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## ENCLOSURE (B) 8

### STUDIES ON THE MANUFACTURE OF AVIATION GASOLINE BY HIGH PRESSURE HYDROCRACKING OF PINE RESIN

by

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Research Period: May - Aug. 1945

Prepared for and Reviewed with Authors by  
the U. S. Naval Technical Mission to Japan

December 1945

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SUMMARY

The object of this study was to find the optimum operating conditions for the manufacture of aviation gasoline, by high pressure hydro-cracking of pine resin. The semi-solid fraction of pine resin distilling above 300°C was hydro-cracked in an autoclave using Molybdenum Sulphide ( $\text{MoS}_3$ ) catalyst and a 70% yield of cracked oil was obtained containing 40% of aviation gasoline with an octane number of 93-95 (0.15% lead).

I. INTRODUCTIONA. History of Project

Very recently, in response to the urgent demands of the war, pine resin was investigated as a source of aviation gasoline. No previous data were available on this subject. The key point of this research was to select proper reaction conditions for hydro-cracking the very stable pine resin, with high content of acidic matter (phenolic acid and abietic acid), so that high octane aviation gasoline could be obtained.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. S. INABA

II. DETAILED DESCRIPTION

A rotating autoclave of 2-5 liters capacity was used for these tests. Continuous pilot plant experiments were not made.

Properties of the raw pine resin are given below. The fraction boiling above 300°C. (about 50% of the raw pine resin), was used in these experiments. This fraction at room temperature was a hard solid of brownish color. Upon heating to 80-90°C, it became a viscous liquid.

|                                    |       |
|------------------------------------|-------|
| Specific Gravity, $d_4^{15}$ ..... | 1.023 |
| Initial Boiling point (°C).....    | 95    |
| 10%                                | 155   |
| 20%                                | 169   |
| 30%                                | 228   |
| 40%                                | 309   |
| 50%                                | 318   |
| 60%                                | 333   |
| 70%                                | 346   |
| 80%                                | 346   |
| F.B.P.                             | 354   |
| Acid Value .....                   | 122   |
| Saponification Value .....         | 135   |

Physical and chemical properties of products are tabulated in Tables I(B)8 and II(B)8.

III. CONCLUSIONS

As the result of the autoclave tests, it was found that by high pressure hydrocracking of pine resin under the conditions of 200 kg/cm<sup>2</sup> hydrogen pressure, 430-450°C temperature, 2 hours reaction period, and using Molybdenum.

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Sulphide catalyst, a good quality gasoline with 93-94 octane number (0.15% lead) could be produced in yield of 28%. This work was cut short due to the end of the war. It was planned to investigate this process on pilot plant scale, particularly to develop methods for handling the high viscosity melted pine resin in continuous operation. Further work to develop stronger and more active catalysts also was planned.

Table I(B)8  
CONDITIONS OF REACTION AND PROPERTIES OF PRODUCTS  
(Autoclave Test)

|  | Exp. No.         |                  |
|--|------------------|------------------|
|  | 1                | 2                |
| Catalyst   | MgS <sub>2</sub> | MgS <sub>3</sub> |
| Reaction Conditions                                  |                  |                  |
| Reaction Temperature, °C                             | 430              | 450              |
| First Reaction Pressure, kg/cm <sup>2</sup>          | 100              | 93               |
| Final Reaction Pressure, kg/cm <sup>2</sup>          | 65               | 63               |
| Highest Reaction Pressure, kg/cm <sup>2</sup>        | 220              | 225              |
| Reaction Time, hours                                 | 2                | 2                |
| Products   |                  |                  |
| Absorbed Hydrogen wt. % of Raw Oil                   | 4.3              | 4.6              |
| Yield of Cracked Oil wt. % of Raw Oil                | 68               | 70               |
| Water wt. % of Raw Oil                               | 12.5             | 13.5             |
| Acidic Matter vol. % in Cracked Oil                  | 1.0              | 0.5              |
| Specific Gravity of Cracked Oil                      | 0.7869           | 0.7200           |
| 1. B. P. of Cracked Oil °C                           | 39               | 38               |
| 10% Boiling Point of Cracked Oil °C                  | 72               | 68               |
| 20% Boiling Point of Cracked Oil °C                  | 94               | 89               |
| 30% Boiling Point of Cracked Oil °C                  | 105              | 104              |
| 40% Boiling Point of Cracked Oil °C                  | 118              | 116              |
| 50% Boiling Point of Cracked Oil °C                  | 137              | 133              |
| 60% Boiling Point of Cracked Oil °C                  | 153              | 150              |
| 70% Boiling Point of Cracked Oil °C                  | 186              | 182              |
| 80% Boiling Point of Cracked Oil °C                  | 199              | 192              |
| 90% Boiling Point of Cracked Oil °C                  | 210              | 203              |
| 97% Boiling Point of Cracked Oil °C                  | 233              | 220              |
| Final Boiling Point of Cracked Oil °C                | 263              | 252              |
| Total Distillate (vol %)                             | 95               | 98               |
| Residue (vol %)                                      | 2                | 1                |
| Loss (vol %)   | 2                | 1                |
| Residual Gas Composition (vol %)                     |                  |                  |
| CO <sub>2</sub>                                      | 0.2              | 0.3              |
| O <sub>2</sub>                                       | 0.3              | 0.4              |
| C <sub>n</sub> H <sub>2n</sub>                       | 0.9              | 0.5              |
| CO   | 0.4              | 0.3              |
| C <sub>n</sub> H <sub>2n</sub> <sup>*2</sup>         | 16.5             | 17.5             |
| H <sub>2</sub>                                       | 78.2             | 76.2             |
| N <sub>2</sub>                                       | 3.5              | 4.8              |
| n. (Carbon number)                                   | 0.9              | 0.6              |
| Yield of Aviation Gasoline from Cracked Oil<br>vol % | 37               | 40               |

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**Table II(B)8**  
**PROPERTIES OF AVIATION GASOLINE**  
**(Autoclave Test)**

|   | Exp. No. |        |
|---|----------|--------|
|   | 1        | 2      |
| Reaction Temperature, °C                      | 430      | 450    |
| Specific Gravity D <sub>4</sub> <sup>15</sup> | 0.7778   | 0.7614 |
| Acidic Substance in Aviation Gasoline, vol. % | 0.2      | 0      |
| Fractional Distillation, °C                   |          |        |
| Initial Boiling Point                         | 42       | 33.4   |
| 10% Boiling Point                             | 84       | 63.8   |
| 20% Boiling Point                             | 94       | 80.2   |
| 30% Boiling Point                             | 101      | 97.4   |
| 40% Boiling Point                             | 108      | 105.6  |
| 50% Boiling Point                             | 110.4    | 108.6  |
| 60% Boiling Point                             | 120.5    | 118.5  |
| 70% Boiling Point                             | 132      | 130.8  |
| 80% Boiling Point                             | 147      | 147    |
| 90% Boiling Point                             | 160      | 162    |
| 97% Boiling Point                             | 170.4    | 168.5  |
| Final Boiling Point                           | 172.5    | 171.5  |
| Total Distillate vol. %                       | 95       | 98     |
| Residue                                       | 3        | 1      |
| Loss  | 2        | 1      |
| Composition vol. %                            |          |        |
| Unsaturated Hydrocarbon                       | 3.0      | 0      |
| Aromatic Hydrocarbon                          | 21.3     | 24     |
| Naphthenic Hydrocarbon                        | 24.3     | 30.4   |
| Paraffinic Hydrocarbon                        | 51.4     | 45.6   |
| Aniline Point                                 | 60.7     | 1.2    |
| Octane Number                                 |          |        |
| Clear   | 78.0     | 79.0   |
| With 0.15% of Lead                            | 93.6     | 94.2   |