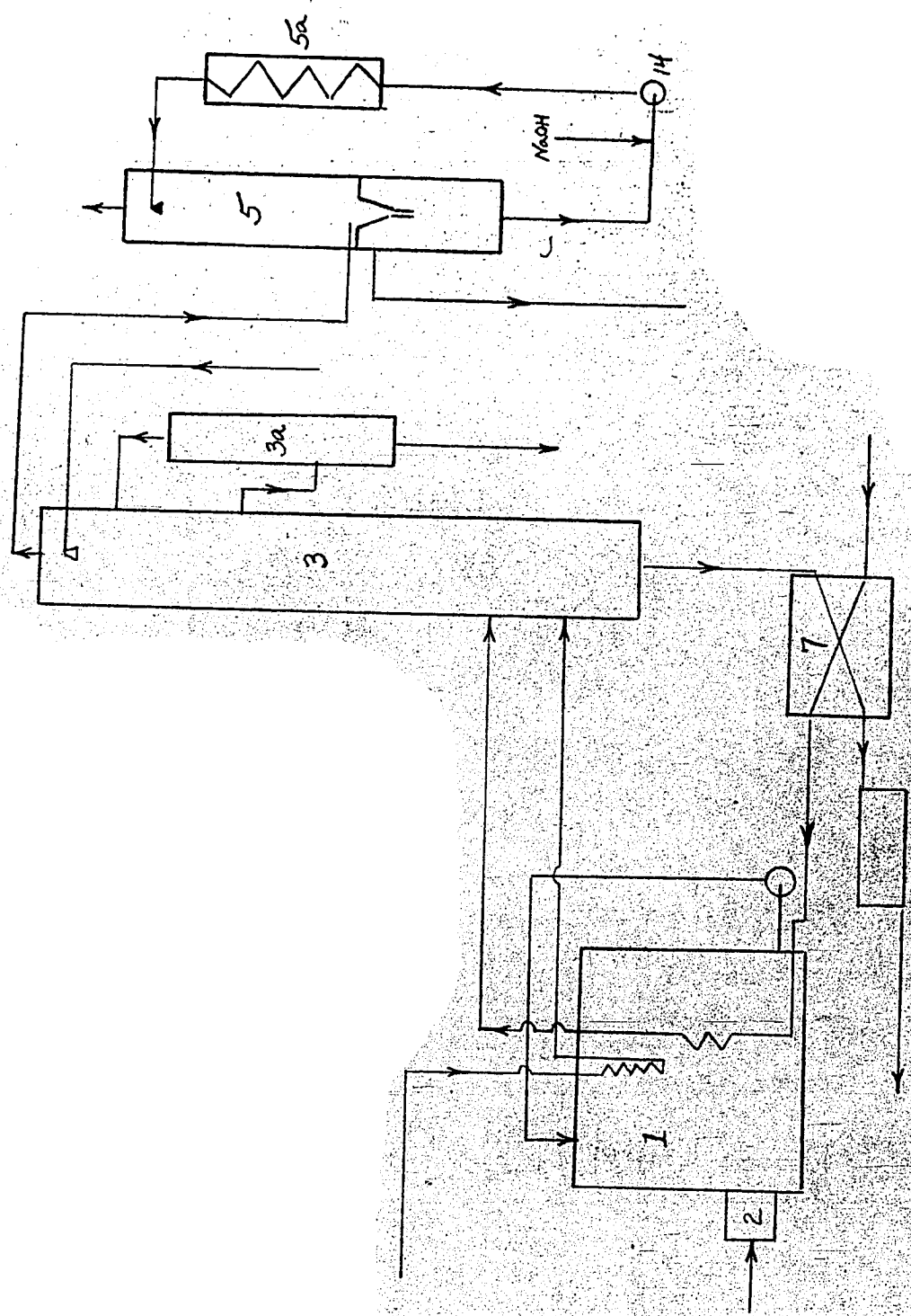
This plant produces as bottom product an SS oil boiling above 330°, alternatively 300°, and having a viscosity of 6°Egg and 3°Egg, respectively. The yield of this oil based on feed to distillation is 50-55%. Superheated steam (10% on feed to column) is injected into the bottom of the column to raise the flash point of the oil above 230°. The remaining 45-50% of the feed is taken off as top product. The small amounts of chlorine compounds remaining in the filtered crude product are converted by the steam to HCl which caused severe corrosion in the condenser. Ammonia injected into the top of the column prevented this corrosion but caused plugging of the top product cooler with  $\text{NH}_4\text{Cl}$ . Therefore an injection type condenser 5 (Einspritzkuhler) was employed, in which the circulating water was maintained slightly alkaline. The only precaution to be observed in using this arrangement is to see that no vapors condense in the top of the column or in the vapor line leading to the condenser by properly insulating the lines. Condensation then occurs in the Ceramic lined (ausgesteint) condenser. While this condenser is normally kept slightly alkaline, it may in the course of upsets become slightly acid and hence the stoneware was coated with Asplit A, which resists both acid and alkali.

Operation of this condenser 5 is as follows: the mixture of steam and hydrocarbon vapor flows upward in the tower and is condensed by the water, which is cooled in exchanger 5a. The upper part of this tower, the condensing section, is filled with Raschig rings, while the lower part acts as a phase separator. In the lower part of the tower or in the water outlet at the bottom is located an electrode which is used to control the pH. The alkalinity of the water is controlled by adding very weak (less than 5%) NaOH solution to the suction of the water circulating pump 14. Water which is withdrawn from the bottom of the separator is circulated through the cooler 5a to the top of the tower. The condensed hydrocarbon phase is drawn off from the separator through a higher outlet and led to another separator, 5b, where additional water is settled out. The forerunnings surge tank 5c assures a constant supply of reflux for the column, which is returned to the top of the tower through the preheater 6 by means of the pump 11. The distillate goes through the upper forerunnings line through the Laval centrifuge 13 to storage, from which it is returned to the polymerization plant as solvent. Water must be carefully removed if the distillate is used for this purpose.

The following describes the construction of the Laval centrifuge. This can be used in two ways:

1. As a purifier for the separation of two liquids of different densities.
2. As a clarifier for liquids, i.e., for the separation of solids such as dirt particles or bleaching clay or even small amounts of liquids, provided the amount is not greater than the volume of the outer part of the drum.

Fig. 57



The assembly of the centrifuge for these 2 operations is as follows:

|              | <u>Purifier</u>   | <u>Clarifier</u>     |
|--------------|-------------------|----------------------|
| Upper Disk   | With neck         | Without neck         |
| Regular Disk | Without neck (a)  | With neck            |
| Lower Disk   | With perforations | Without perforations |
| Water Seal   | Yes (b)           | No                   |

- (a) Used as a purifier for the separation of liquids of different densities one uses outlet spouts of different diameters. The opening should be smaller, the denser or more viscous the light liquid component is or the greater the flow rate.
- (b) In setting the machine in operation, make sure the drum is full of the heavier liquid (ordinarily water). The liquid is added slowly to the centrifuge (ordinarily after removal of the filling screw) until it rises in the sight glass. In this way a water seal is formed in the drum which prevents the lighter component from escaping with the heavier through the water outlet.

In assembling the apparatus, be sure that the disks are put on in the proper sequence (number 1 underneath) and that the ring closure (equipped with left hand thread) is screwed down to the mark.

Crude product:

|                 |         |
|-----------------|---------|
| I.B.P.          | 100°    |
| Off at 330°     | ca. 45% |
| d <sub>20</sub> | 0.820   |
| M.W.            | 400     |

|                 | <u>Forerunnings</u> | <u>V120</u> | <u>S.S. Oil</u> |
|-----------------|---------------------|-------------|-----------------|
| Boiling range   | 130-250°            | 250-330°    | > 330°          |
| d <sub>20</sub> | 0.778               | 0.815       | 0.850-55        |
| M.W.            | 155                 | 238         | 800             |

The most important temperature to observe in the SS oil distillation process is that of the oil tubes in the pipe still which should not exceed 400° if decomposition of the oil is to be avoided. The following additional points should be observed:

If the furnace is allowed to cool, the temperature should be raised again very slowly (one to two days) to avoid cracking the brickwork.

Light the furnace only in the presence of the foreman. Purge the furnace with air for 15 minutes before lighting.

If the cylindrical gas blower is used proceed as follows (see sketch 58):

1. Cut in the cylindrical gas blower.

2. Close the damper K<sub>2</sub>. After flushing, open K<sub>1</sub> and K<sub>2</sub> until the manometer shows a vacuum of 40 mm. in the burner. Introduce the igniter and open the gas cock slowly. After the burner is lit, adjust K<sub>1</sub> and K<sub>2</sub> to their normal positions.

#### Procedure for Rapid Shutdown of the Plant

1. Turn gas down as far as possible (oil exit temp., 150°) or shut off entirely.
2. Put residue in the circulating system.
3. In case the liquid level in the column disappears, restore by adding crude product through the charging pump.

#### Power Failure

1. Vent gas from system.
2. Switch in bottoms duplex pump.
3. Start bottoms circulating.
4. Switch in tops duplex pump.
5. Switch off pumps, centrifuges and blowers simultaneously.

Sudden pressure increases in the furnace caused by water or methanol in the feed, which are vaporized suddenly in the tubes, happen sometimes upon feeding from a new tank. Switch to the next tank. If the differential pressure recorder on the column shows a sudden pressure and the temperature of the individual plates falls one after the other from the bottom upward, flooding of the column is indicated.

#### Causes :

1. Bottoms pump not operating.
2. Bottoms liquid level controller not operating.
3. Residue cooler at too low a temperature.
4. Line from column bottom to heat exchanger plugged.

The pressure increase may also be due to plugging of the leads to the pressure recorder.

Electrode: Addition of alkali to the water circulating system should occur when the pH drops to 7 (-27 M.V.), as below this value the water becomes acid and corrosive. Values above +30 M.V. should also be avoided, as too strongly alkaline water causes emulsion formation in the separator. The concentration of NaOH added

to the water should not exceed 5%. If hydrocarbon vapor vents from the top of the condenser, the water pump is not operating properly or the circulating system does not contain sufficient water.

By varying distillation conditions it is possible to compensate in some degree for variations in the viscosity of SS oil caused by variations in the C<sub>2</sub>H<sub>4</sub> purity, catalyst quality, or operating conditions in the batch part of the process. To show the influence on the V.I., flash point and pour point of the SS oil of the distillation conditions, various polymers were distilled to different cut points and the properties of the bottoms determined:

Table 62

Distilled in vacuum to:

| <u>150°</u> | <u>t. °C</u> | <u>Wt. %</u> | <u>°Egg</u> | <u>V.I.</u> | <u>Flash Point</u> | <u>Pour Point</u> |
|-------------|--------------|--------------|-------------|-------------|--------------------|-------------------|
| 2.4°Egg     | 110          | 65.8         | 1.77        | 132.0       | 148                | -53               |
|             | 120          | 64.8         | 1.84        | 130.8       | 158                | -51               |
|             | 130          | 62.0         | 1.94        | 126.6       | 169                | -48               |
|             | 140          | 59.0         | 2.08        | 123.7       | 176                | -45               |
|             | 150          | 54.5         | 2.41        | 119.4       | 184                | -41               |
| 4.4°Egg     | 110          | 77.0         | 2.42        | 128.5       | 160                | -50               |
|             | 120          | 70.0         | 3.12        | 120.5       | 173                | -48               |
|             | 130          | 67.4         | 3.52        | 117.9       | 190                | -46               |
|             | 140          | 66.0         | 3.57        | 116.8       | 195                | -45               |
|             | 150          | 62.0         | 4.43        | 114.6       | 210                | -40               |
| 5.8°Egg     | 110          | 74.5         | 2.21        | 124.0       | 154                | -56               |
|             | 120          | 71.2         | 2.39        | 118.2       | 170                | -52               |
|             | 130          | 62.2         | 4.04        | 108.9       | 190                | -41               |
|             | 140          | 56.6         | 4.75        | 107.5       | 206                | -36               |
|             | 150          | 54.4         | 5.66        | 106.2       | 214                | -34               |
| 6.5°Egg     | 110          | 75.2         | 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        | 109.0       | 247                | -28               |
|             | 160          | 61.2         | 7.17        | 108.0       | 246                | -27               |
|             | 170          | 59.7         | 7.49        | 108.0       | 254                | -28               |

#### IV. Refining

Originally Tonsil AC clay from Bavriechen Bleicherdefabrik was used for refining; later "A Special" clay from Moosbierbaum was used. Clay treating is carried out at 90°. When treating heavy oil such as SS 906 the treatment must be at 120° to permit rapid filtration rates. The dark SS 903 oil requires a treat of 3-5% clay while only 0.7-1.0% is required for SS 906. For neutralization of the weakly acid clay 10% of Ca(OH)<sub>2</sub> is added.



The charging of the clay is done pneumatically (with  $N_2$ ) from a cone-bottom container; unlike the charging of lime to the main hydrolyzer, no elaborate precautions are necessary as the refining kettle does not contain light hydrocarbon vapors, and operates at atmospheric pressure. The kettle is completely filled with oil and the clay is introduced under the surface of the oil to avoid blowing the fine powder about. Clay treating requires 30 min. Filtration is done in a flame filter press, and since there are no volatile products, presses with individual compartments and open flow are used. In this way the slightest leakage can be detected by darkening of the filtrate and the offending compartment can be detected at once, a big difficulty with the previous filtration step following hydrolysis. Another advantage of the open filtration is that the filtration process need not be interrupted if rupture of the filter cloth in one of the chambers occurs (provided the chamber is not entirely full). The contaminated filtrate is returned to the treating kettle and the remaining chambers are allowed to run.

The use of PC cloth as filter cloth is not possible at these high temperatures, but it is unnecessary anyway as the oil is neutral. Fairly thick cotton, cellulose wool-cotton, or 100% cellulose wool cloths have proven satisfactory. These cloths are durable even at the  $120^\circ$  temperature at which SS-906 oil is filtered. Using a 1000  $\phi$  press with 24 chambers (requiring 50 m. of filter cloth) the filter cloth serves for 1000 cu.m. of oil. When the presses reach 8 atm. compression the chambers are full and the cake is washed with fore-runnings and blown dry with  $N_2$ . It has been found that this washing process operates best when the water content of the clay is limited to 8%. Hence the clay should be stored in the absence of moisture.

#### V. Residual Oil Treatment

In the section on the working up of the crude polymer the separation of the oil-aluminum chloride sludge was described (p. 78). The residual oil thus obtained has the following properties:

|                              |                     |            |      |
|------------------------------|---------------------|------------|------|
| d <sub>20</sub>              | 0.8510              | Coke-test  | .63  |
| V <sub>38</sub> <sup>°</sup> | 125.3E <sup>°</sup> | Acid No.   | 0.1  |
| V <sub>99</sub> <sup>°</sup> | 5.39E <sup>°</sup>  | Sap. No.   | 0.17 |
| V.I.                         | 80.2                | Iodine No. | 122  |
| Fl.P.                        | 185                 | A.P.       | 82   |
| P.P.                         | -23                 |            |      |

On the basis of the high iodine number it was decided to hydrogenate the oil over Cat. 3076 at 10-18 MV. The catalyst was poisoned very quickly. An increase in the hydrogenation temperature brought no improvement in the life of the catalyst. The used catalyst was in part decomposed and in part incrustated with coke.

The improvement of these oils by hydrogenation was abandoned and an after treatment with  $AlCl_3$  was tried. The water-free neutral oil and 5-7%  $AlCl_3$  was heated to  $120-150^\circ$  with stirring for 3 hours. Upon cooling, the  $AlCl_3$ -hydrocarbon complex separated and was removed by decantation.

The acid oil was neutralized with lime and methanol, and through distillation brought to the desired Fl. P. If this acid oil is neutralized with lime without the use of alcohol the properties of the oil are better, as shown in Table 63.

Table 63. Neutralization with and without Methanol

| <u>Date</u> | <u>Exp. No.</u> | <u>Conrad. C.</u> | <u>Iodine No.</u> |      |                  |     |            |            |
|-------------|-----------------|-------------------|-------------------|------|------------------|-----|------------|------------|
| 12/8/42     | I               | .188              | 16.5              |      |                  |     |            |            |
|             | II              | .216              | 17.1              | I    | Plant Sample Oil | -   | Lab-Lime   |            |
|             | IV              | .237              | 17.4              | II   | " "              | "   | " " + MeOH |            |
|             | 53              | I                 | .157              | 16.6 | III              | " " | "          | Plant-Lime |
|             |                 | II                | .200              | 27.5 | IV               | " " | "          | " " + MeOH |
|             |                 | IV                | .234              | 24.2 |                  |     |            |            |
|             | 54              | I                 | .242              | 27.3 |                  |     |            |            |
|             |                 | II                | .285              | 30.0 |                  |     |            |            |
|             |                 | III               | .218              | 26.4 |                  |     |            |            |
|             | 55              | I                 | .169              | 15.1 |                  |     |            |            |
|             |                 | II                | .204              | 15.7 |                  |     |            |            |
|             |                 | III               | .180              | 15.2 |                  |     |            |            |
| 56          | I               | .180              | 15.5              |      |                  |     |            |            |
|             | II              | .215              | 16.2              |      |                  |     |            |            |
|             | III             | .175              | 15.6              |      |                  |     |            |            |

Table 64 shows that the higher boiling material is more unsaturated than the lower.

Table 64

| <u>b.p./0.1 mm.</u> | <u>Iodine No.</u> |             |
|---------------------|-------------------|-------------|
| < 160               | 2.28              |             |
| 180                 | 4.80              | Iodine No.  |
| 190                 | 5.25              | Sample 6.53 |
| 200                 | 5.98              |             |
| 210                 | 7.32              |             |
| 220                 | 9.70              |             |
| 240                 | 12.55             |             |
| 250                 | 15.05             |             |

This light fraction can be put in again with the SS oil in the polymerization process.

One obtains out of 100 parts of crude R oil, 60 parts refined R oil and about 27 parts R oil forerunnings. One obtains further material from R oil refining by washing the  $AlCl_3$  sludge with hot water - 5 parts of a so-called R-R oil.

The refined R oil has the following properties:

|                   |        |            |      |
|-------------------|--------|------------|------|
| d <sub>20</sub>   | 0.8457 | Coke Test  | 0.12 |
| V <sub>38</sub> ° | 60.4   | Acid No.   | 0    |
| V <sub>99</sub> ° | 4.33   | Sap. No.   | 0.18 |
| V.I.              | 106.3  | Iodine No. | 32   |
| Fl. P.            | 194    | A.P.       | 157  |
| P.P.              | -39°   |            |      |

It is used for the production of cold-resistant axle oil for the German Railways.

The  $AlCl_3$  sludge obtained in treating R oil consists of 65 parts oil and 35 parts  $AlCl_3$ . The sludge will not react with cold water but will decompose vigorously with hot water. One obtains then a dark, very viscous oil which has the following properties:

|                   |          |            |       |
|-------------------|----------|------------|-------|
| d <sub>20</sub>   | 0.960    | Coke Test  | 5.68  |
| V <sub>80</sub> ° | 2622.OE° | Acid No.   | 3.58  |
| V <sub>99</sub> ° | 26.4     | Sap. No.   | 8.06  |
| V.I.              | 67       | Iodine No. | 137   |
| Fl.P.             | 188      | A.P.       | 60-69 |
| P.P.              | 1°       |            |       |

Table 65. U.V. Absorption Spectra

% Transmission  
between 2,500 and 2,800Å

|                                  |      |
|----------------------------------|------|
| R Oil Crude                      | 5.8% |
| R Oil H <sub>2</sub> with 3096   | 27.5 |
| R Oil H <sub>2</sub> with 3390   | 68.0 |
| R Oil Treat with $AlCl_3$        | 29.7 |
| R-R Oil Crude                    | 5.0  |
| R-R Oil H <sub>2</sub> with 3390 | 40.5 |
| SS Oil (Oven VIII/41)            | 58.0 |
| SS Oil (Oven VIII/41)            | 47.5 |

The R-R oil was hydrogenated with 3390 catalyst at 17 MV.

A small amount of cracking took place. A 68% yield of water-clear weak blue fluorescent oil was obtained with the following properties:

|                   |       |            |      |
|-------------------|-------|------------|------|
| d <sub>20</sub>   | 0.881 | Coke Test  | 4.55 |
| V <sub>38</sub> ° | 15.58 | Acid No.   | 0    |
| V <sub>99</sub> ° | 1.816 | Sap. No.   | 0    |
| V.I.              | 51    | Iodine No. | 137  |
| Fl.P.             | 163   | A.P.       | 143  |
| P.P.              | -35   |            |      |

One sees on comparing this product with the starting material that the viscosity has decreased sharply, the V.I. decreased slightly, the coke test is still very high, and the iodine number is practically unchanged. It is remarkable that the pour point has decreased from -1° to -35°. The most important of these results is that the constituents responsible for the high coke test are not removed through hydrogenation. Table 65 shows that the R-R oil differs from the R oil in that it possesses a much higher aromatic content. These are responsible for the high coke test.

As the R-R oils had high iodine numbers, they were given to Dr. Heidinger to test as drying oils. He succeeded, with our help, to produce a lacquer which,

according to the choice of solvent, produced a dry shiny coating, whereupon it was concluded that the R-R oil could be used as a drying oil. However, it appeared that the oil did not take up oxygen in drying as a vegetable oil would do but rather formed a bituminous-like material. If, for example, the R-R oil is mixed with 2% Cobalt-Lead-Manganese siccative and blown with air for two days at 20°, there is no uptake of oxygen, as the following elementary analysis shows:

|          | <u>Original R-R Oil</u> | <u>R-R Oil after 48 hrs.</u> |
|----------|-------------------------|------------------------------|
| Carbon   | 87.60                   | 87.10                        |
| Hydrogen | 10.89                   | 10.72                        |
| Oxygen   | 1.25                    | 1.23                         |

The bituminous-like character of R-R oil is also shown by the fact that if it is heated with Vinoflex a glistening thick lacquer is produced.

The R-R oil has been accepted by the lacquer commission and advertised as a lacquer ingredient under the name of "Karboresin R". It serves as a base for paint on wood and brick.

The R-R oil is also very useful as a plasticizer for Buna compound-ing, as has been shown in the rubber laboratories at Schkopau. It can also be used together with mineral filling; for example, with ground shale, it produces a linoleum-like surface if applied to rough cement.

## VI. Experiments for After-treatment of Manufactured SS Oil

### a. Effect of Hydrogenation on Properties of the Oil

It was desired to determine whether hydrogenation of the SS-oil would produce an alteration in the stability of the oil or its cold properties. Out of a great number of experiments at different temperatures and pressures over catalyst 3390 and 3076 only the following one need be described:

| Hydrogenation over K 3090 at 150 atm. | Not Hydrogenated | 5 MV      | 6 MV  | 7 MV  | 8 MV  | 9 MV  | 10 MV     |
|---------------------------------------|------------------|-----------|-------|-------|-------|-------|-----------|
| $d_{20}^{20}$                         | 0.848            | 0.848     | 0.846 | 0.846 | 0.847 | 0.847 | 0.847     |
| Viscosity 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                                    | 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 meas. |       | 20490 |       |       | not meas. |
| V.I.                                  | 121.7            | 122.6     | 122.6 | 122.8 | 122.5 | 122.1 | 123.3     |
| P.P.                                  | -39°             | -16°      | -17°  | -19°  | -15°  | -17°  | -16°      |
| Fl.P.                                 | 169°             | 174°      | 178°  | 190°  | 185°  | 184°  | 188°      |
| Iodine No.                            | 5.21             | 1.77      | 1.40  | 1.04  | 0.74  | 0.39  | 0.0       |
| Conrads on C.                         | 0.114            | 0.038     | 0.034 | 0.036 | 0.030 | 0.028 | 0.024     |

The product after 5 and 6 MV hydrogenations was a pale yellow oil; after 7 MV it became a colorless oil. For complete saturation 10 MV were required. The latter material has been tested with Paraflow in order to determine its effect on pour point and viscosity.

1) SS 903, 2.49E°/99 Hydrogenated at 10 MV

| °C  | <u>Without Paraflow</u> | <u>0.05% Paraflow</u> |
|-----|-------------------------|-----------------------|
| 0   | 362                     | 340                   |
| -10 | 1435                    | 952                   |
| -15 | 3430                    | 1163                  |
| -20 | 10600                   | 3190                  |
| -25 | not meas.               | 6960                  |
| -30 |                         | 16800                 |

2) SS 903 Hydrogenate without Paraflow

|                  | P.P. |
|------------------|------|
|                  | -20° |
| + 0.02% Paraflow | -27  |
| 0.04% "          | -30  |
| 0.06% "          | -35  |
| 0.08% "          | -35  |
| 0.10% "          | -34  |

3) P.P. Lowering with Paraflow using Synthetic Oil SS 902

| <u>Amt. Paraflow</u> | <u>P.P. °C</u> | <u>V<sub>-30°E</sub></u> |
|----------------------|----------------|--------------------------|
| 0                    | -39°           | 10950                    |
| 0.01                 | -40            | 9749                     |
| 0.02                 | -45            | 6296                     |
| 0.05                 | -47            | 4912                     |
| 0.075                | -47            | 4702                     |
| 0.10                 | -47            | 4250                     |

4) Effect of Oppanol and Paraflow on SS 902

| <u>Amt. Oppanol</u> | <u>Amt. Paraflow</u> | <u>P.P.</u> | <u>Viscosity, °E</u> |             |
|---------------------|----------------------|-------------|----------------------|-------------|
|                     |                      |             | <u>-99°</u>          | <u>-30°</u> |
| 0                   | 0                    | -39         | 2.18                 | 4940        |
| 0.5                 | 0                    | -49         | 2.42                 | 6160        |
| 0.5                 | 0.5                  | -51         | 2.42                 | 4560        |

b) Effect of After-Polymerization on SS Oil

In order to improve the properties of the oil, especially to raise the thermal stability or lower the viscosity, the crude polymer was heated further in the autoclave before the pressure was released and in the presence of the reactive addition compound.

The first experiment of this kind was carried out in February, 1938, in the 1000 C autoclave.

After the end of the normal polymerization at 110°, the autoclave without further gas introduction was heated an hour at 130° as well as at 140°. The AlCl<sub>3</sub> addition compound in the crude polymer should act as a condensing agent. Some of the results are shown in the following table. Since no analytical test showed any change, the product was not subjected to motor tests.

Table 66

| No. | Heating |     | E°/99 | V.I.  | Pour Point | Flash Point |
|-----|---------|-----|-------|-------|------------|-------------|
|     | Hours   | °C  |       |       |            |             |
| 254 | 0       | -   | 4.14  | 116.1 | -36        | 201         |
|     | 1       | 130 | 4.05  | 116.6 | -36        | 195         |
|     | 2       | 130 | 4.15  | 115.8 | -36        | 201         |
| 257 | 0       | -   | 4.23  | 118.1 | -37        | 207         |
|     | 2       | 120 | 4.52  | 118.4 | -37        | 197         |
|     | 3       | 120 | 4.27  | 116.1 | -36        | 201         |
|     | 4       | 120 | 4.70  | 117.1 | -34        | 205         |
| 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         |

In a similar manner, higher temperatures and longer times were tried in the 4500 l. N<sub>6</sub> autoclave. The oil obtained was tested for oxidation stability. The oxidizing conditions were as follows: 255 g. SS oil was heated 200 hours at 170° with 10 l. air passing through per hour.

Table 67

| After Polymerization | Oxidation | E°99  | V.I.  | P.P. | F.P. | AN   | SN    | CC    |
|----------------------|-----------|-------|-------|------|------|------|-------|-------|
| None                 | None      | 4.55  | 108.6 | -34  | 218  | 0.0  | 0.0   | 0.026 |
|                      | 200 hours | 8.37  | 103.2 | -27  | 213  | 7.73 | 20.61 | 0.832 |
| 4 hours at 155°      | None      | 5.52  | 108.3 | -33  | 221  | 0.0  | 0.0   | 0.030 |
|                      | 200 hours | 10.15 | 101.0 | -25  | 198  | 7.06 | 19.38 | 0.817 |
| 10 hours at 155°     | None      | 4.49  | 108.5 | -35  | 214  | 0.0  | 0.0   | 0.022 |
|                      | 200 hours | 8.92  | 96.3  | -24  | 208  | 7.06 | 22.18 | 0.677 |

Although the after-polymerization was extended beyond the ten hours, no important effect on the thickening was observed. A small improvement in the Koketest was observed. Experiments at still higher temperatures are continuing and their products will be tested.

VII. Survey of the Leuna Production in the Years 1938 - 43

The following table shows a collection of oil yields in the different autoclaves based on 100 parts of ethylene.

Table 68

|                 | <u>45 l.</u> |  | <u>1000 l.</u> |  | <u>4500 l.</u> |
|-----------------|--------------|--|----------------|--|----------------|
| SS Oil          | 78.4%)       |  | 77.2%)         |  | 76.0%)         |
| Forerun         | 10.3 )93.7%  |  | 8.6 )91.4%     |  | 7.7 )91.0%     |
| Residual Oil    | 5.0 )        |  | 5.6 )          |  | 7.3 )          |
| Uncondensed Gas | 2.3          |  | 3.2            |  | 2.7            |
| Loss            | 3.7          |  | 5.4            |  | 6.3            |

The above yields were obtained from early work, 1936-38. Table 69 is a survey of the improvement in yield and energy consumption from 1938-1942. The drop in yield in 1942 is due to the variations produced by the production of SS 903 and to the fluctuation of the gases received.

Table 69

|   | 1938    |      | 1939    |      | 1940    |      | 1941      |      | 1942         |         |
|---|---------|------|---------|------|---------|------|-----------|------|--------------|---------|
|   | t       | %    | t       | %    | t       | %    | t         | %    | t            | %       |
| Ethylene Used   | 700     |      | 2,799   |      | 5,121   |      | 8,512     |      | 11,440       |         |
| Ethylene Residual Gas                                     |         |      |         |      | 278     |      | 309       |      | not measured | 1)      |
| Ethylene Consumption                                      |         |      |         |      | 4,843   | 94.5 | 8,203     | 96.3 |              |         |
| <b>Prod. Based on Consumed C<sub>2</sub>H<sub>4</sub></b> |         |      |         |      |         |      |           |      |              |         |
| SS 906  | 439     | 63   | 1,932   | 69.0 | 3,881   | 80.0 | 6,220     | 75.8 | 8,257        | 72.5    |
| Forerun   | 19      | 2.7  | 115     | 4.0  | 238     | 4.9  | 526       | 6.4  | 708          | 6.2     |
| P Oil   | 73      | 10.0 | 231     | 8.3  | 406     | 8.4  | 729       | 8.9  | 505          | 4.4     |
| Total Yield   | 531     | 75.7 | 2,267   | 81.3 | 4,525   | 93.3 | 7,475     | 91.1 | 9,470        | 83.1 2) |
| <b>Material Used Based on SS Oil</b>                      |         |      |         |      |         |      |           |      |              |         |
| AlCl <sub>3</sub>   | 39      | 9.0  | 151     | 7.8  | 291     | 7.5  | 454       | 7.5  | 621          | 7.5     |
| MeOH  | 12      | 2.7  | 116     | 6.0  | 165     | 4.2  | 268       | 4.3  | 342          | 4.1     |
| Ca(OH) <sub>2</sub>                                       | 38      | 8.6  | -       | -    | 90      | 2.3  | 165       | 2.6  | 270          | 3.5     |
| Clay  | 27      | 6.1  | 72      | 3.7  | 41      | 1.0  | 35        | 0.5  | 73           | 0.9     |
| <b>Energy Total: by SS Oil</b>                            |         |      |         |      |         |      |           |      |              |         |
| Gas (m <sup>3</sup> )                                     | 265,000 | 600  | 750,000 | 390  | 890,000 | 228  | 1,290,000 | 206  | 1,273,000    | -       |
| High P. Steam (t)   | 16,225  | 36   | 31,395  | 16.2 | 6,613   | 2.2  | 9,699     | 1.5  | 12,000       | 1.5     |
| Low P. Steam (t)  |         |      |         |      | 41,067  | 10.5 | 50,406    | 8.1  | 34,818       | 4.3     |
| Electricity (KWH)   |         |      | 379,530 | 222  | 600,130 | 154  | 845,800   | 136  | 894,420      | 111     |
| Water (m <sup>3</sup> )                                   | 320,130 | 730  | 468,360 | 242  | 657,630 | 170  |           |      | 292,460      |         |

1) <387

2) Based on C<sub>2</sub>H<sub>4</sub> used.



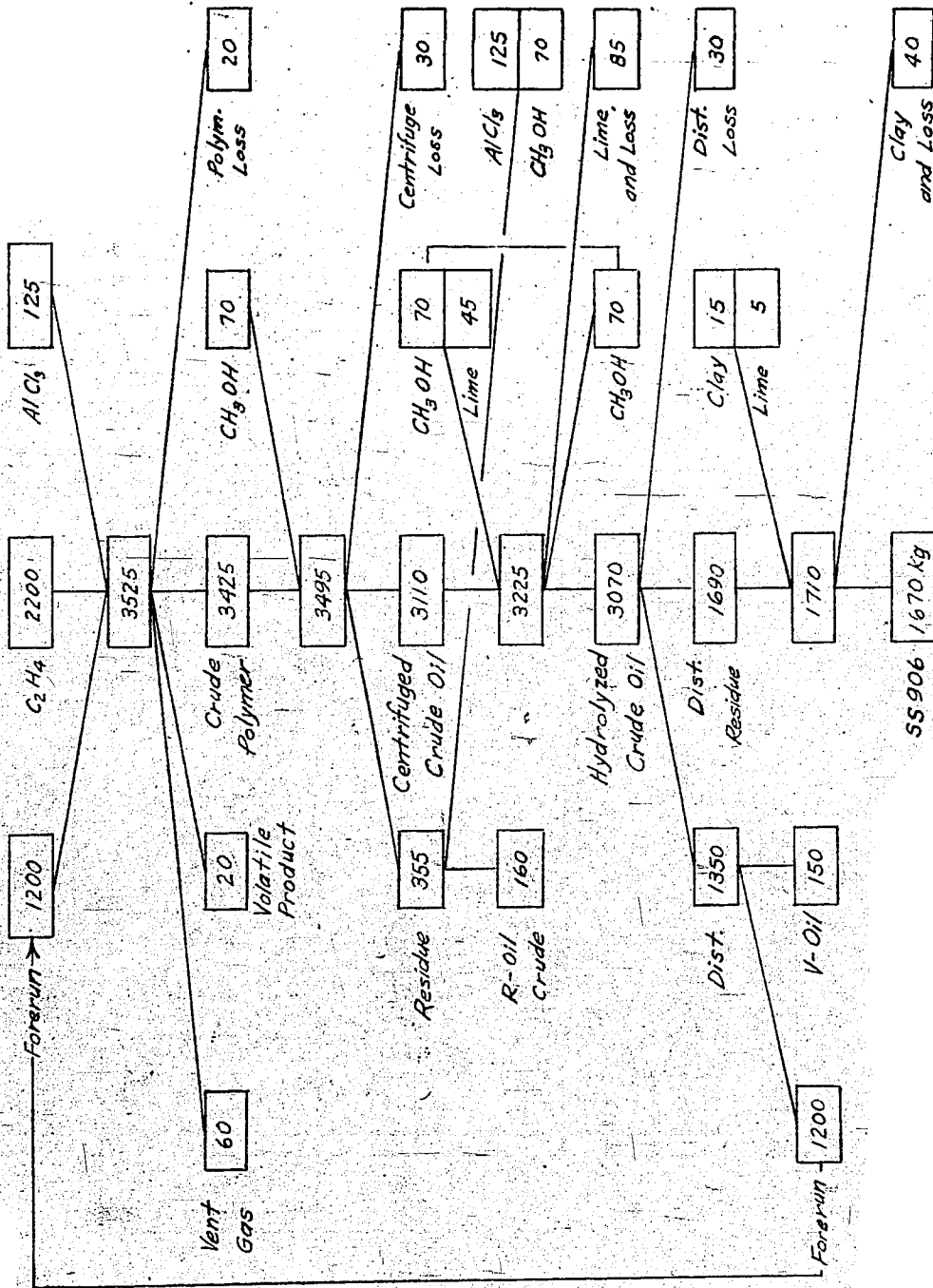
Tables 70a, b, c and d are surveys of the refining of polymer from the 1000 liter and 4500 liter autoclaves.

Table 70a

| <u>Autoclave</u>                          | <u>500 mm. (1000 l.)</u>                     | <u>800 mm. (4500 l.)</u>                      |
|---|--|---|
| <u>C<sub>2</sub>H<sub>4</sub>/Reactor</u> | 470.0 kg. = 100%                             | 2200 kg. = 100%                               |
| SS 906                                    | 362.8 kg. = 77.2%                            | 1670 kg. = 76.0%                              |
| V Oil                                     | 40.4 kg. = 8.6%                              | 150 kg. = 6.8%                                |
| R Oil                                     | 19.3 kg. = 4.1%                              | 160 kg. = 7.2%                                |
| Machine Oil                               | 7.2 kg. = 1.5%                               | -   |
| Volatile Oil                              | -  | 20 kg. = 0.9%                                 |
| Residual Gas                              | -  | 60 kg. = 2.7%                                 |
| Asphalt                                   | 14.2 kg. = 3.0%                              | -   |
| Loss                                      | 26.1 kg. = 5.6%                              | 140 kg. = 6.4%                                |
| At 2 charges/day at                       | 28200 kg./mon. C <sub>2</sub> H <sub>4</sub> | 132000 kg./mon. C <sub>2</sub> H <sub>4</sub> |
| 80% operating time/                       | 17.5 t./mon. SS-906 =                        | 80 t./mon. SS 906 =                           |
| oven                                      | 210 t./yr. SS 906/oven                       | 960 t./yr. SS 906/<br>oven                    |

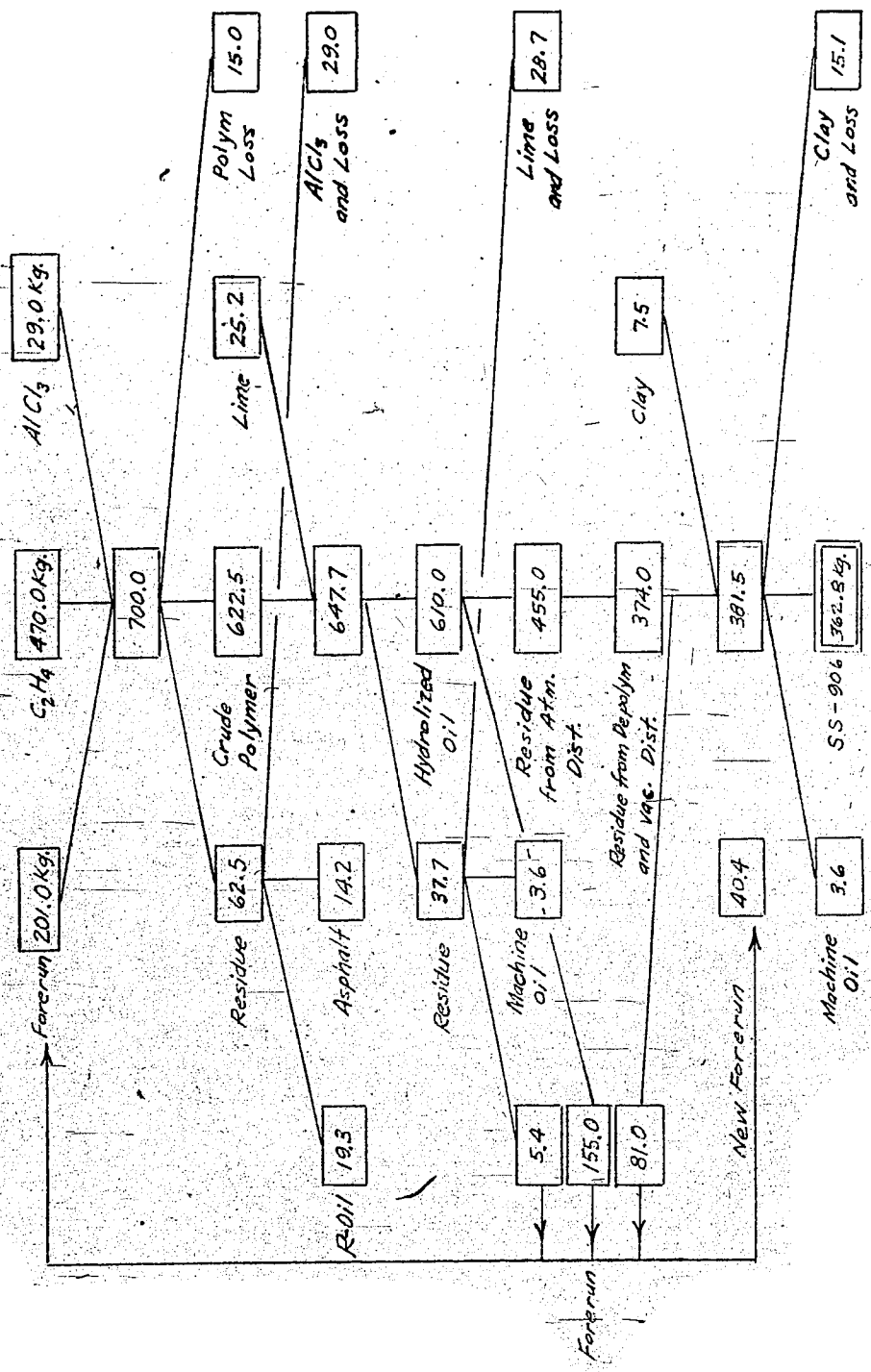
706  
Table 167b

SS Polymerization in the 800mm Autoclave (45000)

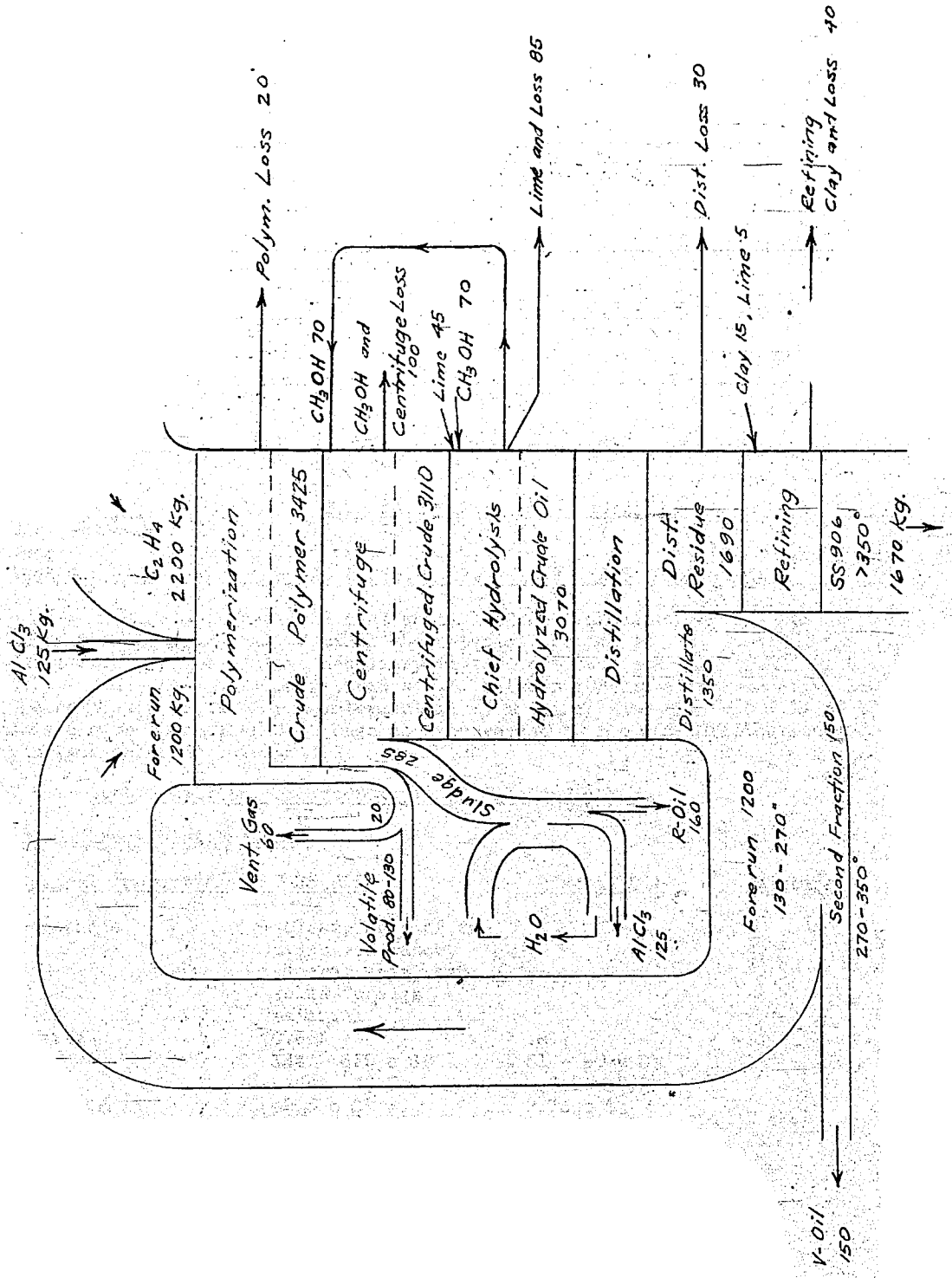


70C  
Table 67e

SS Polymerization in the 500 mm Autoclave (1000L)



70d  
Table 67d



Tables 71a and b show the amounts and quality of finished oil.

Table 71a. Viscosity Indices and Number of Tank Cars of SS 906 Produced at Wifo

| VI Value Over | 106 | 107  | 108  | 109  | 110  | 111  | 112 | 113 | 114 | Total |
|---------------|-----|------|------|------|------|------|-----|-----|-----|-------|
| No. cars      | -   | -    | 13   | 29   | 55   | 14   | 7   | 5   | 1   | 123   |
| 1939 %        | -   | -    | 10.6 | 23.6 | 44.7 | 11.4 | 5.7 | 4.1 | 0.8 |       |
| No. cars      | -   | 10   | 89   | 94   | 48   | 8    | -   | -   | -   | 219   |
| 1940 %        | -   | 4.0  | 35.8 | 37.8 | 19.3 | 3.2  | -   | -   | -   |       |
| No. cars      | -   | 25   | 80   | 86   | 126  | 63   | 17  | 3   | -   | 400   |
| 1941 %        | -   | 6.2  | 20.0 | 21.5 | 31.5 | 15.7 | 4.2 | 0.7 | -   |       |
| No. cars      | 14  | 65   | 161  | 183  | 98   | 10   | 4   | 2   | -   | 537   |
| 1942 %        | 2.6 | 12.1 | 30.0 | 34.0 | 18.3 | 1.9  | 0.7 | 0.4 | -   |       |
| Jan. No. cars | 2   | 28   | 52   | 70   | 76   | 42   | 7   | -   | -   | 277   |
| June 1943 %   | 0.7 | 10.1 | 18.8 | 25.0 | 27.4 | 15.2 | 2.5 | -   | -   |       |

It will be noticed that until 1942 no tank cars went out with a V.I. less than 107. In 1942, 2.6% of the material dropped to V.I. 106. In the first half of 1943, it was necessary to send out two tank cars (0.7%) with V.I. = 106. The chief amount had a V.I. between 108-110 with some above 110. The chief aim of further development is to bring all the oil to a V.I. of 112. This can be accomplished through an improvement in the gas purification and aluminum chloride catalyst.

VIII. Specifications for Products in SS Oil Manufacture

1) SS 906 (Chief Product)

| <u>Physical Properties</u> | <u>SS 906</u>  | <u>Mineral Oil</u>             | <u>Mixture</u>        |
|----------------------------|--|--------------------------------|-----------------------|
| Appearance                 | Clear, free of undissolved water, mineral acid, and solid foreign material |                                |                       |
| Density                    | < 0.862  | < .897                         | < .895                |
| V50°                       | 334 - 350 c St<br>= 44 - 46 E°   | 51 - 60 c St<br>= 6.8 - 7.9 E° | 125 - 143 c St        |
| V100°                      | 42.3 c St =<br>5.63E°  | 9.35 c St =<br>1.77E°          | 19.0 c St =<br>2.75E° |
| V.I.                       | Over 107   | > 88                           | > 98                  |
| Richtungskonstante         | < 3.05   | 3.66                           | < 3.35                |
| Pole Height                | < 1.73   | 2.08                           | < 1.85                |
| Pour Point                 | < -25°   | -15°                           | < -20°                |
| Flash Point                | > 225°   | 225°                           | > 225°                |

VIII. Specifications for Products in SS Oil Manufacture (cont'd)

1) SS 906 (Chief Product) - Cont'd

| <u>Physical Properties</u>    | <u>SS 906</u> | <u>Mineral Oil</u> | <u>Mixture</u> |
|-------------------------------|---------------|--------------------|----------------|
| Fire Point                    | > 263         | 258                | > 225          |
| Acid No.                      | < 0.06        | 0.06               | < 0.06         |
| Sap. No.                      | < 0.30        | 0.17               | < 0.2          |
| Volatility (Noack<br>b. 250°) | < 8%          | < 14%              |                |
| Conradson C.                  | 0.2%          | 0.25%              | 0.25%          |
| Ash Content                   | 0             | 0                  | 0              |
| Asphalt                       | 0             | 0                  | 0              |
| Water                         | 0             | 0                  | 0              |

If SS 906 is to be used for airplane motors, it is mixed with equal parts of mineral oil. The latter must have the properties shown in column 2.

The finished mixture (50 parts SS 906, 50 parts mineral oil, 0.2% inhibitor) should have the properties shown in column 3.

2) SS 903 (3E°/100)

|         |                            |
|---------|----------------------------|
| d20     | 0.860                      |
| V50°    | 106 - 114 c St = 14 - 15E° |
| V100°   | 21 c St = 3E°              |
| V.I.    | 115                        |
| m       | 3.20                       |
| Vp      | 1.60                       |
| P.P.    | -35°                       |
| Fl.P.   | 200°                       |
| Con. C. | 0.20                       |

The SS 903 oil is not used directly as a lubricating oil, but is mixed with esters to produce the following oils:

|           | <u>Air torpedo oil</u>             | <u>LTK 12</u>    |
|-----------|------------------------------------|------------------|
|           | <u>Lube oil for LT instruments</u> | <u>VS 1</u>      |
|           | <u>Cold starting oil</u>           | <u>SS 1600</u>   |
|           | <u>LTK</u>                         | <u>VS 1</u>      |
|           | <u>SS 1600</u>                     |                  |
| SS 903    | 40 pts.                            | 25 pts.          |
| Ester 515 | 57                                 | 72               |
| KSE       | 3                                  | 3                |
| d20       | <.910                              | <.910            |
| V30°      |                                    | <.900            |
|           |                                    | < 7600 s St =    |
|           |                                    | 1000 E°          |
| V20°      | 87-95 c St =                       |                  |
|           | 11.5-12.5 E°                       |                  |
| V50°      |                                    | 16.7-18.5 c St = |
|           |                                    | 2.5-2.7 E°       |
|           |                                    | 23.8-27 c St =   |
|           |                                    | 3.3-3.7 E°       |

|                  | <u>LTK.</u>              | <u>VS 1</u>            | <u>SS 1600</u>           |
|------------------|--------------------------|------------------------|--------------------------|
| V <sub>100</sub> | > 6.25 c St =<br>1.50 E° | > 5.1 c St =<br>1.4 E° | > 6.25 c St =<br>1.50 E° |
| P.P.             | < -50°                   | < -60°                 | < -55°                   |
| Fl.P.            | > 180°                   | > 180°                 | > 200°                   |
| Acid No.         | < 0.20                   | < 0.20                 | < 0.20                   |

Some Mesulfol and KSE may be added to SS 1600 but the amount has not been determined. From the SS 903, one should try to get an oil with V.I > 120, P.P. < -35°, Fl.P. > 200°, and V<sub>99</sub> 2.5 - 3.0 E°.

### 3) V Oil.

This is the low boiling fraction of the SS crude polymer. It shows very good cold properties as it is still liquid at -70°. The V Oils are designated with a number which corresponds to their flash point. The V Oils are used as components for the production of the following oils:

- |                        |         |
|------------------------|---------|
| a) Liquid pressure oil | Do 2000 |
| b) Gun oil             | Blue 44 |
| c) Ice-machine oil     | SV Oil  |

The composition and specifications for these oils are:

#### a) Do 2000

Composition: 73 parts V 120  
25 parts Ester 455  
2 parts KSE  
.006 parts Fluoral 5G  
10 g. phenol phthalein

#### Specifications:

|                  |                      |
|------------------|----------------------|
| d <sub>20</sub>  | < 0.850              |
| V <sub>20</sub>  | > 9.1 c St = 1.75 E° |
| V <sub>-60</sub> | < 4940 c St = 650 E° |
| P.P.             | < -70°               |
| Fl.P.            | > 120°               |
| Volatility       | 120° < 12 wt. %      |
| Acid No.         | < 0.2                |
| Sap. No.         | > 30                 |

Swelling - Liq. Material 5383.7) ± 0 - 2 Vol. % after 24 hours at 80°C  
Swelling - Liq. Material 5344.7)

To meet the above specifications, the V-120 must have the following properties:

|                  |         |
|------------------|---------|
| d <sub>20</sub>  | < 0.816 |
| V <sub>-60</sub> | 330 E°  |
| V <sub>20</sub>  | 1.71 E° |
| P.P.             | < -70°  |
| Fl.P.            | > 120°  |

b) Gun Oil Blue 44

Composition: 45 parts SV 120  
 45 parts Ester 455  
 3 parts S = 10 parts Mesulfol II  
 0.05 parts Sudan blue

SV 20 or VK 20 is a mixture of V 120 with SS 906. Tables 72a, b and c show the properties of mixtures of SS 906 with V 120 as well as with V 140.

d20 < .895  
 V<sub>20</sub>° > 10.8 c St = 1.9 E°  
 V<sub>-60</sub>° < 7600 c St = 1000 E°  
 Fl.P. > 125°  
 Volatility at 120° < 7.5%  
 S Content > 3 wt. %  
 Acid No. < 0.3

Table 72a and b. Mixtures of SS 906 and V 120

| Composition |       | Viscosity |       |       |       | V.I.  | Flash Point | Pour Point |
|-------------|-------|-----------|-------|-------|-------|-------|-------------|------------|
| SS 906      | V 120 | 20°       | 38°   | 50°   | 99°   |       |             |            |
| 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     | 53.5  | 28.1  | 4.42  | 113.1 | 168         | -37        |
| 90.0        | 10.0  | 149.6     | 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  | 112.9 | 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 | 142.3 | 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        |
| 47.5        | 52.5  | 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         | under -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         | "          |



Table 72a and b (cont'd)

| Composition |       | Viscosity |       |       |       |       | V.I. | Flash Point | Pour Point |
|-------------|-------|-----------|-------|-------|-------|-------|------|-------------|------------|
| SS 906      | V 120 | 20°       | 38°   | 50°   | 99°   |       |      |             |            |
| 27.5        | 72.5  | 3.15      | 2.02  | 1.695 | 1.237 | 185.7 | 114  | Under -73   |            |
| 25.0        | 75.0  | 2.93      | 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  | 2.16      | 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 | 1.239 | 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  | "           |            |

Table 72c. Mixtures of SS 906 and V 140

| Composition |       | Viscosity |       |       |       |       | V.I. | Flash Point | Pour Point |
|-------------|-------|-----------|-------|-------|-------|-------|------|-------------|------------|
| SS 906      | V 140 | 20°       | 38°   | 50°   | 99°   |       |      |             |            |
| 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 | 185  | -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  | under -73   |            |
| -           | 100   | 2.08      | 1.55  | 1.389 | 1.123 | -     | 139  | under -73   |            |

4) R Oil.

Obtained from the  $AlCl_3$  sludge. These serve for the production of Y-axle oil -red for the railways. The R Oil must have the following properties:

- $d_{20}$  < 0.85
- $V_{50}$  42.0 c St = 5.6 E°
- P.P. < -50
- Fl.P. > 140
- Con. C. < 0.3

Y Axle Oil.

Composition: 60 parts R Oil  
20 parts V 160  
20 parts Ester 504  
0.02 parts Sudan red

Properties: V<sub>50</sub>° > 3.4 E°  
V<sub>-30</sub>° < 900 E°  
V<sub>-40</sub>° < 3300 E°  
P.P. < -60°  
Fl.P. > 140

