

FILM STUDY GROUP  
SUBJECT INDEX AND REPORT

T.O.M. REEL NO. 11

Prepared by

THE TEXAS COMPANY

# The Texas Company

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Item No.

Solvent Extraction

To increase A-K of aviation gasoline (SO<sub>2</sub>)

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Desulfurizing

Water gas with alkazid caustic, corrosion

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Isomerization

Butane to isobutane

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T.O.M. REEL 11  
Bag No. 2247, Target No. 30/4.09 - Scholven

- ITEM 1-5  
Inclusive: Auditor's report for Scholven, calendar years 1938-9.
- ITEM 6: 1942 Production data, covering aviation and motor gasoline, fuel gas.
- ITEM 7: Podbielniak analyses of hydrogenation gases (March 20 1940)
- ITEM 8: Coal analyses, Scholven, also dependence of coal residue on alkalinity of coal ash (February 28, 1944).
- ITEM 9: Design data for coal hydrogenation: Regenerators, heat exchangers, preheaters. Discussion held at Scholven Oct. 21, 1941, between I.G., Scholven, Leuna, Poelitz.
- ITEM 10: Estimated costs Scholven coal hydrogenation plant (March 16, 1942)
- ITEM 11: Tankage and building for Gladbach or Scholven III, also high pressure gas flow sheet, Nov. 13, 1941 and April 22, 1941.
- ITEM 12: Preparation of gas for Scholven III or Gladbach; dated from 1938 to 1942.
- ITEM 13: Material quantities to be handled in Scholven III (Gladbach) April 9, 1942.
- ITEM 14: Aromatics determination in CV<sub>2</sub>B-Gasoline Scholven, Nov. 23, 1940.

In Scholven the aromatic content of gasolines is calculated from the aniline point before and after removal of the olefins and aromatics by the method of the IG-Leuna. The product (AP I minus AP II) x 0.95 gives the volume percent of aromatics. The aromatics and olefins are dissolved by 1/2 hour shaking of 1 part gasoline with 3 parts of concentrated sulfuric acid (98%).

To check this procedure the method of Dr. Hirschberger at Leuna was used. This consists in extracting the aromatics with liquid SO<sub>2</sub> and determining the aromatics both by volume and by weight after driving off the SO<sub>2</sub>. The composition of the extracted aromatics was also determined by close distillation.

~~For removal of the aromatics 300 cc. gasoline was extracted 3 times with 300 cc. liquid SO<sub>2</sub>, shaken 1/2 hour in a cold bath at -80°C and the SO<sub>2</sub> extract removed after standing 1/2 hour. The aromatic-containing SO<sub>2</sub> was then in a similar manner treated with liquid propane in order to remove any non-aromatics that might possibly have been dissolved out by the SO<sub>2</sub>. The propane extract was then shaken with liquid SO<sub>2</sub> in order to remove the last traces of aromatics and this SO<sub>2</sub> combined with the rest of the SO<sub>2</sub> extract. From this combined extract the SO<sub>2</sub> and propane were driven off in a long reflux condenser cooled with ice water. The aromatics and non-aromatics~~

were washed with caustic and water. The aromatics were separated into individual constituents in a fine fractionating column devised by Dr. Koeppel (Gute Hoffnungshuette, Oberhausen).

The olefins were determined in the aromatic-free mixture with 92% H<sub>2</sub>SO<sub>4</sub>. The content of naphthenes and paraffins were calculated from the aniline point of the olefin-free product. In Table I, results obtained by the two methods are compared, and as seen, the aromatic contents check very well. However, the olefin, naphthene and paraffin contents differ. In the value given under I, the olefins were determined by extraction from the aromatic containing gasoline with 92% acid, while in the second case, the olefins were extracted with 92% acid from the aromatic-free product. Thus, the difference in olefin content. If the gasoline contains besides olefins also aromatics, then these are also partly dissolved by the 92% acid and therefore give a higher olefin content at the expense of the aromatics. On account of the different methods of aromatic removal, the AP of the aromatic-and olefin-free product (AP II) are different and likewise also their naphthene and paraffin contents. If the aromatics are removed with liquid SO<sub>2</sub> and the olefins with 92% acid, then the AP of the aromatic-and olefin-free product is about 2°C lower than in the case of a gasoline freed of aromatics and olefins by means of 98% acid. In the case of the 98% acid, the naphthenes are attacked, while this is less the case with the milder treatment with liquid SO<sub>2</sub> and 92% acid.

As determined by close fractionation, the composition of the aromatics contained in CV<sub>2</sub>b gasoline is: benzene (0.880/d<sub>15</sub>) 17% by volume; toluene (0.866) 33%; xylenes plus ethylbenzene (0.863) 25%; higher aromatics (0.866) 25%.

If the values for aromatics, naphthenes, olefins and paraffins determined by aromatic extraction are considered as correct, then the aromatics determined by the usual methods would be considered as correct, while the olefin and paraffin determinations would be too high and the naphthene content somewhat too low.

TABLE I  
Aromatic Determination from AP I and AP II      Aromatic Determination by SO<sub>2</sub> Extraction

	Aromatic Determination from AP I and AP II	Aromatic Determination by SO <sub>2</sub> Extraction
AP I	-30°C	-30°C
AP II	+ 47°C (after treatment with 98% acid)	+ 45°C (after treatment of aromatic-free gasoline 92% acid)
Aromatics	47.5%	47.7 (d <sub>15</sub> 0.870)
Olefins	3.5	1.6
Naphthenes	37.2	41.9
Paraffins	11.8	8.8

Research on 7019 Catalyst DHD Nov. 23, 1940

This microfilm was concerned with a description of the DHD process as obtained at Scholven. The microfilm was in poor shape but it was evident that the DHD process as described was similar to that described in the TAC Report ZGU-2, Page 105.

ITEM 15: Aviation Gasolines and their manufacture - by M. Pier  
(Jahrbuch der Deutschen Akademie der Luftfahrtforschung  
1941/2, pp. 531-9)

The author first briefly reviews processes used outside of Germany for manufacturing aviation gasoline such as catalytic cracking, alkylation, etc.

The aluminum chloride cracking process is used in Germany partly independently in the petroleum industry, and partly in connection with hydrogenation, with which it can be advantageously combined. Synthetic catalysts have been developed in Germany with a higher activity than the decolorizing earths used up to this time. (No details given).

In Germany, varied raw materials, both rich and poor in hydrogen, have to be converted into aviation gasoline and only catalytic hydrogenation is suitable if high yields are to be obtained. Units constructed for the manufacture of motor gasoline and Diesel fuels can be converted directly to aviation gasoline manufacture. The aviation gasoline produced today (1941) is prepared predominantly by hydrogenation.

In converting a hydrogenation plant to use oil instead of coal, the hydrogen unit and the high pressure chambers require no alteration. The solid or high boiling charge is first processed in the liquid phase with finely divided catalysts giving gasoline and middle oil alone, sometimes fuel oil as well. For aviation gasoline the middle oil is then processed in the vapor phase with hydrogen over a fixed catalyst. The properties of the product obtained in the vapor phase depend on the pressure (which is up to 700 atmospheres), the hydrogen partial pressure, the temperature, and especially on the catalysts. The nature of the charging stock also plays a decisive role. Hydrogen-poor stocks such as anthracite coal, and cracked gas oil residues give higher anti-knock products than hydrogen-rich stocks. However, practically all of the stocks processed in the hydrogenation units give good aviation gasoline of 87 octane number (leaded) and are paraffinic-naphthenic in type and low in aromatics. They have good lead sensitivities. By additional means such as extraction with liquid  $\text{SO}_2$  or the addition of iso-paraffins or aromatics, the quality of the aviation gasoline may be increased, especially that obtained from hydrogen-rich stocks. In practice the A-K of aviation gasoline is improved by lowering the end point. Fig. 1 shows the end points which gasolines produced in similar manner from various stocks must have to give aviation gasolines of the same octane number.

Iso-octane is prepared in Germany from hydrogenation residue gases or from  $\text{H}_2$ -CO. Butane from the hydrogenation gases must be dehydrogenated into olefins for which purpose a catalytic process was developed in which the catalyst was passed concurrently (hindurchgeschleust) through the reaction zones and regenerated outside the chamber and recycled. The method of producing iso-octane from  $\text{H}_2$ -CO has already been developed technically. (No details).

Since, however, iso-octane cannot be produced in sufficient quantities, it is necessary to consider the aromatics which can be

made in large amounts with the equipment already available. By coal hydrogenation a predominantly naphthenic gasoline and by hydrogenation of higher alcohols an iso-paraffinic gasoline (EP about 110°C) were prepared of the same octane number (78 motor method). The coal gasoline appeared by the motor method to be even less lead sensitive; however, when these two gasolines were tested in an engine with varying air-fuel ratios the MEP curve of the former lies above that of the pure paraffinic gasoline (see Figure 2). While having somewhat higher vapor pressure it approaches in quality that of foreign 100 octane aviation gasolines.

Higher aromatics show in general a better MEP curve than benzol. Symmetry of substitution as well as branching and, up to a certain degree, length of the side chain have a favorable effect so that p- and m- xylol as well as toluol are better than benzol, while on the other hand o-xylol is not as good as benzol. The blending value of aromatics in lesser degree increases with the higher boiling point compounds. In 50-50 mixture with 42 octane number gasoline, benzol has a blending value of 96, toluol 99, p-xylol 101, and mesitylene 109. In the case of rich mixtures higher engine output is obtained with aromatics than with iso-octane. Also with lean mixtures the MEP curves of most higher aromatics lie above iso-octane while benzol is somewhat below. The MEP curves of the aromatics contained in technically aromatized gasolines are about the same as that of toluol.

Thus in the case of aromatic fuels an appreciable increase in output of an airplane engine can be obtained in case, through the construction of the engine it is possible to increase the mixture temperature as well as the cylinder and piston temperatures and thus take advantage of the great temperature sensitivity of the aromatics.

Carefully refined motor benzol, so-called aviation benzol, has long been added to aviation gasoline in small amounts. Also still higher fractions of crude benzol, which give greater losses on refining the sulfuric acid, can be added to aromatic fuels after the former have been refined by hydrogenation under pressure. In continued operation, the higher aromatics perform better in higher concentrations than aviation benzol; the latter can lead to early ring sticking.

The production of aromatic gasolines is effected by dehydrogenation of naphthenic and paraffinic gasolines. The non-aromatic portion of these gasolines is also more knock-resistant than that of aromatized gasolines from similar base stocks. This dehydrogenation is carried out under about 50 atmospheres pressure. The yield depends on the charging stock and also on the aromatic content required. Hydrogen-poor naphthenic anthracite gasoline gives an especially high yield. Not only the yield, but also the quality of the dehydrogenated gasoline depends on the gasoline charged. The more knock-resistant the initial material, the higher the output in the engine of the dehydrogenation gasoline of the same aromatic content. Fuels of especially high aromatic content, for example for blending, are obtained by dehydrogenating aromatized gasoline. Such a fuel with clear octane of 92 had octane of 100 on addition of 0.12% volume of lead.

Increasing the end point of aromatic fuels, in contrast to straight run and hydrogenated gasolines, causes no decrease in the octane number.

On the contrary, the higher fractions of this type of fuel are very knock-resistant. Therefore, the end point in the case of these fuels can be raised.

A comparison of iso-paraffinic 100 octane gasoline used abroad shows that the aromatic fuels in the lean zone behave in part appreciably better. In the case of rich mixtures aromatic fuels are throughout better.

It has thus been shown that in German hydrogenation units, large quantities of 87 octane aviation gasoline can be produced and that by slight rearrangement of present hydrogenation units and construction of auxiliary equipment large amounts of high octane fuels can also be manufactured, if necessary, very rapidly. The process described renders it possible to increase the iso-paraffinic content of gasoline within certain limits by using strongly isomerized hydrogenated gasolines or increasing the content of iso-octane or similar materials. In connection with present hydrogenation units, it was easier and time-saving to increase the aromatic content of the gasolines, using aromatization, dehydrogenation and cyclization. Iso-paraffins, aromatics and lead tetraethyl can replace each other to a certain degree in improving engine characteristics so that the necessary amount of lead, for example, can be decreased by increasing slightly the iso-octane or aromatic content. At the present time, (1941) German high aromatic fuels are at least as good as foreign fuels, if not better.



Fig. 1

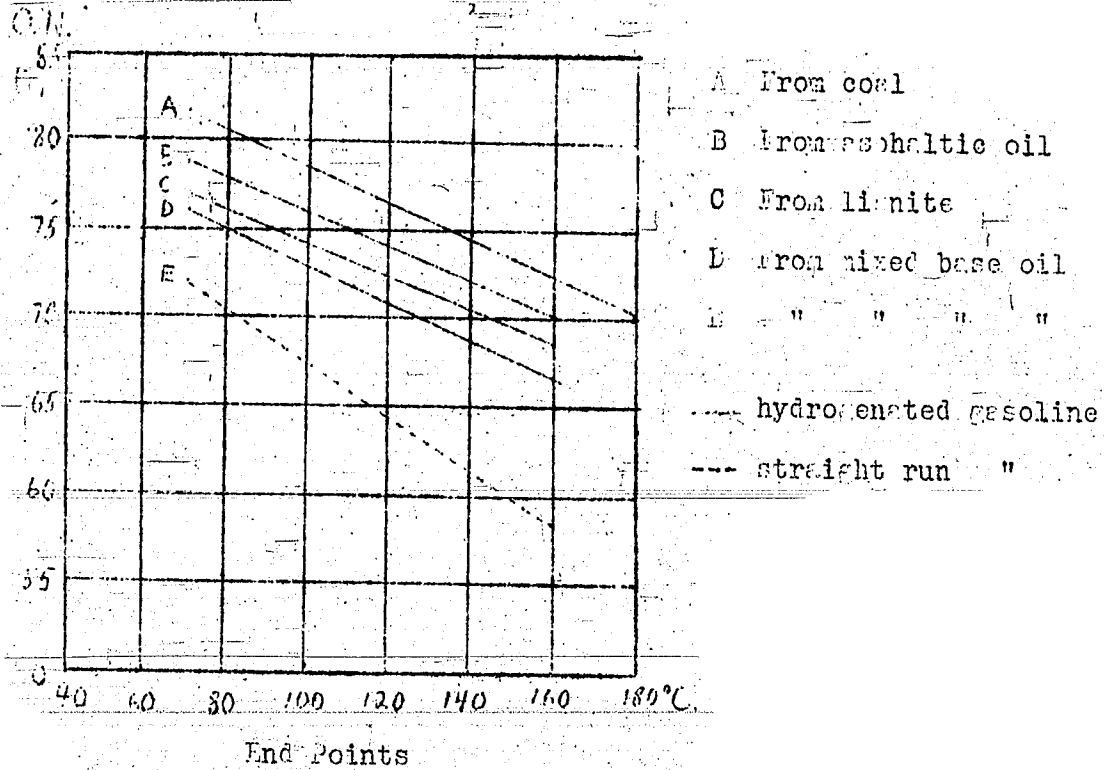


Fig. 2

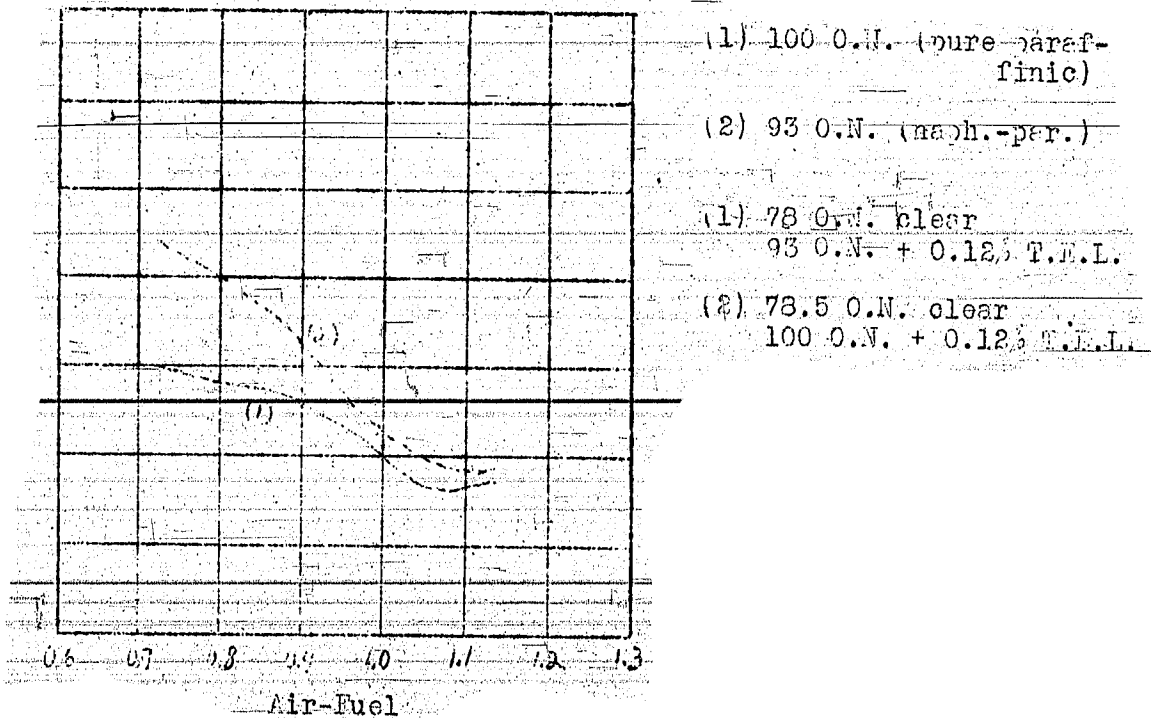
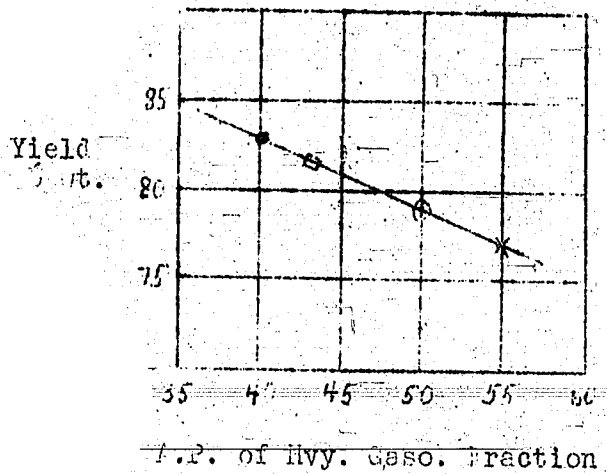


Fig. 3



- Hydrogenated Gasoline - Anthracite
- ◻ " " - Lignite
- ◉ Naphthenic Petroleum Gasoline
- × Paraffinic " "

ITEM 16: Description of method used at Poelitz to determine the corrosive action of alkazid caustic on aluminum based on Leuna method. A method for determining the silicic acid content of the lye is being developed by Leuna. Discussion of aluminum and iron corrosion in connection with the alkazid processes for desulfurizing water gas.

Bag No. 3500, Target 30/4.05, Boehlen  
(Brabag and Saechsische Works)

Index in English of the following:

1. Bound monthly reports on plant operations for 1943 (Boehlen)
2. - 7. Inclusive: Monthly hydrogenation reports Jan-June 1944. Include flow diagrams and material balances; distillation curves of gasoline and diesel fuel stocks.
8. Flow sheet of 1000 ton coal hydrogenation project. Blank form used for reporting above data.
9. Graph showing production of fuels 1936 to May 1944
10. Monthly average analysis of tar, light oil and mixtures Dec. '43
11. Motor gasoline, Diesel fuel tests. Boehlen, May 7, 1945
12. Daily report sheet Tar Stall, June 30, 1942.
13. Daily Report Sheet Gasoline Stall, June 30, 1942.
14. Report on trial of a Stall for T.T.H., Boehlen, June 21, 1941, for increasing Diesel oil production. (TTH is process for hydrogenating brown coal at low temperatures.)
15. Details of Fugal plant and gas systems (no date). Tabulation of centrifuge characteristics for tar.
16. Rough flow diagram of a plant for oil extraction of centrifuge residues (no date).
17. Estimated cost of repair of hydrogenation plant, May 5, 1945.
18. Material balances for Boehlen "Rueckgas", July - December 1941
19. Delivery and Installation of an Isomerization Plant for the Production of Isobutane From n-Butane. Friedrich Uhde A.G. to Brabag - Boehlen (9/25/43),

Capacity of the Plant and Basis of Production - The plant is laid out for a production of 1500 kg./h of isobutane from n-butane on the basis of the present experimental knowledge of the Merseburg Ammonia Works. The exchange of the plant amounts to 25%, i.e., at

each passage of the raw material through the plant 25% of the n-butane is converted into isobutane; the yield of the isomerization process amounts to 25%. The charge supplied to the plant must in respect to n-butane be free of olefins and higher hydrocarbons. The contact time is primarily influenced by this consideration; at higher content (of olefins and hydrocarbons) the conversion and output of the plant also drop. Corresponding to present experimental knowledge, the olefin content of the charge for the plant to be built should be limited to a maximum of 0.4% and the content in respect to higher hydrocarbons to a maximum of 1.0%. The charge must be free of water, although a water content of the order of magnitude of 0.02-0.03% in the butane feed does not work out unfavorably.

Corresponding to the procedure of the AT-Plant with which you are acquainted, the charge stocks for the isomerization plant will be obtained from the sump of the butane separation of the AT-distillation. According to the conditions there defined, the charge stock for the isomerization consists of the sump product from the butane-separator and is about 97% n-butane and about 3% isobutane. According to the attached Plan U 406 b-16 the ingoing n-butane was fed into the isomerization plant which was at 35°C. in a mixture of the following composition:

5720 kg./h. n-butane
180 kg./h. isobutane
<hr/> 5900 kg./h. butane mixture

In the future the isomerization plant will be referred to as the Iso-Plant.

Production - There was produced from a butane mixture of the above composition 1360 kg./h. of isobutane, a percentage yield of 95, in the Iso-Plant.

Layout of the Plant - The Iso-Plant is so laid out that it is able to put out 1,5 tons of isobutane per hour. For this performance all the apparatus and machines are standardized. The later mentioned commercial numbers apply for this purpose. As far as the operation requires, reserve outfits are provided in order to assure continuous operation of the plant. Therefore, for example, of the 5 contact furnaces to be constructed 3 are provided for operation, 1 furnace for operation reserve and 1 furnace for contact charge reserve. You will obtain the remaining details concerning the works reserves from the attached apparatus list.

Description of the Plant - According to the attached Plan U 406 b-16 and U 1493-1 already known to you, the charge (Sump product of the butane separation apparatus) was passed through a circulating pump to the evaporation apparatus of the Iso-Plant. Here the butane mixture was evaporated, brought to a temperature of about 103°C., and at this temperature mixed by means of a tuyere with the HCl containing circulation-head product of the HCl-separation column. The butane-propane-HCl mixture so obtained was cooled to about 90-95°C. in an air cooler and passed into the contact furnace. The contact furnace is a full chamber furnace the contact chamber of which is filled with

aluminum chloride. Here at a pressure of about 16 atmospheres the reaction mixture undergoes a gradual temperature rise of about 100°C. from the heat of reaction. The heat of reaction arises as a result of the partial conversion of the n-butane into isobutane on passage of the charge through the contact layer. The efficiency of the contact chamber is increased by means of a filling body, which confers a greater active surface to the slowly liquefying contact.

After the exchange the material leaving the furnace was liquefied at a temperature of about 30°C. in a condensation apparatus. The product mixture was conveyed through an intermediate reservoir by means of a circulating pump into the HCl-separation column to which suitable heat exchangers are connected. The separation column itself works at an operating pressure of about 23 atmospheres. The HCl from the product mixture was driven off overhead in the column. Besides as much of the propane arising in the furnace and of some of the butane mixtures were driven off overhead as was necessary to make the sump of the column completely free of HCl. The HCl-containing circulation-head product which - as mentioned above - was mixed with the charge stock was obtained in this fashion. In order to compensate for the loss of HCl in the cycle a supply of gaseous HCl is provided in a suitable spot. The column is equipped with a circulation evaporator for boiling out the sump. The sump product is freed of HCl at a sump temperature of about 115°C. The iso-n-butane mixture so obtained is passed over a heat exchanger in counter-stream to the sprayed in charge, and then after cooling the product is passed into a lye bath to be neutralized. The outlet pump conveys the iso-n-butane mixture purified of traces of HCl from the separation receiver of this lye bath to the store-tank of the butane-separation equipment. The butane-separation equipment of the AT-Distillation is so laid out that it separates the product mixture coming from the Iso-Plant into iso- and n-butane.

20. Detailed operating instructions for let-down of hydrogenation unit (undated).
21. Material balance on production of motor fuel from tar and light oils, Boehlen hydrogenation unit, Oct. 19, 1938.