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TECHNICAL REPORT No. 217-45

THE PRODUCTION OF SYNTHETIC FUELS BY THE HYDROGENATION OF SOLID AND LIQUID CARBONACEOUS MATERIALS

SUMMARY

This report describes the various principal methods of producing synthetic fuels by high pressure hydrogenation as practiced in Germany. The various techniques of operation, designs of equipment, and characteristics of the products are described, and whenever possible, the relative merits and best uses of the different items are discussed. No attempt has been made to make an economic survey of the industry, since the subject is greatly confused by German finance and slave labor. However, this report does analyze the important features so that there is a technical basis for evaluation of the various phases in the light of existing local conditions. The data in this report were all obtained either by interrogation or personnel, examination of documents collected from the various plants, or by visual observation.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE.

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THE PRODUCTION OF SYNTHETIC FUELS BY THE HYDROGENATION OF SOLID AND LIQUID CARBONACEOUS MATERIALS

1. Introduction.

The production of synthetic fuels by the hydrogenation of coal and tar under conditions of high temperature and pressure is a comparatively new industry even though the initial experiments were completed by Dr. Bergius before the start of World War I. For a long time, the process of converting solid fuels of low hydrogen content to liquid ones with a high hydrogen content appeared to be of mere scientific interest because of the high investment and operating costs of the necessary plant. In 1933 when Germany started in rapidly to prepare for war, it became imperative to improve the processes, and so an enormous amount of effort was expended in experimental development of better methods for coal hydrogenation. The results of this work were successful in developing techniques for treating coal and tar so that over three million tons of fuel were produced in 1942 by these methods. The cost of gasoline produced by hydrogenation was high (about 15 cents per gallon)(1) but, for a country that had practically no petroleum this was not exorbitant. In order to better understand the changes in practice, it is of interest to briefly trace the development of hydrogenation in Germany.

In 1911, Dr. Friederich Berguis started his first experiments in treating coal with hydrogen under pressure. By 1913 the work had reached the point where he took out his first patents on the subject. The research continued for a number of years, on a small scale, until 1924 when I.G. Farbenindustrie started work at Ludwigshafen on the hydrogenation of tar. Dr. Berguis continued his work until about 1930. He will probably be remembered as the "Father of Coal Hydrogenation", but it was the I.G. Farbenindustrie that developed the industrial applications.

After a brief period of research work at Ludwigshafen, I.G. started the construction of a plant at Leuna in [illegible]

1. Introduction (cont'd.)

to produce 100,000 tons per year of gasoline from lignite, and in April, 1927 the first gasoline was produced. The through-puts of coal were low and the efficiencies poor, but these were gradually improved by new design of equipment and better understanding of the process(2). In 1933 a new high activity pelleted tungsten sulfide catalyst was developed that increased the gasoline yield. The following year another catalyst tungsten sulfide on activated clay was developed, which in combination with the first one, was used throughout the war in most of the plants, and produced high quality gasoline.

Between 1935 and 1941 about ten large hydrogenation plants were created in mid-Germany, the Ruhr, and eastern Germany to hydrogenate coals and tars. Research work had shown the beneficial effect of high pressure on the decomposition of coal, and so most of the new coal plants were built to operate at 700 atmospheres pressure. The research work in this period was largely devoted to methods of increasing production by changes in operating technique and/or equipment, as well as to methods for increasing the octane number of the gasoline. With the start of the war the accent was on production, and every effort was made to obtain the maximum quantity of fuel from a given plant. Most plants hydrogenated quantities of tars in addition to coal, since the specific output of gasoline was greater from tar.

Although the hydrogenation plants were owned by several large companies, the integration of the industry was such that most of them followed the I.G. process, and exchanged information with the I.G. research center at Ludwigshafen for the material benefit of all. The result was that only minor variations in operation were found at the different plants, these having been largely caused either by differences in raw material or older design of equipment.

The following report is intended to present the chief items of interest in the German hydrogenation industry, and to describe features which have not been reported in the literature. It is not intended to be a complete record of

1. Introduction (cont'd.).

German hydrogenation technology, but only to cover the important principles of the art so that the reader can evaluate the process.

2. Sources of Information.

The data in this report were collected by personal inspection, interrogation of personnel, and examination of the documents(3,4,5) of most of the hydrogenation plants in Germany. The plants in the Ruhr area and in middle Germany were covered on two inspection trips, while some data were obtained from operating reports(6,7) on plants in eastern Germany that were in Russian occupation territory. The following is a list of the plants visited, the principal type of material processed, and the important personnel interrogated.(8)

Name of Company	Location	Raw Material Processed	Annual Productions	Principal Personnel Interrogated
1.Braunkohle Benzin AG	Bohlen-Rotha	Brown Coal Tar	180,000 tons Aviation Gas.	Dr. Wolf, Plant director, Dr. Schweitzer, Dir. of Hydrogenation
2.Gelsenberg Benzin AG	Gelsenkirchen-Horst	Bituminous Coal	300,000 tons Aviation Gas.	Dr. Prosst, Plant Dir., Dr. Jacob, Dir. of Hydrogenation
3.Hydrierwerke Scholven AG	Scholven-Buer	Bituminous Coal	200,000 tons Aviation Gas.	Dr. Schmidt, Dir. of Hydrogenation.
4.I.G. Farbenindustrie AG	Leuna	Lignite and Brown Coal Tar	600,000 tons aviation gas & Diesel Oil	Dr. Schneider, Dir.of plant, Mr. Cron, Eng. of Hydrogen.
5.I.G. Farbenindustrie AG	Ludwigshaven	Principal Research Center for Coal Hydrogenation		Dr. Simon, Dir of Exp. Hydro. Plant. Dr. Donath, Dir of Hydrog. Research
6.Wintershall AG	Lutzendorf	High Asphalt Bituminous Coal Tars and Mineral Oil Residues	5,000 tons Gasoline + 10,000 tons Diesel Oil	Plant Director; Hydrog. Director.
7.Ruhröl AG	Bottrop Welheim	Bituminous Coal Pitch	60,000 tons Aviation Gas. 120,000 tons Fuel oil	Mr. Stinnes, owner of plant; Dr. Broche Chem. director; Dr. Döring, Research director.

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Name of Company	Location	Raw Material Processed	Annual Productions	Principal Personnel Interrogated
8. Union Rheinische Braunkohle Kraftstoff AG	Wesseling	Lignite	105,000 tons Auto Gasoline, 120,000 tons Diesel oil	Dr. von Blumenoron Dir of Plant; Dr. Peuchert
9. Braunkohle Benzin AG	Zeitz-Tröglitz	Brown Coal Tar	100,000 tons Auto gas, 120,000 tons Diesel oil, 25,000 tons parffins, 15,000 tons lube oils	Dr. Ville, Plant Dir., Dr. Przybylka Chief Engineer, Dr. Lehman, Physcist

OTHER HYDROGENATION PLANTS

Name of Company	Location	Raw Material Processed	Annual Production
1. Hydrierwek Hermann Göring AG	Brüx	Brown Coal Tar	300,000 tons Auto gasoline, 300,000 tons aviation gas.
2. Braunkohle Benzin AG	Magdeburg	Brown Coal Tar	120,000 tons auto gas; 120,000 tons Diesel oil.
3. Oberschlesien Hydrierwerke AG	Blechhammer	Bituminous Coal	240,000 tons aviation gas; 260,000 tons fuel oil
4. Hydrierwerke Pölitz AG	Pölitz	Bituminous Coal and pitch	200,000 tons aviation gas; 150,000 DHD gasoline.

3. General Outline of Hydrogenation.

The hydrogenation of coal was performed in two stages since it was impossible to treat coal directly with active catalysts without subsequent loss of catalyst activity due to fouling of the surface. Therefore, in order to produce high anti-knock gasoline the coal was first liquefied and the resultant low molecular weight, clean oil was destructively hydrogenated over active catalysts to produce a gasoline of good octane number.

The first stage of the process was commonly called the sump or liquid phase (see drawing No. 1). After the coal had been dried and crushed it was mixed with heavy recycle oil from the process and ground into a paste. Usually about two parts of coal were mixed with three parts of recycle oil plus small amounts of catalyst. The resultant viscous paste was raised to the operating pressure of either 300 or 700 atmospheres in large, hydraulically-operated paste pumps. Most of the plants operated the sump phase at about 700 atmospheres since both the through-put of coal and the decomposition of asphalt were higher. The paste was next mixed with recycle hydrogen and passed through heat exchangers counter-current to the outlet products from the process. The heat exchangers supplied between 50 and 90 percent (depending upon the plant) of the heat required to bring the paste-gas mixture up to temperature. The additional heat was supplied in a tubular, gas-fired preheater.

The paste left the preheater at a temperature of about 425°C and entered the bottom of a series of three or four large, unpacked converters. These converters were large steel forgings about one meter inside diameter by 18 meters long, internally insulated to maintain a relatively cool pressure shell. The hydrogenation of coal was a highly exothermic reaction, and hence sufficient heat was liberated to raise the feed to the reaction temperature of about 470-485°C in the first few meters of travel in the first converter. The temperature was controlled by injecting cold hydrogen at three or four different points in each converter. During the passage of the paste-gas mixture through the reactors, about 95 percent of the carbon in the coal was

DRAWING No. 1

(This drawing has been inserted in an envelope attached at the end of this report)

3. General Outline of Hydrogenation (cont'd.)

converted to gaseous and liquid products, and these latter were destructively hydrogenated to lower molecular weight products. Thus the material leaving the last converter after a contact time of about one hour at approximately 475°C had a viscosity near that of water.

The oil and gas next entered a hot separator which was a large steel vessel internally insulated, where the gaseous products and the liquid plus solids were separated. In the process of separating the two phases, a large proportion of the more volatile oil constituents were stripped out and carried along in the gas stream. The hot separator, therefore, produced a crude separation of the products of the sump phase and simplified the handling of the light oil. The oil and gas vapors, after leaving the separator, were partially cooled by counter-current heat exchange with the incoming paste and gas and then given a final cooling in a water cooler. The condensed liquid was collected in a cold separator, while the gas was purified in a oil scrubber and recycled in the process. The condensed oil was expanded stepwise in either two or three stages to atmospheric pressure. The gas evolved from the first expansion was lean in higher hydrocarbons, and it was usually used for fuel. The gases from the other stages were treated to recover the C_3 and C_4 fractions which could be used as alkylate or bottled gas for vehicles. The oil was distilled and produced a light heads product with an end point of about 325°C called middle oil A. The residue oil was recycled for pasting of fresh coal.

The heavy slurry in the hot separator contained the solids left from the hydrogenation reaction. These solids were largely catalyst, ash, and unconverted coal, and amounted to about 20-25 percent weight of the slurry. This material was cooled to about 200°C and then expanded to atmospheric pressure through special valves that had hard alloy stems and seats to resist abrasion from the solids. The viscosity of the slurry was cut by the addition of about 25 percent of a light oil, such as middle oil A, and the diluted mixture fed to continuous centrifuges. These machines were conventional high gravity, automatic solid ejection-

3. General Outline of Hydrogenation (cont'd.)

type centrifuges, and they produced a clarified oil containing about 5-10 percent of finely divided solids and a residue that had a solid content of 35-40 percent. The oil was recycled for pasting purposes while the thick residue was coked in a steam distillation unit to recover about 75 percent of the oil. This latter oil was also used for pasting, while the dry residue was either discarded or mixed with coal and burned.

The middle oil A which was the chief product of the sump phase, contained too much oxygen, nitrogen and sulfur compounds to be used directly for gasoline. Hence, it was necessary to reduce these compounds and add more hydrogen in order to make satisfactory fuels. This part of the process was called the gas phase and was usually conducted in two stages when aviation gasoline was desired. The oxygen and nitrogen compounds existed in the sump phase oil mostly as phenols and nitrogen bases, respectively. As they were poisons for the active catalyst employed in the gasoline production stage, it was necessary to remove them. This was accomplished in a catalytic process called the prehydrogenation stage. This operation was conducted at 300 atmospheres and 400°C over pelleted tungsten sulfide (catalyst 5058) in a plant that was much like the sump phase. These converters, however, were equipped with trays to hold the catalyst. Between each two catalyst beds was a system of baffles which served to mix the hot oil and gas vapors with cold hydrogen introduced to control the temperature. Usually three or four converters connected in series were used in this stage and a contact time of about 1-1/3 hours was sufficient to hydrogenate the aromatics to naphthenes and to reduce the oxygen, nitrogen, and sulfur compounds to hydrocarbons with the formation of water, ammonia, and hydrogen sulfide, respectively.

The temperature was purposely held low in this stage to avoid excessive cracking, since the function of the prehydrogenation step was only to saturate the oil with hydrogen and to destroy compounds which would poison the gasoline production catalyst. The products of the 5058 stage were distilled giving a small gasoline cut which could

3. [illegible] (Cont'd)

[illegible] processed in the next [illegible] could be removed as a fraction [illegible] usually, however, most of the diesel oil was left in the middle oil B fraction boiling over 190°C and was processed in the next stage to make aviation gasoline.

The middle oil B, which consisted mostly of naphthenes and normal paraffins, was treated in the gasoline production stage over a catalyst consisting of tungsten sulfide and activated clay (catalyst 6434). The equipment for the process was similar to that used in the 5058 stage, but the temperature was a little higher, about 425°C. The oil throughput was a little greater so that the contact time averaged about one hour. The function of the 6434 catalyst was to crack open the naphthenic rings and to isomerize normal paraffins to iso-paraffins. At the same time a reduction in the average molecular weight of the oil occurred so that a huge fraction of the oil boiling over 200°C was converted into gasoline. The liquid product from the gasoline stage was distilled to give aviation gasoline that had an unleaded octane number of 70 to 75. The addition of 0.12 vol% of lead tetaethyl increased this value to between 90 and 95. The heavier oil left after the removal of the gasoline fraction was recycled together with fresh middle oil B to the 6434 stage.

As mentioned in the introduction, a considerable fraction of the German gasoline supply was produced by the hydrogenation of tar and pitch. These materials were easier to handle because they were already in a liquid state, and hence the mechanical problems attendent on the solids removal were much simplified. Furthermore, the hydrogen contents were greater in these materials than in coal, thus both the hydrogen consumption and the operating difficulties caused by coking were greatly reduced.

Tars and pitch were handled in a two step process in much the same manner as the coal. The crude tar was given an initial distillation to remove the gasoline and middle oil. The latter treated either directly over 6434 catalyst,

3. General Outline of Hydrogenation (cont'd.)

if the phenol and nitrogen contents were low or given a prehydrogenation treatment as was done with sump phase oil from coal if they were too high. The heavy distillation residue was processed in the sump phase under conditions very similar to those employed with coal, although the through-puts were a little greater. The treatment of the sump phase middle oil was usually carried out directly over 6434 catalyst, as the phenol and nitrogen contents of the oil were low. The yields and quality of the gasoline so produced were inferior to that produced where a prehydrogenation stage was used, but a considerable saving in investment was realized by the elimination of one high pressure operation.

A new process to produce lubricating oils by hydrogenation was developed in 1936 by the I.G. Farbenindustrie and first put into plant operation at Zeitz in 1939. The low temperature hydrogenation process (known as T.T.H.) treated brown coal tar over an active catalyst such as 5058 in the sump phase at 390-410°C and 300 atmospheres pressure. Very little cracking occurred, but instead a refining of the oil took place through the elimination of oxygen, nitrogen, and sulfur. Brown coal tar has a high paraffin content, and the purpose of the T.T.H. process was to preserve the paraffins, while hydrogenating the aromatics to naphthenes. Therefore, if the temperature was allowed to rise, the yields of lube oils and paraffin wax decreased, and greater quantities of diesel oil and gasoline were produced. The diesel oil manufactured by the process had a cetane number of about 50 and the lube oils had a V.I. of 60-80.

Another new process which attracted quite a lot of attention in the literature, but which actually played a very minor part in the German fuel program, was the Pott-Broche process for the extraction of bituminous coal. Only one unit had been built and the output from this unit was largely coked to make electrode carbon. In practice the bituminous coal was extracted at about 100-150 atmospheres pressure and 420°C in the liquid phase using a tetralin-cresol mixture. The product was filtered to remove solids, the solvent distilled off and recycled, and the asphalt-type residue processed in the sump phase like pitch. The opinion of the operators of this process was that it was better adapted for making special products such as coatings and insulation, than for fuels.

The various steps of the coal hydrogenation processes are discussed in greater detail in sections 4 to 9 enclusive, and in section 10 comparisons of the products and operation of the different methods are presented.

4. Description of Sump Phase Operations.

(a) Processing of Brown Coal.

The German brown coal or lignite occured in large thick beds, which averaged 200 to 300 feet in depth. On account of the thickness and proximity of these beds to the surface, strip mining methods were employed. The brown coal as mined resembled dirt in appearance, since it had a deep chocolate color. The coal preparation, which included drying, grinding, and paste mixing, are discussed in detail in U.S. Naval Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels"(9), and hence only the principal points will be described here.

The raw lignite contained on the average 50 percent moisture content before use. The brown coal when dry was very susceptible to spontaneous combustion in air, and consequently, elaborate precautions were taken to keep an inert atmosphere of carbon dioxide or nitrogen over the coal at all times during the drying, grinding, and pasting. The pulverizing of the coal was accomplished by mixing heavy recycle oil from the centrifuges with dried coal in ball or mixing mills and wet grinding until the coal had been properly comminuted and a homogeneous suspension of coal in oil, known as paste, produced. For best results the oil had a viscosity of 100-150 centistokes at 85°C., and sufficient coal was added to give a paste that had a viscosity of 1500-2000 centistokes at 85°C. Although the viscosities were measured at 85°C., the actual operating temperature of the mills was usually about 120°C, since this reduced the viscosity of the oil and permitted most of the free water in the coal to be vaporized.

The concentration of coal in the resultant paste depended upon several variables such as the type of coal and the quality of the pasting oil. The Wesseling plant, which processed Rhine lignite(10), could only handle 36 percent coal in the feed on account of the "gelation" properties, whereas Leuna which treated middle German lignite, operated with 40-42 percent coal in the paste. The average weight of the coal paste was 1.1 tons per cubic meter.

During the grinding of the coal in the oil, catalysts were added and thoroughly mixed in the paste. Iron and sulfur were the more common catalytic elements used for brown coal hydrogenation, and since most coals contained 3 to 6 percent sulfur, it was usually only necessary to add iron. This was accomplished by the addition of 4-6 percent, based on the weight of coal, of "Bayermasse" or "Roterz" (impure iron oxides produced during the purification of alumina ores.). With the Rhine coal, which was very low in sulfur (0.75 percent), it was necessary to add about 1.25 percent of elementary sulfur to the paste, but in other plants this was not necessary(10). Molybdenum and/or zinc had previously been used for catalysts, but iron and sulfur were nearly as active and had the advantage of being much cheaper.

The coal was ground so that about 40 percent was finer than 250 mesh (English measure) and essentially all of it was under 100 mesh before it left the mill. The paste was fed to the large high pressure paste presses in a recycle system which kept the feed moving throughout the entire manifold, and assured a continuous supply of hot uniform composition paste to each of the several pumps connected in parallel. The paste presses were large, double-acting, hydraulically driven piston pumps, which had capacities varying from 10 to 25 cubic meters per hour maximum, depending upon the different sizes employed at the various plants. In general, the larger capacity pumps were newer; the smaller sizes being old machines still kept in service. In order to better resist the abrasive action of the coal paste, the plungers were hardened to about 400 Brinnel, and the value seats were made of specially hardened alloy steel. The packing material was usually metallic rings of either white metal or lead-calcium alloy, and a lantern ring was located in the packing section so that between 80 and 200 liters per hour of flushing oil could be injected to keep paste out of the stuffing box. By the use of flushing oil the packings had a life of about six months under normal operating conditions.

The paste leaving the presses at either 300 or 700 atmospheres depending upon the method of operation, as will be described later, was joined with recycle gas and entered the first heat exchanger in the coal stall. All of the coal hydrogenation plants were constructed on the basis of individual coal stalls or chambers, and each chamber contained two heat exchangers, one preheated, three or four converters, and a hot separator. These pieces of apparatus were mounted in a tall concrete structure which helped to protect the operators by isolating the equipment and localizing fires that might occur from mechanical failures. The size of the various plants depended upon the number of stalls which they operated, since the output of any one stall did not vary greatly among the various plants. Large plants, such as Leuna, operated nine (9) sump phase stalls, whereas the smaller installations usually consisted of two to four units.

The heat exchangers were large forgings of chrome-nickel molybdenum steel 500 or 600 millimeters inside diameter by 18 meters long; the two sizes differed only in the number of tubes and consequent available heat transfer areas. Inside of the steel forging was a diatomite or brick lining about 65 millimeters thick which insulated the pressure wall from the hot contents. A thin stainless steel tube (0.5mm) was located inside of the insulation, and this liner contained the fluid products and resisted the corrosive attacks of high temperature hydrogen and sulfur. The tube bundle with baffles was placed inside of the liner, and connected to the heads through conical adapters. The tubes were made of galvanized N5 steel (chrome-vanadium

4. Description of Sump Phase Operations (a)(cont'd.)

alloy) and measured 23 by 14 millimeters by 16.5 meters long. The 500 millimeter heat exhanger usually held 151 of these tubes and had a heat transfer area of 145 square meters, whereas the 600 millimeter exchanger had 199 tubes and 190 square meters of surface. The closures were made by the compression of aluminum gaskets in the convential manner, by bolts on each flanged head. The assembly and construction details are shown in drawing no C-1 in Appendix C.

In operation the paste and gas entered at the bottom of the first heat exchanger at about 60 to 80°C, and flowed up around the outside of the tubes, counter-current to the outlet products inside of the tubes. The paste leaving the first exchanger had been heated up to about 200°C, and it then was further heated in a similar manner in the second unit to about 320°C. (Refer to drawing No. 2 for flows in the sump phase). The heat transfer coefficients varied greatly, as would be expected with materials that fouled and corroded the equipment, and hence the average values were difficult to determine. For equipment in good condition, the overall heat transfer coefficient varied from 200 to 250 kilocalories per hour per square meter per degree centrigrade (40-50 BTU per hour per square foot per degree Fahrenheit). After the surface had become fouled from caking or coking of solids, the values might drop to 50-100, at which time it was usually necessary to take the equipment out of service(11,29,30).

After leaving the second heat exchanger, the feed entered a gas-fired preheater where its temperature was raised to about 410-430°C. The preheater was a rectangular furnace about 7 meters long by 4 meters wide by 14 meters high, divided into sections to hold the preheater tubes. Drawing Nos. C-1 and C-2 in Appendix C shows one of the more common types of gas-fired heaters, in which hair pin tubes were located in vertial rectangular sections at one end, and the combustion chamber was at the other end. Fuel gas was burned in the combustion chamber, and the hot gases mixed with hot recycle gas and passed through the sections housing the preheater tubes counter-current to the flow of material being heated. The gas leaving the last tube

DRAWING No. 2

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4. Description of Sump Phase Operations (a)(cont'd.)

section was picked up by recycle blowers and returned to the mixing chamber. This high circulatory system, using two blowers of 50,000 cubic meters per hour each (measured at 1 atm. and 450°C) helped to prevent local overheating and increased the themal efficiency. The heating value of the fuel gas employed was about 2000 kilo calories per cubic meter, and between 3000-4000 cubic meters per hour were required.(12)

The hair pin tubes were constructed of N8 or N10 steel, which were chrome, vanadium, molybdenum, tungsten alloys of high tensile and creep strengths. The tubes themselves were 171 by 120 millimeters in diameter, and about 14 meters long. The number of tubes required varied greatly from plant to plant, the range being from 6 to 20 hairpins. In any case the principle of operation was the same, and the furnace was proportioned to accomodate the number of tubes required. On the outside of the tubes, perpendicular to the central axis, were welded a series of steel fins 300 millimeters square, four millimeters thick, and spaced 14 millimeters apart. These fins added heating surface, and thus raised the heat transfer rate which nevertheless was very low. The heat transfer coefficient averaged 6-8 kilo calories per hour per square meter per degree centigrade.

After leaving the preheater, the hot paste-gas mixture entered the first of a series of three or four converters. The older designs used three vessels, whereas the more modern practice was to use four, and hence this report will discuss the four converter coal stall. Three very common sizes of converters were used, either singly or in combination with each other; however, the only important differences, between them were the overall dimensions, since the internal construction was essentially the same. The details of the construction are shown on drawing no. C-4 in Appendix C. Two of the converters were 800 and 1000 millimeters inside diameters, respectively, by 18 meters long, while the third was 1200 millimeters by 12 meters long. The pressure bodies were forgings of N2 (chrome-molybdenum) steel, heat treated to improve the mechanical strength. The inside surface was insulated with two layers of [illegible] [illegible] [illegible]

4. Description of Sump Phase Operations (a)(cont'd.)

asbestos cement so that the thickness of the insulation was about 65 millimeters. A thin V2A (stainless) steel liner, about 0.5 millimeters thick, was placed inside the insulation and connected with the top and bottom heads through concial adapters. The stainless steel liner was used to contain the reactants, since it was resistant to sulfur and hydrogen corrosion. The closures were of the straight compression type, as in the case of the heat exchangers using aluminum gaskets, since copper would have been corroded by the sulfur and ammonia. In the top head were three or four small inlet connections for introducing cold hydrogen at different points in the converter to control the reaction. A large inlet and outlet connection were located in the center of the bottom and top heads, respectively, and the external piping was connected by means of standard lens ring type points.

The hydrogenation of coal is an extremely complicated chemical process, and since coal is not a homogeneous substance, but is composed of many high molecular weight organic compounds, it is impossible to state exactly what occured during the reaction period. An average analysis of brown coal on a dry basis was 62 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 5 percent sulfur, 18 percent oxygen, and 9 percent ash. The relatively high ratio of hydrogen to carbon, plus the high oxygen content, made the lignites reasonably easy materials to hydrogenate. On the other hand the high oxygen content caused a loss of valuable carbon which was eliminated as carbon dioxide, and also a hydrogen consumption to produce water. The brown coal apparently contained a large fraction of paraffin base substances with carboxylic acid groups, as well as condensed aromatic and naphthenic rings with oxygen, nitrogen, and sulfur included in the rings and in scattered connecting bridges. Under the action of heat and high hydrogen pressure, the large molecules were depolymerized with the loss of a large percentage of the oxygen as carbon oxides from the carboxylic acid groups, and as water from ether type linkages. Similarly part of the nitrogen and sulfur were eliminated as ammonia and hydrogen sulfide, respectively, while a fraction of the nitrogen remained in bases such as

4. Description of [illegible] (cont'd.)

aniline, and the oxygen and sulfur in phenols and thiophenols, respectively. A considerable amount of cracking and hydrogenation of the depolymerized coal oil resulted in the hydrogen content being markedly increased and the average molecular weight of the oil being lowered. During the reaction, part of the carbon in the coal was also converted into gaseous products ranging from methane to butane. Obviously, some of these reactions occurred simultaneously, while others went in series, but the principal overall effect was to convert most of the coal into a lower molecular weight oil having a hydrogen content higher than that of the original coal, and at the same time to form a considerable fraction of gaseous materials.

In the processing of brown coal a pressure of 300 atmospheres was sufficient to handle the middle German coals, such as Leuna used, but 700 atmospheres was needed to properly convert the more refractory Rhine lignites.(10) These latter coals were poor in hydrogen and rich in oxygen, and by experiment were found to require the higher pressure. The overall conversion of the carbon in the coal to gaseous and liquid products was between 95 and 99 percent, but the oil yield was low because of the high oxygen content. It took approximately 2.1 tons of lignite ton produce one ton of middle oil, so that the production per stall was not as great as when treating older coals or tars.

The hot paste and gas mixture leaving the preheater was joined by additional fresh hydrogen, heated in a separate set of "U" bends in the preheater, and then the combined feed entered the bottom of the first converter. The production of hydrogen for the process is described in detail in U. S. Navy Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels"(9). Inside the converter the flow of gas carried a quantity of solids and heavy oil up the center of the vessel to the top, where the gas and part of the liquid products left the converter, and entered the base of the second reactor. Some of the solids and heavy oil, having a higher density than the average fluid contents, sank down the sides until they either reached

4. Description of Sump Phase Operations (a)(cont'd.)

the bottom or were again trapped in the gas and carried toward the top. In this manner the contents of the converter were continuously circulated, thus providing better heat transfer and temperature control, as well as permitting the materials that needed hydrogenation most to remain the longest in the reaction zone. The first one or two converters were usually larger in diameter than the latter ones, since this permitted better circulation during the intial stages of the hydrogenation. For 300 atmosphere operation the 1200 millimeter diameter by 12 meter long converter was usually used first, while at 700 atmospheres the size was usually 1000 millimeters by 18 meters. The last converters in the series were usually 800 millimeters by 18 meters long.

The hydrogenation of coal was a highly exothermic reaction, and the feed was quickly heated up to the reaction temperature of 470-480°C within the first few meters of travel. The average through-put of paste was 1.1 to 1.3 tons per cubic meter of reaction space per hour, and for a four converter coal stall with 27 cubic meters reaction volume, this corresponded to 30-35 tons per hour. The corresponding gas flow was about 25 to 30,000 cubic meters of gas with a hydrogen content of about 80%. In order to control the temperature during the reaction due to the heat liberation of about 400 kilo calories per kilogram of coal, an additional 10-15,000 cubic meters of cold hydrogen were introduced through the connections on the top heads, into the converters at three or four levels. The turbulent cycle in the converters helped the heat transfer, and by adjusting the amount of hydrogen added, it was possible to control the temperature and prevent local overheating. The amount of gas circulated was several times that theoretically required, since only 1500 cubic meters of hydrogen were consumed in the production of one ton of middle oil.

The temperature was usually controlled by the asphalt content of the coal liquefaction products, since a high asphalt oil required a high temperature to give satisfactory conversions to lighter oils. The gas formation, particularly the methane, was greater as the temperature increased, so that it was desirable to operate it the lowest temperature consistent with a satisfactory reaction rate and conversion. Brown coals were usually low in asphalt, and hence high conversions and little trouble from this material were experienced.

One of the most troublesome problems with lignite was the formation of little solid balls of calcium carbonate which settled to the bottom of the converters and caused stoppages. These globules were called "caviar" or account of their resemblance to the real product, and means had to be supplied for their removal.(13,14) Usually the formation was most troublesome in the first converter where the coal was undergoing the initial decomposition. By means of a line tapping into the base of the first converter, a small amount of sludge, such as 100-200 liters per hour, could be withdrawn and treated in the solids removal unit. Usually only the first converter needed this simple sludge withdrawal line, but the plant at Wesseling had more difficulty with the Rhine brown coal, and more elaborate methods were needed to cope with the "caviar" problem. For more complete details on "caviar" refer to U.S. Naval Technical Mission in Europe Technical Report No. 87-45, pages 52-58.(15)

After passing through the converters in series, the gaseous and liquid products, together with a small amount of unconverted coal, ash, and catalyst, entered a large high pressure vessel called the hot separator. This apparatus performed a very important function besides merely separating the gases from the heavy oil and solids. Operating at a temperature of about 450°C, practically all of the water and a large fraction of the more volatile oil constituents were stripped from the solids containing heavy oil. This separation of a light overhead oil from the heavy oil was, of course, not as sharp as would be obtained by a distillation of the total product, but the fractionation of such a heavy oil containing solids would have presented formidable difficulties. Approximately 80 percent of the oil boiling up to 350°C was stripped from the heavy slurry by this process.

4. Description of Sump Phase Operations (a)(cont'd.)

The hot separator was a vessel of N1 (chrome-molybdenum) steel 800 millimeters inside diameter by 9 meters long. (See drawings nos. C-5 and C-6 in Appendix C. for details of construction) As in the converters and heat exchangers it was necessary to insulate the walls and use a stainless steel liner to hold the fluid contents. In the top head were inlet and outlet connections for the converter products, and gas plus oil vapors, respectively, as well as connections for a thermocouple well and liquid level regulator pipes. The lower head contained the outlet for the heavy oil plus solids. The inlet pipe was brought in and down one side of the vessel instead of being centered, since this apparantly gave better separation of the gas and liquid products. The volume of the separator up to the feed downpipe was approximately 1.5 cubic meters. In operation the liquid level was held reasonably constant by an automatically-operated liquid level controller.

There were several minor variations in design of the separator; the chief differences being in the inlet pipe and the bottom cone. One of the more common models employed a steep conical bottom connector to prevent solids from adhering to the wall of the liner, thus aiding in the removal of the solids from the separator. Cooling coils were inserted in both the top and bottom sections, and part of the fresh hydrogen for the process was given a little preheat here. By control of the quantity of cooling hydrogen, it was possible to regulate the amount of oil stripped out of the product, and hence the solids concentration and viscosity of the residual oil could be adjusted. In normal operation the solids content in the slurry was held between 20 and 25 percent.

The gas and oil vapors leaving the top of the separator passed down inside of the tubes of the second or hot heat exchanger countercurrent to the warmed paste and gas feed. With an inlet temperature of 430-450°C., the products were cooled to about 275°C, and then entered an intermediate separator to collect the condensed oil. This vessel was a forging of the same size and shape as the hot separator, but the internal apparatus was much simpler, since only clean light materials were handled. The bottom head had a rather flat conical adapter, and there were no cooling coils employed. The condensed oil volume was controlled by a liquid level regulator connected to the apparatus.

The gaseous products leaving the intermediate separator next passed to the top of the first or cold heat exchanger. Frequently, it was necessary to add water to the gas stream at this point to prevent inorganic salts, such as ammonium carbonate and sulfide from condensing and causing crusts or stoppages. About 1000 liters per hour of water were usually sufficient, but with certain coals, such as Rheine brown, it was necessary to use so much as 2100 liters.(15) The products were cooled in passing through the heat exchanger to between 175-200°C.

Further cooling was provided in trombone water coolers, which consisted, of between 4 and 6 sets of 6 tubes each operating in parallel. The pipes were 58 millimeters inside diameter by about 16 meters long, so that the total surface was 80 to 120 square meters. Frequently, part or all of the previously mentioned water was injected at the inlet to the cooler, the difference depending upon plant operation.

The products leaving the cooler at about 70°C entered another large vessel known as the cold separator. This apparatus was a cylindrical forging usually 800 millimeters inside diameter by 6 to 9 meters long. See drawing no. C-7 in Appendix C., for details of construction. The ends were partly swedged so that the size of the openings into the vessel were about one-half of the inside diameter, and removable closures were used on each end. In operation the longitudinal axis was inclined at about 5 to 10° from the horizontal in order to provide a larger gas-liquid interface, and thus reduce the entrainment of froth in the outlet gas. The lower head had two connections, the upper one for the gas and liquid inlet, and the lower one for the liquid outlet. On the inside of the vessel there were two thin tubes connecting with the inlet and outlet parts on the head, and these tubes were curved so that the inlet stream impinged on the upper surface of the separator, while the liquid outlet

4. Description of Sump Phase Operations (a)(cont'd.).

line naturally dipped down toward the bottom. On the upper head there was a gas outlet connection, and this head also carried an internal pipe to take gas out of the top of the chamber. The separator was equipped with a liquid level control to automatically regualte the fluid volume.

The non-condensable gases, still at high pressure, entered the suction ring of the recycle gas system. This suction ring connected the outlet sides of several coal stalls and helped to simplify the gas purification and recirculation system by equalizing the pressures and reducing the number of control instruments. The hydrogen content of the outlet gas had been reduced to about 60 percent, and it was necessary to partially purify it before using it again in the sump phase. An oil scrubbing system operating at the system pressure, was used to selectively remove part of the methane and higher hydrocarbons and thus maintain the purity of the recycle gas. The principal parts of the purification system consisted of absorption towers, solvent circulating pumps, and power recovery engines with necessary gas-liquid separators. The towers were steel forgings that varied in size from 1000 millimeters by 12 meters to 1300 millimeters by 15 meters long. They were usually packed with Raschig rings and adapted for gas inlet and liquid outlet connections at the base and gas outlet and solvent inlet at the top. The usual hourly through-puts were about 75 cubic meters of solvent to 50,000 cubic meters of gas for the larger size tower, although the liquid to gas ratio was adjusted to give an outlet hydrogen purity of 70-75 percent.

The solvent, containing dissolved hydrocarbons and hydrogen, was next expanded to about 50 atmospheres in expansion engines, and the power recovered was used to circulate part of the solvent within the process. The gas separated at this pressure was lean in higher hydrocarbons, and was used for cracking or fuel purposes. The liquid was then [illegible] down to atmospheric pressure, and this gas, which con[illegible] an important propane-butane fraction, was treated to [illegible] these materials as is described in Section 6. The [illegible] solvent was then recirculated to the towers.

4. Description of Sump Phase Operations (a)(cont'd.).

As previously explained, the gas outlet streams from several coal stalls were connected, and this header fed impure gas to a series of washers all operating in parallel; the number of units of course varied with the quantity of gas to be treated. The gas outlet streams from the washers were also connected into a manifold that served several booster compressors. These were single stage machines that handled between 50-80,000 cubic meters per hour at differential pressures from 50-80 atmospheres. The outlet gas from the circulating compressors was mixed with fresh paste and started another cycle through the apparatus.

The light liquid products in the intermediate separator and the cold separator were expanded stepwise in two or three stages to atmospheric pressure. When a two step system was used, the intermediate pressure was usually 50 atmospheres, and the flashed gas, being quite lean, was used for fuel. The gas from the atmospheric pressure expansion was treated to remove C_3-C_4, as described in Section VI, while the liquid was distilled to yield a heads fraction of 325° E.P. called middle oil A, and a heavier residue oil that was recycled for pasting of coal. The middle oil A was treated in the gas phase, as described in Section V, to make gasoline and diesel oil, and this middle oil constituted the primary product from the sump phase. The distillation procedures and gas treatments are both covered in more complete detail in Section VI on Products Separation.

The heavy oil and solids that were left in the bottom of the hot separator were cooled by counter-current heat exchange with part of the fresh hydrogen make-up gas and finally by water to about 200°C. The slurry was then blown down to atmospheric pressure through special valves operated by the liquid level controller. These valves had replaceable stem faces and seats of tungsten carbide, to resist the abrasions of the solids. See drawing no. C-8 in appendix C for the details of construction of the expansion valve. A large expansion chamber was used after the seat to reduce the pressure drop across the valve and increase the life of the seat. In operation the valves were opened wide for a few moments and then shut, for if they had been used to

4. Description of Sump Phase Operations (a)(cont'd.).

throttle, the seats would have been cut out in one to two hours. By operating the valves in pairs, each one working singly for about 15 minutes, the average working life was about 500-600 hours. The replacing of the seats and stems was not difficult, for a valve could be reconditioned in about 15 minutes while the twin was operating.

The gas evolved from the sludge was usually used for fuel, and the slurry after dilution with oil was centrifuged to recovery the pasting oil for the next cycle. The solids containing residue from the centrifuges was caked to recover additional pasting oil. These operations are covered more completely in Section VII, on Solids Removal and Oil Recovery.

(b) Processing of Bituminous Coals.

The bituminous coal fields in Germany were located in two principal areas, the Ruhr and Silesia; and in both of these districts the Germans had large coal hydrogenation plants for the production of motor fuels. Bituminous coals differed in composition from the previously discussed lignites, since they were much older geologically, and had lost a major portion of the oxygen as well as part of the hydrogen so that the hydrogen-carbon ratio was lower than that of lignite. The condensed ring structure of the coal gave the resultant oils higher aromatic and naphthenic contents than those from lignite. An average analysis of bituminous coal, on a dry basis was 5 percent ash, 78 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 3 percent sulfur, and 8 percent oxygen. In general the Ruhr coals were a little older than the Silesian and had a slightly lower hydrogen to carbon ratio, but this difference did not seem to affect the coal through-put greatly.

The mechanical operation of the sump phase for bituminous coal hydrogenation differed in a few respects from that employed with lignites. However, since the same types and sizes of equipment were used, and since most of the major features were similar, only the points of difference will be described in this section. There were two systems

4. Description of Sump Phase Operations (b)(cont'd.).

of operation which varied chiefly in the manner in which the feed paste was heated. The first or older method, as practised at Gelsenberg and Scholven used only one heat exchanger, but had two preheaters. Bituminous coal paste of the desired concentration could not be used in a heat exchanger, as was done with brown coal, on account of the swelling and fouling of the tubes, and hence it was necessary to heat the paste plus a small stream of gas in a gas-fired preheater section. The major portion of the hydrogen stream passed through the heat exchanger counter-current to the outlet products, as in the case of brown coal, and was then united with the hot paste. This mixture of gas and paste, was then heated in a second preheater section up to 425°C. before entering the converters.

This system was obviously less thermally efficient than the standard brown coal process, and this was aggrevated by the extremely low heat transfer coefficient of about 6 kilo calories per square meter per hour per degree Centigrade which was obtained in the gas-fired preheater. Therefore, research was conducted to try to adapt the brown coal technique to bituminous coal.(16,17,18) It was found that coal pastes of about 35 percent concentration operated satisfactorily in the heat exchangers with heat transfer coefficients similar to those obtained with brown coal paste.(17) Therefore, a new method of operation was developed in which the total coal paste was made up into two batches. A thin coal paste of 36 percent fresh coal was preheated together with about 90 percent of the recycle hydrogen in a series of three heat exchangers. A thick coal paste containing about 48 percent coal was heated with 10 percent recycle hydrogen in a gas-fired preheater, and then the two streams were combined. The composite mixture was heated to 425°C. in a preheater in exactly the same manner as was done with brown coal. The ratio of thin paste to thick was usually about 1.1 to 1.2 and the combined paste contained about 41 percent coal. This second method of operation, as practiced at Pölitz and Oberschlesien, reduced the heat requirements by nearly 50 percent, and at the same time it greatly lowered the pressure drop through the unit.

4. [illegible] (b)(cont'd.)

The asphalt contents of bituminous coals were considerably higher than those of lignites, and since these materials were very refractory toward hydrogenation, it was necessary to operate the sump phase converters at 485°C. In most of the plants the operating pressure was 700 atmospheres,(19) since the higher hydrogen pressure had a very pronounced effect on the asphalt decomposition. The catalysts used were 1.5-5 percent of "Bayermasse" or "Roterz", 1.3 percent iron sulfate, and 0.3 percent sodium sulfide, all based on the weight of coal. These materials were mixed with the coal and ground in a mill in the same manner as was done with lignite.

Each coal stall usually contained four 1000 millimeter diameter by 18 meter long converters giving a total reaction volume of 36 cubic meters. The coal paste through-puts averaged between 33 and 37 tons per hour, which gave a contact time of very nearly one hour. The gas volumes were 30,000 cubic meters per hour circulated with the paste, and 20,000 for temperature control in the converters. The hydrogen consumption per ton of middle oil produced averaged about 1600 cubic meters, while the conversion factor for middle oil from coal was 0.6 tons per ton. The conversion of bituminous coal was quite high, about 95 percent of the carbon being transformed into gaseous and liquid products.

At Scholven the hydrogenation plant operated at 300 atmospheres pressure, since a more active catalyst was used. A mixture of tin oxalate and ammonium chloride, 0.06 and 1.0 percent, respectively, based on the weight of coal was added to the paste. This catalyst gave the less favorable conversion of 90 percent of the coal at through-puts comparable to those used in other plants. There were, however, mechanical difficulties in operation, since the chloride was quite corrosive.(20) The two points where the maximum corrosion occurred were in the preheater tubes, and in the coolers where water started to condense and gave an acid solution of chloride salts. On account of the corrosion difficulties, the tin-chlorine system was not popular in Germany, and Scholven was the only plant so operated.

4. Description of Sump Phase Operations (b)(cont'd.)

Bituminous coal middle oils were richer in aromatics and naphthenic compounds than those obtained from brown coal, and the gasoline made from them had good octane ratings. The description of the further processing of these middle oils to produce fuels is described in Section V.

(c) Processing of Tars and Pitches.

The hydrogenation of coal tars and pitch played an extremely important part in the German fuel program for the war. There were at least six large plants which processed only tars and pitches from the numerous coke ovens, and in addition to these, nearly every coal hydrogenation plant used some tar mixed with the paste to increase its production. Low temperature tar from brown coal was the principle raw material, and this tar contained about 81 percent carbon, 11 percent hydrogen, 1.5 percent sulfur, 0.5 percent nitrogen, and 6.0 percent oxygen. The phenol content was about 10-15 percent.

The crude tar as received, contained about 2 percent water and 1 percent of fine dirt. These materials were separated in centrifuges, since it was necessary to remove the water to prevent crusting and overheating of the tar in the still preheater. The latter was caused by sudden vaporization of the water with subsequent stagnation and carbonizing of the tar. The dirt was removed to protect the sump phase catalyst from being fouled and its activity reduced. After removal of the dirt and water, the purified tar was distilled, giving a middle oil plus gasoline fraction boiling below 320°C, and a heavy residue. This latter material, which amounted to about 55 percent of the tar, was treated in the sump phase, to produce additional middle oil.

The catalyst most frequently employed for tar hydrogenation was iron sulfide on coke breeze such as that obtained from coke ovens or Winkler generators. About 0.5 - 1.0 percent of this powder was made into a paste of about 40 percent concentration using freshly stripped tar residue oil for a vehicle. This paste was mixed with about one hundred

4. Description of Sump Phase Operations (c)(cont'd.)

times its volume of heavy slurry from the hot separator at the entrace to the heat exchangers and pumped with the fresh tar through the unit. The catalyst concentration therefore was about 4-5 percent of the tar feed.

The operation of the sump phase with tar was nearly the same as with brown coal, the chief difference being the greatly reduced solids removal problem. (See drawing no. 3) A small bleed, corresponding to approximately the quantity of fresh catalyst paste, was withdrawn from the hot separator and centrifuged to recover the oil. A hot recycle oil pump, located in the system, recirculated slurry from the hot separator back to the inlet of the preheater and thus increase the turbulence in the converters.

In general the hydrogenation of tars and pitches could be classified into two chief types of operation. The brown coal tars which were low in asphalt (2-5 percent) required less drastic condition than did the pitches and cracking residues which were high in asphalt. For materials in the first category a reaction temperature of about 450-460°C and a pressure of 300 atmospheres were employed. The through-put of fresh tar averaged about 0.5 tons per cubic meter of reaction volume per hour, and for each ton of tar, approximately 1000 cubic meters of gas were circulated. The heat of reaction was much less, averaging about 120 kilo calories per kilogram of middle oil produced, and hence the temperature control in the converters was much easier. Since coal tar had a higher hydrogen content and lower molecular weight than coal, greater yields of oil could be obtained than with coal. About 30 percent more middle oil was produced in a given unit (that used coal tar) and the hydrogen consumption was approximity 250 cubic meters per ton of middle oil, or about 15 percent of that required for coal. In general the brown coal tars were easily handled in the sump phase, and they were a desirable raw material for gasoline production.

The hydrogenation of high asphalt tars and cracking residues was conducted at Lutzkendorf, where a pressure of 700 atmospheres and a temperature of 500°C. was required to

DRAWING No. 3

(This drawing has been inserted in an envelope attached at the end of this report)

4. Description of Sump Phase Operations (c)(cont'd.).

give satisfactory conversion. On account of the refractory nature of the material being processed, the through-put was low. It averaged about 0.35 to 0.40 tons per cubic meter per hour. A very high hydrogen partial pressure (92 percent) was maintained in the gas in order too accellerate the asphalt decomposition, but outside of the more drastic conditions required, the rest of the operation was the same as with brown coal tar.

The hydrogenation of pitch, as typified by the operation at Welheim (See drawing no. 4) was conducted at 480°C and 700 atmospheres pressure. The feed consisted of 60 percent fresh pitch with a 70°C melting point plus 40 percent heavy recycle oil from the process. The feed rate averaged 25 cubic meters per hour of liquid, and 45,000 cubic meters of gas were used per stall of four converters having a total reaction volume of 36 cubic meters. The hydrogen consumption was considerably greater than in plants processing brown coal tar, since pitch was a material relatively poor in hydrogen. On the average, 700-800 cubic meters of hydrogen were required to convert one ton of pitch to middle oil and fuel oil. The overhead oil collected in the cold separator was distilled to give a middle oil fraction for processing in the gas phase, while the residue was sold for fuel oil. This last operation was quite different from that practised in plants treating coal tars, since there the distillation residue was recycled. The high asphalt content of the pitch, and its low susceptibility to hydrogenation made further treatment of the heavy oil less attractive than in the case of tar. With a market for fuel oil, this provided a convenient way of keeping the asphalt content in the system from becoming too great. The gasoline produced from pitch had a good octane rating on account of its high aromatic content. The preparation of gasoline from pitch middle oil is described in Section V.

5. Description of Gas Phase Operation.

As previously mentioned, the purpose of the gas phase was to take the liquified coal or middle oil from the sump

DRAWING No. 4

(This drawing has been inserted in an envelope attached at the end of this report)

phase and, by a combination of hydrogenation and cracking, convert it into gasoline. At first this operation was conducted in one step over a molybdenum-magnesium-zinc catalyst (No. 3510) at temperatures around 460°C. This catalyst, however, produced too much gas and its activity was rather low, so that the through-put of oil was small. In 1933, after laboratory tests at Ludwigshaven, the I.G. plant at Leuna first tried pelleted tungsten disulfide catalyst (No. 5058) in the place of 3510.(21) This new material was about three times as active as the first catalyst, and hence it was possible to operate at a lower temperature and obtain a superior product with better yields. The tungsten sulfide was very active in hydrogenating aromatics to naphthenes as well as reducing phenols, nitrogen bases, and sulfur compounds to hydrocarbons. However, the high proportion of naphthenes and paraffins in the gasoline produced by this method gave a low octane number of about 60. By the addition of lead this could be made into motor gasoline, but not aviation grade. The diesel oil on the other hand was of fair quality, the cetane number falling between 35 and 50.

Since the German emphasis was upon aviation grade gasoline, a search was made for a catalyst that could convert naphthenes and normal paraffins into isoparaffins. In 1937, Leuna started to use a tungsten sulfide-activated clay catalyst (No. 6434) to convert the product from the 5058 stage into aviation gasoline. The unleaded gasoline produced by this material had an octane number of 70 to 75, which by the addition of tetraethyl lead, could be easily raised to aviation grade. This latter catalyst could not treat middle oil from the coal sump phase directly, since the phenols and nitrogenous bases in the oil poisoned and drastically reduced its activity. Therefore, it was necessary to pretreat the sump phase oil with 5058 catalyst to remove the oxygen and nitrogen compounds before using the 6434 catalyst. This resulted in a two stage gas phase operation which continued with only minor changes throughout the war. However, when only auto gasoline or diesel oil were required, a one step process using 5058 catalyst was employed. Obviously, many variations of these processes could be used, depending

5. Description of Gas Phase Operation (cont'd.)

upon the particular demands, but the use of 6434 to make aviation gasoline, and of 5058 to make diesel oil and motor gasoline became the basis of the German synthetic fuel program for coal hydrogenation.

(a) Prehydrogenation Stage.

The feed for the prehydrogenation was usually middle oil from the sump phase hydrogenation of brown or bituminous coals and tars. To this was added a recycle middle oil from the distillation of the product. A typical analysis of a bituminous coal middle oil was: specific gravity 0.956 at 20° C.; aniline point -12.5° C.; phenol content 17%; and distillation range 145-322° C.

The oil was pumped up to the operating pressure of 300 atmospheres in large pumps quite similar to those used for handling coal paste. The maintenance on these oil pumps was less, however, on account of the absence of solids and the consequent reduction in abrasion of the pistons and packings. Hydrogen was next added to the oil from the pressure header which contained recycle plus make-up hydrogen.(9) About 1500 cubic meters of gas containing between 70 and 80 percent hydrogen were circulated for each cubic meter of oil feed.

Referring to drawing no. 5, which shows a typical flow for the gas phase, it will be seen that the oil and gas mixture entered the bottom of the first of two heat exchangers. These pieces of equipment were built exactly like the ones used for the sump phase, and operated in the same manner with the inlet material on the outside of the tubes flowing upwards and the outlet products on the tube side flowing down. The sizes varied with the plant, but two of the most common were the 500 millimeter diameter with 151 tubes, and the 600 millimeter diameter with 199 tubes. These two exchangers were both 18 meters long and had heat transfer surfaces of approximately 145 and 190 square meters, respectively. A new design of the 600 millimeter heat exchanger had been made in which there were 241 tubes having a total surface area of 228 square meters. This later ap-

DRAWING No. 5

(This drawing has been inserted in an envelope attached at the end of this report)

paratus had probably been planned for new gas phase installations since its use was not in evidence in the plants visited.

With a feed rate of approximately 20 cubic meters of oil plus 20,000 cubic meters of gas per hour entering the cold heat exchanger at near room temperature, the heat transfer warmed the feed to about 180° C. In the second or hot exchanger the feed was further heated to about 300° C. The overall heat transfer coefficients were usually about 250-300 kilo calories per hour square meter degree centigrade (51-61 BTU per hour per square foot degree Fahrenheit), al**though at times under favorable circumstances** the values **went as high as** 400-500 metric units.

As in the sump phase, it was necessary to give the feed a little additional heating in order to warm it to the point where the heat of reaction was sufficient to carry the temperature up to the reaction zone. In the sump phase, gas-fired tubular preheaters were used exclusively. In the gas phase, gas-fired preheaters similar to those employed in the sump phase were used in some installations, while in others electrical heat was used. The former type has been described in section IV, but the latter equipment was employed only in the gas phase operation.

The preheater consisted of four to six 120 by 90 millimeter tubes of N8 steel, approximately 15 meters long, encased in a thin steel cylindrical shell. (See drawing no. C-9 in Appendix C). Instead of using heating elements, the tubes themselves were the electrical resistors, thus increasing the thermal efficiency. Steel lugs were welded on the outside of the tubes, and electrical connections **were** made to them through bus bars backed up with steel plates. The tubes were supported by ring clamps insulated from each other and from the steel shell at the top end. Rock wool insulation was packed around the tubes inside of the shell to reduce the heat losses. The transformers used to reduce the electric current operated on a primary voltage of 6000-7000 volts, and usually one was required for each pair of hair pin bends or four straight lengths. The hot side of the secondary winding of the transformer was connected to the binding post connecting the tops of the two inside lengths of tubing, while the negative or grounded side of the transformer was connected to binding posts at the top of each outside length. Thus the electrical current flowed through one complete "U" bend, heating up the tube by reason of the I^2R loss in the steel. For obvious reasons, a low potential of about 70 volts and a high ampere current were employed in this type of apparatus. In general the electrical type of heater was satisfactory when its limitations were not exceeded.

One of the big advantages of the electrical type of preheater was that the heat input could be quite accurately measured, and thus better control could be obtained. The electrical type was also somewhat less expensive to build, and where the power load was not too high, the operating costs were reasonably favorable. However, there were several rather serious disadvantages connected with the electrical preheater. If the material being heated inside the tube started to carbonize, polymerize, or cake on the walls in any way such that the heat transfer was reduced, then the wall temperature of the tube increased, since the electrical input remained constant. The higher wall temperature increased the local electrical resistance, so that the greatest amount of heat was being liberated in the section where the heat transfer was the lowest, and this still further raised the local pipe temperature. If the contents in the tube continued to cake or coat, as was usually the case when the local temperatures became excessive, then the preheater tube would become heated to such a point that it would rupture and possibly cause a serious fire. For this reason, the electrical preheater could be used only on clean materials such as distilled oils, but even then gas-fired preheaters were often used.

Another liability, although not as great as the first, was caused by the increase in electrical resistance of the steel with temperature. Thus the greatest heat density in the tube was at the outlet end, whereas the reverse situation would have been more desirable on account of carbonization. This defect was partially overcome by heating the total length in short sections, as has been previously des-

5. Description of Gas Phase Operation (a)(cont'd.)

cribed.

The oil and gas after having been heated up to approximately 350° C. in the preheater entered the first of a series of either three or four converters. The early converters were packed solid with catalyst, but the highly exothermic heat of reaction caused local overheating and made the temperature difficult to control. The next step was to introduce cold hydrogen at several points in the reaction zone by the use of internal down pipes of appropriate lengths. This method worked moderately well for the less active catalysts, but the mixing of the hydrogen and the reation products was not as good as desired. The more recent designs, therefore, supported the catalyst on several grates with a space between the top of one catalyst bed and the grate of the next one above. Cold gas was introduced to each section and mixed with the oil and hot gas vapors by means of baffles in the unpacked section, and better control of the temperature was obtained.

The new converters used for the gas phase hydrogenation (See drawing nos. C-10 and C-11 in Appendix C) were forgings of S_2 steel, 1000 millimeters internal diameter by 18 meters long, and were fitted with an internal lining of diatomite insulation 65 millimeters thick, similar to that used in the sump phase converters. A thin stainless steel liner was used inside of the insulation to contain the reaction materials and resist the corrosive attack of high temperature hydrogen and hydrogen sulfide. The catalyst was held on grates, usually seven in number, although some designs used as few as four. These grates consisted of a series of steel strips set on edge with parallel spacing of about 10 millimeters. The ends were welded to the internal circumference of a steel hoop. Fastened to the lower side of the grating were two sets of baffles with slots set 90° to each other. Under the baffles was a perforated distributing plate. The previously mentioned cold gas lines were brought in through the top head and carried down in the insulation lining to points between the catalyst grates and the baffles. One line was used for each catalyst bed except the bottom, and the cooling gas was introduced through the stainless

5. Description of Gas Phase Operation (a)(cont'd.)

steel liner into the space between the baffles and the grate. The thermocouple well was located in the center of the converter and temperature measurements were taken at the entrance and in the middle of each catalyst bed. The materials of construction of the internal parts were of stainless steel when available, but galvanized N5 steel was used when the former was unobtainable.

The early catalytic converters employed an upward flow of oil and gas, but it was found that the dust formation was too great, especially with the lighter catalysts, due to agitation of the particles by the ascending gas stream. Therefore, the newer practice employed downward flow. Between 7.2 and 7.6 cubic meters of catalyst could be changed to a converter, the difference depending upon whether seven or four beds were used. The 800 millimeter converter was constructed like the one just described, but of course the catalyst volume was less, amounting to about 5 cubic meters.

The standard prehydrogenation catalyst consisted of cylindrical pellets 10 millimeters in diameter by 10 millimeters high of tungsten disulfide. This material was prepared by dissolving tungsten trioxide in ammonium sulfide solution, and heating the resultant ammonium thiotungstate in a stream of hydrogen to give tungsten disulfide. This material was pelleted and used for the prehydrogenation stage.(21) For more complete details on the preparation of 5058 catalyst see Appendix B. During the war tungsten became quite scarce in Germany, and hence research work was conducted to find a substitute catalyst which could replace 5058.(22) One of the better new materials was prepared from activated alumina plus 25 percent of tungsten sulfide and 3 percent of nickel sulfide.(23) This composition, called 7846W250, was more active than 5058 in hydrogenating the lower boiling constituents in the oil, but less active in the reduction of phenols, and it was much weaker as a cracking catalyst. The usual practice was to use a combination of 5058 and 7846W250 in order to take advantage of the good characteristics of each.

The standard method of operation was to fill all con-

5. Description of Gas Phase Operation (a)[illegible]

verters with 5058 catalyst and use a pressure [illegible] pheres and a temperature of 390-410° C. However, [illegible] tion was obtained when the first one or two [illegible] charged with tungsten disulfide and the others with [illegible] The advantage of using the 5058 first was that it [illegible] reduced the phenol content of the oil and made the [illegible] ture easier to control, whereas if the diluted catalyst [illegible] been used first, about 90% of the phenols would have been reduced in the first converter and the exothermic heat of reaction would have been difficult to dissipate.

When the prehydrogenation stage was properly operated at a temperature not over 410° C. the gas production was quite low, and the concentration of C_3 and C_4 hydrocarbons was very high. About 10 percent of the carbon would be converted to gaseous products of which about 50 percent would be C_4, 20-30 percent C_3, and the rest C_2 and C_1. The C_4 cut contained about 40 percent isobutane which was useful for alkylation. The liquid product from the prehydrogenation stage contained about 10 percent aromatics, 40 percent naphthenes, and 50 percent paraffins. The normal catalyst life was at least one year, but under favorable conditions it might last two years.

The mechanical operation of the gas phase was very similar to that of the sump phase. The through-put of oil averaged about 0.6-0.8 kilograms per liter of catalyst per hour, and the ratio of gas added as recycle was about 1500 cubic meters of gas per cubic meter of oil. An average hourly through-put, therefore, for a gas stall having four converters of 28 cubic meters catalyst volume, would be 20 tons of oil plus 30-35,000 cubic meters of recycle gas having a hydrogen content of 80-85 percent. Approximately 20,000 cubic meters of cooling gas would be divided between the four converters for temperature control. Each of the catalyst beds had its individual cooling gas line, and by regulating the amount of gas introduced into the baffled vapor mixing chamber below each bed, it was possible to keep the temperature under control. As previously mentioned, the usual flow was from top to bottom to prevent dust formation due to attrition of the pellets. The heat of reaction

5. Description of Gas Phase Operation (a)(cont'd.)

in the prehydrogenation stage was highly exothermic on account of the large amount of hydrogen added in saturating the products. The hydrogen consumption was about 500 cubic meters per ton of middle oil, and the heat of reaction was about 100-150 kilo calories per kilogram of middle oil.

About one cubic meter of water was injected into the hydrogenated middle oil and gas vapors after leaving the last converter to prevent salt formation, and the products were then cooled by countercurrent heat exchange with the inlet material. This was followed by a final cooling with water in a set of four to six parallel trombone coolers. The condensed oil was separated in a cold catch pot, and the gas recirculated without any purification. Where the same gas compression system was used for both the prehydrogenation and gasoline production stages, a water scrubber was used to remove the ammonia from the gas, but where each gas system was separate, it was not necessary to use the scrubber. Usually the outlet and inlet gas lines from several stalls operating on the same material were connected to a manifold, and a booster compresser was used to make-up the pressure drop in the cycle.

The liquid product from this stage, after reducing the pressure, was distilled (as described in Section VI) into gasoline which had an E.P. of 165° C. and the low octane number of 60. This gasoline could be improved by the addition of tetraethyl lead to make a satisfactory motor gasoline. The more modern treatment, however, was to take the prehydrogenation gasoline and treat it in a D.H.D. plant(24) in order to dehydrogenate naphthenes to aromatics and isomerize some of the normal paraffins to isoparaffins. By this treatment the octane number of 5058 gasoline could be raised to about 80.

The fraction of the prehydrogenation product boiling higher than gasoline was called middle oil B. This material was high in naphthenes and paraffins and hence a satisfactory diesel oil could be made from it. When the latter was desired, a side stream boiling from 200 to 300° C., was withdrawn from the still and sold. This diesel fuel had a cetane number of about 35 to 50.

5. Description of the [illegible] Operation (cont'd.)

(b) Gasoline Production Stage.

In the earlier days of coal hydrogenation the internal combustion engines did not require as high quality fuels as were needed during the war. It was possible therefore, to use the gasoline made by the tungsten disulfide catalyst directly after the addition of lead. Later, however, when aviation gasoline of 87 to 100 octane was required, it was necessary to use another stage to convert the middle-oil B into aviation gasoline.

The mechanical equipment and method of operation of this second or gasoline production step were identical with those used in the prehydrogenation stage, and hence will require very little explanation. The catalyst for this process (no. 6434) consisted of 10 percent tungsten sulfide plus 90 percent activated clay made into cylindrical pellets 10 by 10 millimeters. Fullers earth was activated with a hydrogen fluoride solution and a solution of ammonium thiotungstate in ammonium polysulfide added. After evaporating to dryness the product was heated in a hydrogen atmosphere to give tungsten sulfide and clay. The mixture was then pelleted and ready for use. For more complete details of the method of preparation, see Appendix B.

The middle oil from the prehydrogenation stage was mixed with recycle middle oil from the gasoline stage and processed at about 400-420° C. and 300 atmospheres pressure. The oil throughput was about 1.2 kilograms per liter of catalyst per hour, or 30 to 35 tons per hour in a four converter stall. The gas requirements were decidedly less, since the hydrogen consumption was about 200 cubic meters per ton of feed. The total gas recycled with the feed averaged about 20,000 cubic meters, while only 6 to 7,000 cubic meters of hydrogen were required to control the temperatures in the converters.

The sulfide catalysts required a partial pressure of hydrogen sulfide in the gaseous products in order to prevent reduction of the tungsten sulfide to inactive metal. The sump phase middle oil usually contained enough sulfur con-

5. Description of Gas Phase Operation (b)(cont'd.)

pounds, which upon hydrogenation supplied sufficent hydrogen sulfide to maintain the activity of the 5058 catalyst. The feed for the gasoline stage, however, was nearly sulfur free, and it was necessary to add hydrogen sulfide to the reactor. Hydrogen sulfide could be added in any of several ways, such as mixing with the feed gas, pumping liquefied hydrogen sulfide, or by using a hydrogen-hydrogen sulfide gas mixture for cooling in the converters. The latter method was quite popular, since it reduced the corrosion in the heat exchangers and preheater. The optimum sulfur content was about 2 percent, but in practice it was usually between 0.5 and 1.0 percent, since the last 1 percent only added slightly to the activity.

This catalyst was very active in opening naphthenic rings, in reducing the molecular weight of the oil, and in converting normal paraffins to isoparaffins. Despite the cracking that occured, only a small amount of gas was formed. Approximately 8 percent of the carbon in the oil was converted to gaseous products which analyzed about 70 percent C_4, 20 percent C_3, and 10 percent C_1 and C_2. The C_4 cut furthermore contained approximately 75 percent isobutane. The C_5 fraction of the gasoline contained 80 percent iso and 20 percent normal pentane. All of these results were achieved only when the catalyst was properly operated. If the catalyst was accidentally poisoned and the temperature was raised, then the yield of methane increased, and the ratios of iso to normal paraffins dropped sharply. The normal life of 6434 catalyst was about one year, but much depended upon the type of feed. Unless the phenol, nitrogen, and high molecular weight compounds were kept to a minimum, the loss of activity was rapid. The first two types of compounds caused a temporary loss of activity, whereas the latter formed condensation products that could not be desorbed, and thus caused permanent impairment.

The liquid product was distilled to produce aviation gasoline and middle oil B for recycle. The gasoline had an E.P. of 150° C. and an octane number of 70 to 75. (Later in the war the E.P. was raised to 175° C. to increase production.) The lower octane value was obtained from brown

[illegible]tion of Gas Phase Operation (b)(cont'd.)

[illegible] from [illegible] on account of the high paraffin [illegible] whereas the condensed ring structure of bituminous coal gave a naphthenic type of gasoline with a higher rating. By the addition of 0.12 volume percent of lead tetraethyl, the octane ratings were raised to between 89 and 92.

Several variations of the gasoline production stage were used. Among the more important were the use of 5058 catalyst to make gasoline, and the treatment of brown coal tar middle oil without prehydrogenation. In the former case the temperature was usually raised to about 420-430° C., and the residue middle oil recycled so that the end product was gasoline that could be converted into aviation fuel by DHD or leaded to motor grade. Since the DHD process could produce gasoline with an antiknock rating of 78 to 80, the single high pressure step for gasoline production was being more extensively used.(24)

Since coal tars did not contain a very high percentage of phenols or nitrogenous bases, several plants treated the mixture of middle oil from the distillation of the raw tar and sump phase product directly over the 6434 catalyst, thus producing gasoline in one gas phase step. The through-put was lower and, as must be expected, the catalyst life was shortened, but a saving in investment cost was realized. The octane rating of the gas was slightly poorer, the value being 69, but this could be made into an acceptable aviation fluid by raising the octane to 89 with the addition of lead.

The Ruhröl AG had a quite different method of producing gasoline from middle oil obtained from the sump phase hydrogenation of pitch. They had developed a molybdenum-zinc-chromium-activated clay catalyst which was packed in a continuous bed in each of four converters with four interal tubes per converter to introduce cooling hydrogen at suitable points in the beds. (See drawing no. 6) The feed averaged 14 cubic meters of oil plus 30,000 cubic meters of gas per hour, with an additional 7-8,000 cubic meters of gas for temperature control in the converters. The reaction temperature was approximately [illegible] C. and the operating pres-

DRAWING No. 6

(This drawing has been inserted in an envelope attached at the end of this report)

5. Description of Gas Phase Operation (b)(cont'd.)

sure was 700 atmospheres. The equipment and method of operation, outside of the details mentioned, were quite standard. This catalyst was not nearly as active as the tungsten-containing ones, and hence the higher temperature was required to produce a suitable reaction velocity. At 500° C., however, the equilibrium was unfavorable for complete hydrogenation, so that the resulting gasoline was rich in aromatics. Thus a product was produced that had an octane rating of about 80 which could be raised to 92 by the addition of lead.

More complete details, including tables of analyses, on the various products produced in the gas phase may be found in Section X.

6. Hydrogenation Products Separation.

(a) Gaseous Products.

The principal constituents in the gases from the various phases of the hydrogenation process consisted of saturated hydrocarbons methane to butane and higher, carbon dioxide, carbon monoxide, ammonia, and hydrogen sulfide together with hydrogen and a little nitrogen. In general the gases were divided into two groups, called lean and rich depending upon the relative amounts of propane and heavier which they contained and the degree of saturation. The amounts of heavier hydrocarbons carried by the gases depended upon the temperature and pressure of the mixtures, or more simply on the ratio of the partial pressure of each constituent to the total pressure. Gases from the intermediate expansion stages (50 atm.) of the cold and intermediate separator oils and circulating gas stream scrubber liquid were usually used for fuel directly. Since they contained chiefly hydrogen and methane, there were insufficient heavier hydrocarbons to warrant the expense of treatment.

The gases from the atmospheric pressure gas-liquid separators in the light oil and solvent systems previously mentioned were combined into a rich gas fraction. When an

6. Hydrogenation Products Separation (a)(cont'd.)

intermediate expansion of liquid from 50 atmospheres to about 6 atmospheres was used ahead of the final atmospheric pressure break-down, the gas from this 6 atm. stage was also combined with the rich gas fraction. These gases contained the major portion of the propane and butanes produced during the sump and gas phase operations, and were treated to recover these materials.

The first step usually was an Alkazid treatment to remove hydrogen sulfide and carbon dioxide from the gases. The Alkazid process consisted in "scrubbing" the gases with an alkaline solution of either alanine or glycocol derivatives in a system that operated in approximately the same manner as the conventional triethanolamine process. Further details on this step may be found in the gas purification [illegible] of U. S. Naval Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels".(9)

The gases were next treated in a combination absorption distillation column at 15 atmospheres to remove the gasoline fraction which consisted of pentanes and heavier hydrocarbons. The lighter hydrocarbons and hydrogen were then given a water wash under pressure to remove ammonia before they passed to the butane column. In this unit butane and the small amount of pentane in the gas were removed from the base of the column while the lighter materials passed on to the propane column. Here the gases were separated into fuel gas and propane fractions. If desired the ethane could be separated from the fuel gas, but in most plants this was not done.

All of these hydrocarbon gas separations were performed in conventional equipment and according to standard practice, hence, there is no necessity to go into further detail concerning the technique of operation. The propane-butane fraction was either processed into high octane aviation gasoline by alkylation or polymerization or compressed, liquefied, and sold as motor fuel (Treibstoff). The output of this latter fuel usually amounted to about 40 percent of the gasoline production and hence represented

6. Hydrogenation [illegible]

a sizeable contribution to the German fuel program.

(b) Liquid Products.

The liquid products described in this section were those obtained from the cold and intermediate separators in the sump phase and the cold separator in the gas phase. The treatment of the heavy oil slurry from the hot separator is discussed in Section VII. The liquid products from the cold separator were expanded to atmospheric pressure and the gas removed for separate treatment as has been previously described. The oil and water phases were then separated by decantation. The water, containing phenols, hydrogen sulfide, carbon dioxide, and ammonia, was usually treated with either tricresyl phosphate or phenolsolvan solution to remove the phenols in the same manner as aqueous liquors from coking plants. Then the water was given an Alkazid treatment to remove the hydrogen sulfide before discharging to avoid polution of the river. Further details on the treatment of water prior to discharge from hydrogenation plants may be obtained in U. S. Naval Technical Mission in Europe Report No. 87-45.(15)

The oil phase from the sump stage cold separator was sent to the "A" distillation unit. See drawing no. 7 for a diagrammatic flow sheet of the distillation process. Here the crude oil was partially preheated by counter-current heat exchange with the vapors from the still and then the hot still residue before it was further heated in a gas-fired preheater. This unit was similar in principle to the preheaters used in the gas and sump phases of the hydrogenation process. About 10 percent of steam was injected with the oil during the preheating in order to reduce cracking of the oil and carbon deposition on the tubes. The hot feed then entered a packed distillation column where it was separated into middle oil "A" and residue fraction.

The fractionating column was about two meters in diameter by 30 meters high and packed with Raschig rings. With a reflux ratio of 2 to 1 the average through-put was 65 tons [illegible], the maximum 80 tons per hour. The end point of

DRAWING No. 7

(This drawing has been inserted in an envelope attached at the end of this report)

6. Hydrogenation Products Separation (b)(cont'd.)

The heads product was usually held at about 320°C, and the separation was such that there was an overlap of about 10°C between the end point of the middle oil and the initial of the residue. The vapors were condensed in a series of three units, the first using the crude feed as the cooling medium, and the latter two using water. The gases were sent to the rich gas separation unit and treated as previously described, while the middle oil was separated from the water. The latter contained sufficient phenols so that is was treated to recover these materials in the same manner as the aqueous phase from the hydrogenation units.

The whole distillation process was quite conventional and simple. The fractionation was not very sharp, since the principle object was to produce a light oil for the gas phase process, that was free of high molecular weight tarry materials. The condensed oil collected in the first or oil cooled condenser was usually blended with the rest of the oil, but part of it could be kept out for pasting purposes if desired. The residue was used for pasting in the sump phase.

The distillation of the gas phase cold separator product was conducted in essentially the same type of apparatus, but there were more variations depending upon the desired products. When brown coal or brown coal tar was hydrogenated the product of the 5958 prehydrogenation stage was often fractionated into a gasoline of 140-150°C E.P. which was then processed in the DHD unit to make aviation gasoline and a residue of middle oil B for treatment in the 6434 stage. Sometimes a portion of the middle oil was taken out as diesel fuel, a cut from 200°C to 300°C usually being removed for this purpose. When bituminous coal was processed, it was customary to pass the whole product of the 5058 stage to the 6434 stage unless a DHD gasoline stock was removed.

The oil product from the 6434 phase was also distilled in similar equipment to produce aviation gasoline of 150-165°C end point and middle oil which was recycled to the same hydrogenation stage. The gasoline was stabilized and the lighter materials sent to the rich gas treatment unit.

6. Hydrogenation Products Separation (b)(cont'd.)

All of these distillation stages were quite conventional in operation, and hence this phase of the coal hydrogenation process is not discussed in detail. Some of the important properties of the various motor fuels and gasolines are presented in tables in Section X of this report, but for more detailed information about aviation gasoline the reader is referred to U. S. Naval Technical Mission in Europe Report entitled "The Manufacture of Aviation Gasoline in Germany" (24) U. S. Naval Technical Mission in Europe Report entitled "German Diesel Fuels" gives more complete information on the characteristics of diesel oils produced by hydrogenation.

7. Sump Phase Solids Removal and Oil Recovery.

(a) Centrifugation of Slurry.

In the hydrogenation of the coal a small fraction was not converted during the passage through the converters, and this together with the coal ash and catalyst had to be removed from the cycle. The most common way was to centrifuge the slurry from the hot separator into a clarified recycle product plus a heavy sludge that contained most of the solids.

The hot slurry from the hot separator, after having been cooled to about 200°C and blown down to atmospheric pressure, as described in Section IV, was diluted with a lighter oil to reduce the viscosity. The solids content in the original slurry was usually about 20-22 percent, and approximately 25 percent of diluent oil was added, so that the resultant solids content was about 16 percent. The choice of thinning oil played an important part in the operation of the sump phase, since the characteristics of the pasting oil could be controlled at this point. The composition of the oil could be a blend of clarified oil from the centrifuging, the residue from the cold separator distillation after removing the middle oil, and middle oil itself. The use of the clarified centrifuge oil helped to reduce the asphalt content in the system, since on a second pass through the machine an additional quantity was removed with the solid residue. The use of some middle oil in the diluting feed helped to thin the slurry more, and at the same time it pre-

7. Sump Phase Solids Removal and Oil Recovery (a)(cont'd.)

cipitated some of the heavier asphalts so that they could be removed from the system. Combinations of these methods were used depending upon the existing conditions at the plant, but in any case it was always necessary to thin the viscous slurry prior to centrifuging.

After dilution the slurry passed to continuous centrifuges where it was separated into an oil containing 6 to 10 percent finely divided solids, and a heavy residue containing 35 to 40 percent solids. The ash content of the solids in the oil averaged about 35 percent, the balance of the solids being asphalt type constituents and fusain. The solids in the residue contained about 50 percent ash plus the major fraction of the unconverted coal. The centrifuges employed were commercial machines, many of them made by DeLaval, which operated on the automatic solid ejection principle. The inside diameter of the housing was about 480 millimeters and the vertical rotating shaft carried about 200 perforated conical disks spaced about one-half millimeter apart. The rotor turned at about 3200 r.p.m. so that a very high centrifugal force of about 10,000 times gravity was obtained. Tungsten carbide valves were employed at the residue discharge to resist the abrasion of the solids. The slurry capacity of these machines was approximately 2.5 tons per hour so that a coal hydrogenation plant had a large battery of them handling the hot separator product.

The lack of complete removal of the solids in the centrifuges was caused by the relatively viscous medium, the low density difference between some of the solids and the oil, and the extremely fine size of many of the particles. The operation of the centrifuges was a compromise between through-put and completeness of purification, since longer contact times resulted in more complete elimination of the solids. It was necessary to remove the residue as a thick slurry in these machines, since too thick a sludge caused the automatic discharge valves to become fouled. This method of centrifuging divided the feed into approximately two-thirds recycle oil and one-third residue, and the large amount of oil in the latter material constituted a heavy load on the sludge coking plant. The Germans realized the liabilities in the process, had done some research work on the problem, but had apparently not found a better solution.

In 1938 the Leuna plant of the I. G. Farbenindustrie conducted tests on the filterability of the slurries using three different types of equipment, a Wolf cell filter, a cartridge filter, and a Dorr rotary filter.(25) The cartridge type unit gave the highest filtering rate of about 130 kilograms of slurry per square meter per hour, while the cell filter averaged 100, and the Dorr machine only 50. The solids content in the pasting oil, the washing of the filter cake, and the wash oil requirements were most favorable with the cartridge filter. The results of these tests, however, were not sufficiently attractive to warrant the installation of filter equipment in the new hydrogenation plants built in 1940-1943.

(b) Coking of Centrifuge Residue.

As previously mentioned the residue from the centrifuges contained 60 to 65 percent oil, which if it had been discarded, would have been a serious loss. It was therefore necessary to further treat the sludge in order to recover the oil content for recycle in the system. This operation was carried out in coking ovens where the material was heated and the oil distilled off leaving a dry, high ash residue which could be burned by mixing with fresh coal.

The sludges from brown coal, which were low in asphalt were frequently processed in a screw type oven. See drawing no. C-12 for construction and operation of this unit. The apparatus consisted of a gas-fired furnace which contained two steel drums each about one meter in diameter by 16 meters in length, so supported, one over the other, that the upper drum discharged into the lower drum. The feed inlet to the upper drum and the coke discharge from the lower drum were at one end of the unit and the inter-connection between the two drums at the other end. Inside of each drum was a screw that turned at about one revolution

7. Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)

per minute. In the lower part of the furnace a set of steam superheater coils were located. Auxiliaries consisted of a feed pump, and a traveling rake to remove the solids as they were discharged from the lower section of the kiln. The gases and vapors evolved were freed from dust, and were then cooled. The condensed oil was recovered in a series of heat exchangers and coolers, and collected in settling tanks. The gaseous products were used for fuel.

In operation the sludge was pumped through a heat exchanger counter-current to the outlet oil, gas, and water vapors before it entered the oven. Ordinarily the warmed material entered the hollow shaft of the top screw, and passed through the length of the oven where it was discharged into the drum. It was possible, however, to inject the feed directly into the kiln, should the lines become stopped up with material. Superheated steam equivilant to 5-10 percent of the charge was injected into each tube to lower the partial pressure and reduce cracking of the oil. After the residue had been moved by the screw from the inlet end to the rear of the top drum, it dropped down into the lower drum and was carried forward until it finally was discharged into a sump where it was cooled by water. A traveling rake then carried it out and loaded it into cars for disposal.

The oil vapors, gas, and steam together with a small amount of dust left through a connection at the rear of the kilns. The dust was removed in a cyclone separater and was discharged by gravity into a water sump and was pumped or carried away for disposal. The gaseous products were next partially cooled in the heat exchanger by the feed material, and then in to a water cooler. The condensate from these two units was a heavy oil suitable for recycle as a pasting medium. A light oil as well as most of the water vapor was condensed in an after cooler using water and the noncondensable gases were used for heating purposes. The light oil, after separation from the water was sent to the distillation building and blended with the sump phase overhead product to recover an additional quantity of middle oil.

7. Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)

The operating temperature of the oven was about 550°C, and its through-put was approximately two tons of sludge per hour. About 75 percent of the oil was recovered. The major difficulty in operation was coking up of the screws especially in the lower tube. Usually the on-stream time was about 100-120 days for the top section and only 17 to to days for the bottom between cleanings. These furnaces would not handle high asphalt content feeds on account of coking of the screws. Even with relatively good feed stocks the operating time was quite short between maintenance periods.

In order to handle the sludges from bituminous coal hydrogenation plants, a combination ball mill rotating oven was employed. This apparatus consisted of a large drum about two meters in diameter by 11 meters long inclined at about 6° from the horizontal, and mounted in a gas fired furnace. See drawing no. C-13 for flow details of this type of system. The mill oven was lined with high chrome abrasive-resistant steel and held about 9-10 tons of balls. The feed and part of the steam were injected through pipes in the hollow trunnion at one end, and the remaining steam was introduced at the opposite end in a similar manner. The vapors left through the trunnion at the feed end of the oven. The solid coke was removed at the end opposite the feed and collected in a water-sealed sump. In the upper section of the furnace setting were coils for superheating steam and also for preheating the feed. The auxiliaries were essentially the same as those employed for the screw type furnace, the dust collector and the heat exchanger being combined into one unit.

The operating temperature was usually a little higher, about 560-590°C, than that used for the screw coking oven, but the oil recovery was essentially the same. About 10-15 percent of steam was added to the charge to reduce cracking and gas loss. These ovens coked up in about five days of operation, but due to the grinding action of the steel balls they were self cleaning by merely shutting off the feed and continuing the rotation for 10-12 hours.

The sludge through-put was considerably greater than

7. Sump Phase Solids Removal and Oil Recovery (cont'd.)

in the screw-type furnace, 3.2 tons as compared with 2 tons per hour. Another big difference was the much lower oil content in the residue, about 1-2 percent as compared with 20-25 percent. The higher temperature produced more gas so that the overall oil recovery was essentially the same. It was of interest, however, that the ratio of heavy oil to light oil was greater in the ball oven than in the screw type, despite the fact that the gas yield was almost double. The ratios of heavy to light oils were 4.8 and 3.4, respectively, from the two units operating on the same feed.

Table No. 8 in Appendix A contrasts the operation of these two types of furnaces.

8. Description of the T.T.H. Process.

The T.T.H. process or Tief Tempratur Hydrierung (low temperature hydrogenation) represented a markedly different approach to the hydrogenation of coal tar to obtain diesel fuel and lubricating oils. In 1935 experimental work was started on the problem of preparing lube oils from brown coal tar by means of a limited hydrogenation so as not to destroy the paraffinic nature of the tar. By 1938 the work had reached the stage for commercial application, and in 1939 the first and only plant in Germany was started at Zeitz.

The feed for the process consisted chiefly of brown coal tar from low temperature carbonization with about 10 percent of light oil added. The raw tar contained about 0.5 percent finely suspended dirt and 0.4 percent water which were largely removed by centrifuging. The clarified tar was next filtered and the dirt content reduced to a maximum of about 0.01 percent. An analysis of the tar feed showed that it contained 83.4 percent carbon, 10.5 percent hydrogen, 2.0 percent sulfur, 0.4 percent nitrogen, and 3.7 percent oxygen. The specific gravity at 50°C was about 0.95, and analytical distillation showed that 6 percent boiled up to 180°C, 33 percent up to 325°C, and 52 percent up to 350°C.

8. Description of the T.T.H. Process.(cont'd.)

The equipment in which the conversion was conducted was essentially the same as that used in the gas phase hydrogenation. The hot equipment was located in a stall which held two heat exchangers, an electric preheater and three catalytic converters. The Zeitz plant had five of these stalls operating on the T.T.H. process during the war. Since the equipment was nearly the same as that previously described, only those items which were different will be discussed.

The reaction occured in the liquid phase over an active catalyst at between 300 and 390°C. under a total pressure of 300 atmospheres. A partial pressure of hydrogen of about 85 percent was maintained at the converter inlet, but at the outlet it had dropped to about 80 percent. The through-puts were relatively low averaging 0.35 and 0.4 tons of tar per cubic meter of catalyst per hour. In a three converter system having 25 cubic meters of catalyst, the tar through-put was therefore about 9-10 tons per hour. Approximately 25,000 cubic meters of gas per hour were mixed with the tar and heated in the exchangers and preheaters, while an additional 14,000 cubic meters were required for temperature control in the converters. The hydrogen consumption was approximately 550 cubic meters per ton of tar.

A hot separator was not used in this system, even though it was a liquid phase process since there were no solids to be removed. The whole product was collected in the cold catch pot and distilled.

The converter design was a little different from that employed in the gas phase, although the general features were similar. (See drawing no. C-14 in Appendix C). A forging 1000 millimeters in diameter by 18 meters long was insulated and lined as was done with both the sump and gas phase reactors. Only one grating, similar to that used in the gas phase converter was installed in the lower section so that the catalyst bed was continuous instead of being divided into sections. The catalyst volume was increased to 8.4 cubic meters by this means. It was still necessary to introduce cooling gas to control the reaction temperature,

8. Description of the T.T.H. Process. (cont'd.)

so six down pipes located at strategic points were used. A ring with holes around the circumference was connected to the lower end of each of the cooling gas pipes and used to distribute the gas throughout the catalyst bed. As in the gas phase reactors the thermocouple well was located in the center.

A rising flow of oil and gas were employed in the converters, since the velocities were not as great as in the other hydrogenation processes and the liquid phase tended to cushion the catalyst and reduce attrition. The catalyst most frequently used, when available, was no. 5058 tungsten disulfide pellets, the same as used in prehydrogenation. The complete preparation of this material is given in Appendix B. When tungsten became scarce, the substitute catalyst No. 7846W250, sometimes referred to as 8376, was used. This latter material was a mixture of 25 percent tungsten sulfide plus 3 percent nickel sulfide on activated alumina. As mentioned in Section V under the prehydrogenation process, this catalyst was very active in reducing oxygen and nitrogen compounds as well as hydrogenating the lower boiling constituents, but it was less effective in cracking and hydrogenating higher boiling materials. The milder cracking was desirable, but the reduced hydrogenation activating was a liability, so that altogether the Germans felt that 5058 catalyst was the better material to use whenever available.

The average catalyst life depended very greatly upon the purification of the feed tar. As previously explained, the dirt content was reduced to about 0.01 percent by centrifuging and filtration, and great care had to be exercised to keep this dirt value low. This suspended solid matter would gradually foul the catalyst surface together with condensed polymerization products that could not be desorbed. Soluble ash, such as iron phenolate, also caused trouble by being reduced and deposited on the catalyst surface. The only way to avoid the latter difficulty was to choose feed tars that contained very little soluble inorganic compounds. If proper precautions were taken, a catalyst life of six months to one year was obtained. Regeneration of the catalyst in situ was not possible, but instead fresh material was charged,

8. Description of the T.T.H. Process (cont'd.)

and the active ingredients recovered at the catalyst plant.

The purpose of the process was to very carefully refine the high molecular weight paraffinic substances without cracking and destroying them, so that they could be recovered as lube oils and waxes. For this reason the low temperature was absolutely necessary, as the lube oil fraction decreased rapidly above 390°C and at 420°C it practically disappeared being converted into gasoline and diesel oil. Under actual condition approximately 80 percent of the fresh tar was converted into desired products with the following distribution: 27 percent gasoline, 43 percent diesel oil, 5 percent lube oil, 9 percent wax, 0.5 percent $C_3 + C_4$ gas, and 14 percent residue which could be processed in a sump phase tar hydrogenation plant.

The gasoline, as produced, was not useable directly, but had to be further treated in either the gas phase plant or in a DHD process. Its average composition was 5 percent aromatics, 30 percent naphthenes, and 65 percent paraffins, and consequently the octane rating was low, about 55. The diesel oil fraction boiled from 200 to 320°C and had a cetane rating of 45-50. Its composition was similar to that of the gasoline, but it was a satisfactory fuel as produced, whereas the gasoline was not. The phenol and sulfur contents averaged 1 percent and 0.1 percent, respectively.

After removing the gasoline and diesel oil cuts, the residue oil was vacuum distilled to produce lube oils. The total lube oil fraction had a VI of 60 to 80, but it was usually fractionated to produce a spindle oil and a machine oil. The relative yields were approximately two-thirds of 4° Engler spindle oil and one-third of 6 to 8° Engler machine oil.

The waxes were extracted from the residue by means of the conventional propane process. These were divided into soft and hard wax. The former constituted about one-third of the product with a melting point of 40-45°C; the latter two-thirds with a melting point of 52°C. These waxes were used for the production of fatty acids, or were cracked

8. Description of the T.T.H. Process.(cont'd.)

and the olefines polymerized to make lubricating oils.

A complete report of the operation of the T.T.H. process including actual yields for 1944 at the Zeitz plant was obtained, and further information on the process, if desired, may be obtained from this document.(27)

9. Description of Pott-Broche Process.

Although this method for treating coal was more like a solvent extraction than a hydrogenation, however, its similarity in operating conditions and its use in conjunction with coal hydrogenation plants makes this report the logical place for presentation. Briefly, the theory of the operation was to contact finely ground coal with a suitable solvent at a temperature and pressure high enough to dissolve a major portion of the coal. The untreated coal and ash were removed by filtration and the solvent recovered by distillation leaving a high molecular weight coal extract which could be fed to a coal hydrogenation plant to produce fuels.

In 1927 research work on the commercial application of solvent extraction to bituminous coals was started by Drs. Pott and Broche. The work progressed slowly, but by 1934 it had reached the point where it was deemed advisable to build a pilot plant for testing the process on a larger scale. In 1936 the Ruhröl A.G. constructed the first commercial unit with a capacity of 26,000 tons per year of bituminous coal extract. On account of difficulties and peculiarities in the process, which will be discussed later, this was the only plant built and operated in Germany for coal extraction.

The feed material was Ruhr bituminous coal which had a moisture content of 5-10 percent and an ash content of 5-7 percent. On a dry, ash-free basis the coal contained 86.7 percent carbon, 5.1 percent hydrogen, 1.2 percent sulfur, [illegible] percent nitrogen, and [illegible] percent oxygen. The volatile matter content averaged [illegible] percent, which was markedly lower than the 38 percent obtained from bituminous coals used in nearby hydrogenation plants. The coal was dried to 0.5 to 1.0 percent moisture content, and then ground in ball mills so that 95 percent was finer than 100 mesh, and about 65 percent was finer than 250 mesh. See drawing no. 8 for process flows.

The coal was next mixed at about 90°C with twice its weight of solvent in large steam-heated, agitated tanks. The solvent originally used was a mixture of 80 percent tetralin and 20 percent cresols, while the newer operation was to use a sump phase middle oil which was rich in these materials. After the coal had been thoroughly suspended in the oil, the paste was pumped to the extraction apparatus. This consisted of a preheater and an extraction section mounted in a single furnace. A gas-fired furnace similar in construction only larger, than these employed as preheaters in the coal hydrogenation plants, was used to heat 48 hairpin tubes approximately 15 meters long. The first 24 tubes were finned exactly like the hydrogenation plant preheater tubes and served to bring the materials up to reaction temperature. The last 24 tubes, which were slightly smaller, did not have fins and these served as the extraction chamber. All of the tubes were connected in series with the preheat section forming a circle around the outside of the reaction section. The rest of the construction was standard practice such as the use of hot recycle flue gas blowers and lens ring joint connections between "U" bends.

The average through-put of the unit was 16 tons per hour of which 5.3 tons was coal. The temperature at which the solution of the coal occurred rapidly was about 420-430°C and the pressure 100 to 150 atmospheres. Since this process was operated without the addition of gaseous hydrogen, the maximum temperature was lower than that employed in coal hydrogenation plants; the operating conditions being a compromise between rate of reaction and coking of the contents. After one hour contact time in the tubes, about 75 percent of the ash-free coal was dissolved in the solvent, the residue consisting of refractory

DRAWING No. 8

(This drawing has been inserted in an envelope attached at the end of this report)

bitumens and fusain.

The theory of the action of the solvent was that under the influence of heat and catalyzed by the cresols, the coal was depolymerized. The four loosely-bound hydrogen atoms in the tetralin were available to stabilize the decomposition products and prevent them from repolymerizing into higher molecular weight cokes. The tetralin, therefore, acted as a doner of hydrogen; or stated in another way, the use of tetralin provided a means of introducing hydrogen into the system without the use of gaseous materials. Naphthene and paraffin type compounds, such as decalin or decane, were entirely unsuited since the hydrogen atoms were too tightly bound to be available for hydrogenating the deploymerized coal substances.

In the original process the tetralin would be nearly all converted to naphthalene during the reaction, and consequently it was necessary to use another step to hydrogenate the naphthalene back to tetralin before it could be used again in the extraction. The newer practice took advantage of the proximity of the adjacent pitch hydrogenation plant and the fact that the sump phase middle oil contained a large percentage of partially hydrogenated aromatics as well as phenolics. Therefore, it was possible to substitute sump phase middle oil for the tetralin-cresol mixture, and thus simplify operation. The recovered solvent was then processed in the gas phase hydrogenation unit, and interestingly enough the octane rating of the gasoline was raised. The exact cause for the latter effect was not known, but it appeared to be connected with an increased aromatics content.

The slurry of coal solution and solids after leaving the reaction chamber was filtered to remove the solids. Three ceramic cartridge filters containing about 35 elements each were employed to filter the slurry at 150°C and six atmospheres differential pressure. The filter medium was a poraus stone annular ring, about 125 by 80 millimeters in diameter by 33 millimeters thick. Approximately 60 of these were mounted on tubes, and so arranged in the filter that the oil passed through the stone into the inner hollow section and was then collected in filtrate tanks. The solids were collected on the outside of the ceramic cartridge, and after about 13 tons of slurry had been filtered, the cake was discharged by carbon dioxide introduced inside of the element. The filters worked reasonably well, and about 4000 batches could be handled before the mediums became so dirty that they had to be replaced.

The ash and solid free solution was next vacuum distilled at 50 to 100 millimeters too recover the solvent. The residue, which amounted to 3.7 tons per hour, was a high molecular weight material that resembled asphalt in appearance. It had a melting point of about 200° C. and a volatile matter content of 40-42 percent. The ultimate analysis of the extract averaged 89.2 percent carbon, 5.3 percent hydrogen. 1.5 percent nitrogen, 1.1 percent sulfur, and 2.9 percent oxygen, while the ash content was reduced to about 0.05 percent. This extract was the primary product of the process, and it was further treated as well be described later.

The heads fraction from the vacuum distillation was again distilled at atmospheric pressure to give recycle solvent with an E.P. of 220°C, and a residue that was sent to the sump phase for hydrogenation. Part of the solvent recovered was sent to the gas phase hydrogenation plant, while the rest was mixed with fresh sump phase middle oil and used for pasting coal.

The filter cake containing about 65 percent oil by weight, was coked in a rotary kiln at about 400°C to recover the oil. The solid residue was either mixed with coal and burned or discarded, as it was very difficult to ignite and had a low heating value on account of its high ash content.

The original intention of the Ruhröl Company had been to use the coal extract in the sump phase process to make synthetic fuels. It was an easier material to handle than coal on account of the absence of ash and materials very difficult to hydrogenate. However, it was not as readily

9. Description of Pott-Broche Process (cont'd.)

processed as tar or pitch which were further along the path toward middle oil. Since Germany required the maximum production of gasoline from each plant, it was more expedient to process pitch than coal extract. Therefore, the extraction process was not operated to produce stocks for hydrogenation, but rather for special purposes. It was found that the extract could be coked to give a carbon that made good electrodes for use in the aluminum industry, and hence most of the production was diverted to this purpose. The Ruhröl Company felt that the future of the process lay in the production of special purpose materials rather than in the manufacture of motor fuel. They felt that the extract might be used as molding plastics, fillers in structural material, or as insulating coatings for wires and cables. In order to dissolve the extract a solution of cresol, tetralin, benzol, and pyridine was used since ordinary solvents were not suitable. This process may find greater commercial application in the future, although to date its record has not been very impressive.

10. Discussion of the Products of Hydrogenation.

As has been described in the previous sections of this report the Germans made a variety of synthetic fuels by hydrogenation of coals, tars and pitches, but each of the raw materials had its own characteristics which made it a better stock for certain products than for others. This section of the report, therefore, is an endeavor to rationalize the various hydrogenation processes and contrast the variations in the products. Although the German fuel program for the war was a complicated series of balances, yet there were several general principles which governed the production program, and this section will attempt to show how these operated.

All of the five main sources of raw material, namely brown coal, brown coal tar, bituminous coal, bituminous coal tar, and pitches plus cracking residues, could be treated to produce various yields of aviation grade gasoline. There were three main ways of preparing aviation gasoline, namely,

10. Discussion of the Products of Hydrogenation (cont'd.)

by the three step hydrogenation process for coals and tars, the two step hydrogenation process for pitch as practiced at Welheim, and the two step hydrogenation of coals and tars followed by a DHD treatment. The last mentioned operation was becoming increasingly important in Germany from 1939 until the close of the war, and for further details on this subject the reader is referred to U. S. Naval Technical Mission in Europe Report entitled "The Manufacture of Aviation Gasoline in Germany."(24)

The following table shows the principal characteristics of aviation gasoline produced by the first two methods from brown coal, brown coal tar, bituminous coal, bituminous coal tar, and pitch.

TABLE I

CHARACTERISTICS OF AVIATION GRADE GASOLINE BY HYDROGENATION

Raw Material	Brown Coal	Brown Coal Tar	Bituminous Coal Tar	Bituminous Coal	Pitch
Approximate yield, tons/ton*	0.42	0.72	0.75	0.47	0.23
Specific Gravity, 15°C	0.72	0.71	0.73	0.74	0.78
Distillation:					
Initial °C	45	48		46	
% to 70°C	25	17		15	
% to 100°C	67	64	65	58	38
% to 120°C	89	88		78	

*Includes only the coal processed in the high pressure sump phase.

TABLE I (cont'd.)

Raw Material	Brown Coal	Brown Coal Tar	Bituminous Coal Tar	Bituminous Coal	Pitch
% to 150°C	--	--		96	--
E.P.°C./1%	139/98	134/98	160	151/98	165
Vapor Pressure, atm.	0.39	0.42		0.50	0.45
Composition:					
% Paraffins	52.5	58.0	37	36.5	35
% Aromatics	8.5	10.5	8	9.0	45
% Naphthenes	38.0	30.5	55	54.0	20
% Unsaturates	1.0	1.0	--	0.5	--
Octane No. (Motor Method)	71	69	76	73	80
Octane No. (+.12% T.E.L.)	90	89	94	91	95

This table shows the relatively high paraffin content of the gasolines produced from brown coal and brown coal tar and the resultant lower octane ratings compared with those produced from bituminous coal and pitch. The yield of gasoline from bituminous coal was also greater on account of the lower oxygen and higher carbon content. Coal tar of course gave the highest conversion to gasoline, while the high asphalt content of the pitches made it more profitable to sell a major portion of the surplus product as fuel oil instead of recycling. The aviation gasoline produced, however, had a very good octane rating on account of its high aromatic and isoparaffin contents.

The German fuel program for the war required consider-

10. Discussion of the Products of Hydrogenation (cont'd.)

ably more aviation gasoline than motor fuel, and only 25-30 percent of the total gasoline production from the hydrogenation plants was motor fuel grade. Since bituminous coals were superior raw materials for aviation gasoline, those plants processing that material produced only aviation gasoline. Part of the production of the brown coal and brown coal tar plants went to motor fuels, as the high paraffin contents of the oils gave them lower octane ratings. Then, too, it was more difficult to produce a high quality material in the single gas phase treatment of brown coal tar. The following table shows the principal characteristics of motor gasolines.

TABLE 2

CHARACTERISTICS OF MOTOR FUEL BY HYDROGENATION

Raw Material	Brown Coal	Brown Coal Tar
Approximate yield, tons/ton	0.47	0.80
Specific gravity, 15°C	0.77	0.74
Distillation:		
Initial °C	35	43
% to 70°C	21	15
% to 100°C	45	38
% to 120°C	61	57
% to 150°C	81	85
E.P. °C/%	191/98	168/99
Vapor pressure, atm.		**0.63 at 40°C**
Composition:		
% Paraffins	**59.0**	**56.0**

TABLE 2 (cont'd.)

Raw Material	Brown Coal	Brown Coal Tar
% Aromatics	8.5	17.0
% Naphthenes	30.5	26.5
% Unsaturates	2.0	0.5
Octane No. (Motor Method)	60.5	about 60
Octane No. (+.12% T.E.L.)	about 75	

Some diesel oil was produced by hydrogenation of brown coal and brown coal tars, since the high paraffin contents of the oil gave it a good cetane value. Only the sump phase plus the first gas phase hydrogenation were employed, as the object was to obtain a product high in normal paraffins and naphthenes. The TTH process gave a high conversion of brown coal tar to diesel oil which had the same characteristics as that made by the two stage hydrogenation.

TABLE 3

CHARACTERISTICS OF DIESEL OIL BY HYDROGENATION OF BROWN COAL AND BROWN COAL TAR

Specific Gravity	0.84
Aniline point, °C	45
Distillation:	
Initial °C	194°C
% to 220°C	33
% to 240°C	55
% to 260°C	72
% to 280°C	84

TABLE 3 (cont'd.)

E.P.°C/%	312/99
Phenol	less 1%
Sulfur	less 0.1%
Cetane NO	45-50

The T.T.H. process using brown coal tar was the only combination of raw material and hydrogenation processes that was used to produce lube oils and waxes, as direct hydrogenation destroyed the paraffin constituents in the other coal substances processed. The Zeitz plant produced two grades of lube oils, a light 4° Engler (180 SSU) spindle oil and a heavy 6-8° Engler (215 SSU) machine oil. The yields were approximately two parts of the former to one of the latter. The waxes were also of two grades, a hard wax and a soft wax. The former, which had a melting point of 40-45°C, constituted one-third of the production, while the other two-thirds had a melting point of 52°C.

Fuel oil was produced in limited amount almost exclusively by the hydrogenation of pitch. As has been previously mentioned, the high asphalt content of the heavy residue oil from the sump phase distillation would have been difficult to hydrogenerate, if it had been recycled. Therefore, this product was sold for fuel oil. The yield of fuel oil was approximately twice that of gasoline. The Welheim plant (Ruhroel AG) was the only large unit to operate on pitch.

11. Operation and control of the Units.

(a) Introduction.

This section of the report deals with mechanical operation of the equipment. It will include a summary of operating sequence for starting up and shutting down the high pressure chambers, safety measures, an outline of control methods, and a brief discussion of instrumentation. Operations which are common to all chemical industry, such as operation of pumps and compressors will not be covered except for conditions peculiar to this particular process.

(b) Sump Phase Starting Procedure.

Before a new sump phase unit is first put into operation, all masonry and internal insulation must be dried. This ordinarily requires about two days at 120°C, during which time nitrogen is pumped through the system. Instrument checking and servicing requires about 8 hours.

The entire sequence of starting up is as follows:

(1) Purge system with nitrogen, after purging is complete, build N_2 pressure to 300 atm. and check for leaks. It is important that nitrogen be used, not only to avoid explosive mixtures within the equipment, but also to prevent fires in case there is leakage in the piping or equipment.

(2) Expand N_2 to 50 atm, using the excess for testing other equipment.

(3) Start gas circulators.

(4) Dry out preheater masonry.

(5) Check all meters and instruments.

(6) Blow down the nitrogen and fill the system with circulating gas at 300 atms.

(7) Put meters and instruments into service.

(8) Start heating the system with 12,000 m^3/hr of circulating gas, of which about 1/6 goes through the heat exchangers. The temperature at the inlet to the first converter is slowly increased at a rate of about 15 - 18°C per hour.

(9) When the temperature reaches about 300°C the slurry of oil and catalyst (30 percent of catalyst) is

11. Operation and Control of the Units (b)(cont'd.)

started to the preheater at a rate of 1000 liters/hr, rapidly increasing to 3000 liters. At the same time about 1000 liters per hour of oil are started through the heat exchangers.

(10) Start up the hot oil circulating system at 2000 liters/hour, increasing to 6000 - 7000 liters in about 30 minutes.

(11) When the separators are filled to the normal operating level, the expansion valves are used to hold this level.

(12) As the temperature rises, the use of fresh oil increases, and when it amounts to 6000 - 7000 liters/hour the catalyst slurry is turned through the heat exchangers.

(13) Turn cooling water on slowly.

(14) Control temperature out of the heat exchangers by increasing gas through-put.

(15) The rate of temperature rise is the system is slowed down as the normal operating temperature is approached.

(c) Shutting Down a Sump Phase Unit.

(1) Drop temperature at a rate of 15 - 18° per hour. Cut back on fresh feed, at the same time leaving the gas through-put and circulation unchanged.

(2) Stop catalyst addition at 425°C.

(3) Hold the cold separator temperature constant, unless the product becomes too viscous.

(4) When temperature reaches 250 - 220°C all heat can be removed from the preheater and the flue gas blower shut down. The combustion chamber is purged with nitrogen, and if the shut-down is to be of long

II. Operation and Control of the Units (c)(cont'd.).

duration the fuel lines are blanked off.

(5) All oil circulation and fresh feed is stopped at 165 - 185°C. The preheater is flushed with oil, then blown out with nitrogen. The chambers must remain hot enough to permit complete removal of the sludge.

(6) Gas circulation is containued for 10 minutes, then shut off. The liquid is blown out in sequence from the hot separator, the converters 4 to 1, and the regenerator. The gas is blown down through the expansion valve, taking care that the pressure difference across the entire unit does not exceed 15 atm.

(7) Purge the system with nitrogen for about 50 minutes until no more than 5 percent combustible is found in the outlet.

(8) Blank off all connections to the apparatus to be repaired.

(d) Starting a Gas Phase Unit with Electric Preheater.

(1) Test the electrical system with about 20 volts from the transformer, checking the resistance by comparison of voltage and amperage.

(2) Flush the system with nitrogen to 0.5 percent maximum oxygen.

(3) Build up nitrogen pressure, increasing the pressure from 1 to 20 atm in 1½ hours, and from 20 to 300 atm in 2 more hours. This slow buildup is necessary to protect the catalyst pellets from destruction caused by unbalanced pressures inside and outside the pores, and from damage by physical disturbance from excessive gas velocities. Check all piping for leaks. 30 atm. is sufficient pressure for this purpose if the unit has previously been in operation.

(4) The gas circulator cannot be operated with N_2 over 50 atm because of its greater density compared to

Operation and Control of the Units (d) (cont'd.)

H_2. Drop the pressure to 50 atmospheres slowly, then start the circulator.

(5) Blow off the nitrogen to other equipment, and fill with circulating gas. Care must be taken to prevent overheating of the catalyst as heat is released during adsorption of H_2. The pressuring velocity must not exceed that given above for nitrogen.

(6) Start the circulator when the pressure is up to normal, and circulate about 10,000 m^3/hr.

(7) Heat up the inlet to the first converter at a rate of about 10° per hour.

(8) When the temperature is 220°, open the cold hydrogen valves to the converters, and check the temperature at each inlet point to be certain that the lines are clear and the cold gas is actually entering the converter. Start the oil feed at a rate of 1 to 2 m^3 per hour per converter, checking its progress through the system with the temperature elements. Put water on the coolers.

(9) Control the temperature to the first converter by adjusting the cold hydrogen to the feed. If necessary, the current can be shut off of the preheater.

(10) Increase the oil feed by about 500 liters per hour to a value of about 7 m^3 per hour.

(11) If the temperature in the converter falls off much when the oil feed is started, cut the feed in half and increase the heat. Otherwise a sudden reaction may overheat the chamber with a high oil throughput.

(12) Hourly samples of the oil at the pump and at the separator should be taken for specific gravity determination. If the gravity increases suddenly the feed must be reduced or cut off until an explanation is found. Too heavy oil or water in the feed will permanently damage the catalyst.

11. Operation and Control of the Units (d)(cont'd.)

(13) As the converter temperature approaches the normal range, gradually increase the hydrogen and oil feeds to the unit to full volume.

(e) Shutting Down a Gas Phase Unit.

(1) Cut back the feed by 2-3m^3/hour, holding the catalyst temperature constant until all oil feed is stopped.

(2) Reduce the inlet temperature to the first converter by about 10-12°C per hour.

(3) Follow the procedure of liquid removal and gas expansion as outlined for the Sump Phase.

(f) Temperature Control in the Converter.

If the temperature rises in some part of a gas phase converter, the normal control is increase of the cold gas injection at that point. If the temperature shows signs of going out of control, and this condition is verified by the gas density recorder, as many of the following steps are taken in sequence as are necessary to bring the temperature under control:

(1) Heat is cut off of the preheater.

(2) Oil feed is shut off.

(3) Gas circulation temperature is decreased, and if this does not suffice, gas feed is cut off.

(g) Operating Safety.

Equipment or piping that has been removed from service is always carefully tested before operation is again undertaken. This testing includes hydrostatic tests of 1½ times the normal working pressure on equipment that has been repaired, leakage tests on heat exchangers, converters and piping systems. The entire system is tested with nitrogen at the working pressure of the unit before hydrogen is

11. Operation and Control of the Units (g)(cont'd.)

turned in. The flushing and purging procedure has been mentioned in the preceding pages.

The large high pressure equipment is installed in concrete cells enclosed on all sides, but with a removable door for installation or removal of equipment. The walls extend to the top of the vessels, and there is no roof. This arrangement has protected the operators and as far as is known no one has ever been hurt in the control room by an accident or explosion in the cell. However, the cells are so close to buildings on the opposite side from the control room, where the door is located, that on one occasion an explosion in the cell killed seven men in the coal paste pump building. A disadvantage of the cells enclosed on four sides is that explosions of gas in the cell are much more violent than if one side were open. On several occasions the converters have been blown or have fallen out through the door of the chamber. The open construction with only one main fire wall, as at Billingham England, appears to be much more desirable, but of course requires more space both for the cells and for the protective area in front of the cells.

An emergency blowdown system was installed in most of the plants. This arrangement was intended as a method of minimizing bomb damage, but is also useful in case of accident. The liquid is drawn off to an underground receiver from which the gas is vented to the air.

The following list of accidents in high pressure plants since 1930(38) shows only the major incidents, and is probably not complete, but it will give an idea of the causes and results of failures.

Plant	Year	Description
Leuna	1930	One chamber (cell) destroyed by failure of an S2 tube which had been installed in a hot location.

11. Operation and Control of the Units (g)(cont'd.)

Plant	Year	Description
Leuna	1935	Expansion machine cylinder failed, killing one man, shutting down the plant completely for two weeks and partially for three months
Scholven	1937	Dust explosion in the coal drying plant.
Nordstern	1940	Preheater fire, due to splitting of an N10 return bend.
Nordstern	1940	Preheater explosion due to plug on a return fitting blowing out.
Nordstern	1940	Fire in a sump phase chamber due to destruction of an emergency blowdown line following failure of a checkvalve and a blow down valve.
Nordstern	1940	Building explosion in the CO_2 absorption plant caused by operating failure of a level indicator on the absorber and breakage of a line to the expansion machine--Due to thawing out the equipment during extremely cold weather--One death.
Nordstern	1940	Leakage in the circulating system caused by foundation sinking.
Pölitz	1940	Gas was accidentally turned into a cell under repair. Explosion followed, killing three.
Pölitz	1941	Circulating gas line plugged with hydrate, causing overheating of the converter. Two converters were blown out of the chamber by the explosion.

11. Operation and Control of the Units (g)(cont'd.)

Plant	Year	Description
Pölitz	1942	Gas inlet line plugged off, overheating converters. The resulting explosion blew two converters out of the cell, and a flame 30 meters long followed. Seven men in the upper part of the coal paste pump house opposite the cell were killed.

It will be noted that most of the accidents occurred when the various plants were new, and could possible be traced to inexperienced operators.

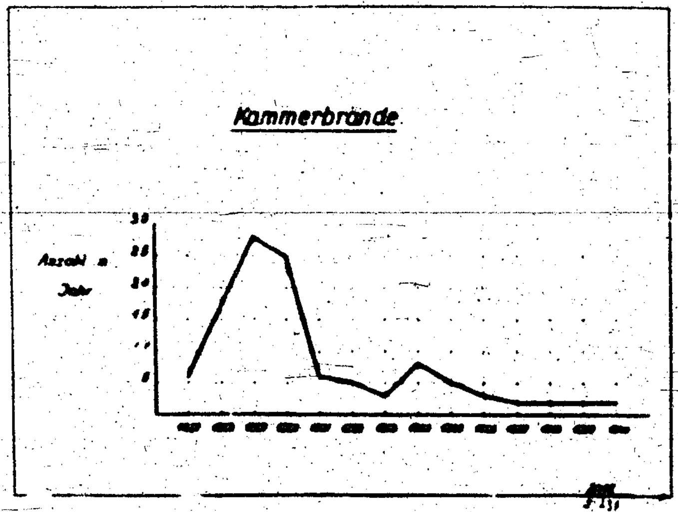
Chart No. 1 on the following page shows the frequency of cell fires in Leuna from 1927 to 1940. An examination of this chart will show that the curve increases with the increasing size of the plant until 1929, when operating experience and development of improved alloys and better design brought a sharp decrease. The increase in 1934 is probably again due to plant expansion. The fires in the last several years amount to only about two a year for all units.

In conclusion it should be emphasized that widely spaced units with cells open on one side would prevent the majority of series accidents. Cell and preheater fires, while spectacular, rarely cause serious damage to equipment or injury to personnel in the Billingham plant of I.C.I. which uses this principle.

(h) Control and Control Instruments.

Free use was made of indicating and recording instruments in the coal hydrogenation plants, particularly of temperature instruments. Automatic control was much less extensive, and only in the last four or five years has it been used to any large extent. The automatic control instruments were all specially built and were usually of somewhat crude design when compared to industrial instruments of the United States. A brief description of the use and operating principle of the various instruments is given below.

CHART No. 1



Frequency of Cell fires in Leuna from 1927 to 1940.

11. Operation and Control of the Units (h)(cont'd.)

The "Ringwaage" (Fig. 1) was almost universally used for fluid flow indication or recording.(40) The primary element is an orifice plate or flow nozzle installed in the line in the usual way. The "Ringwaage" merely shows the differential pressure across the orifice, which is proportional to the square of the flow for any given installation. The Leeds and Northrup "Centrimax" and possibly other American makes operate in a similar manner. The instrument was used to record all gas and clean oil flows necessary for material balances or for control, such as fresh hydrogen, circulating gas, cold gas to each point, and the various product gases and liquids.

The coal paste charge quantity was determined by measurement of the stroke velocity of the pump. The instrument (Fig. 2) records an average velocity every three minutes. The "Eckhardt" piston displacement meter was used for some liquid measurements, and utilized a similar mechanism for recording the flow.

Coal feed to the paste mixer and catalyst feed to the slurry were weighed on "Dosierbandwaagen" (Fig. 3) which was a rather conventional automatic scale.

Pressure indication is by gauges with heavy steel spiral bourdon tubes, or by dead weight piston gauges. The piston gauges can be spring loaded or pendulum weight loaded. Accuracy of a fraction of an atm at 700 atm pressure was claimed for some of these instruments.

A differential pressure recorder (Fig. 4) was used to determine pressure drop across various parts of the system during operation. These were sometimes installed with remote oil-controlled valves so that they could be easily switched from one service to another. The photograph shows a piston instrument shomewhat similar to the pressure instrument described above. Another type which was sometimes used operated with two steel coil bourdon tubes controlling air pressure through a moveable nozzle. The air pressure was proportional to the pressure difference and was recorded. A gas density instrument (Fig. 5) operating on the Bunsen law principle recorded two gas densities on

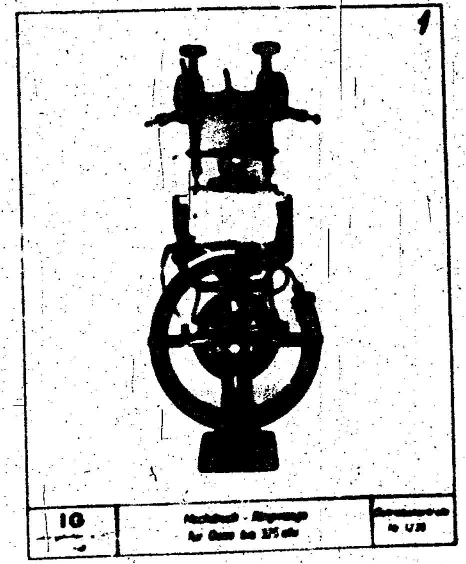


Fig. 1

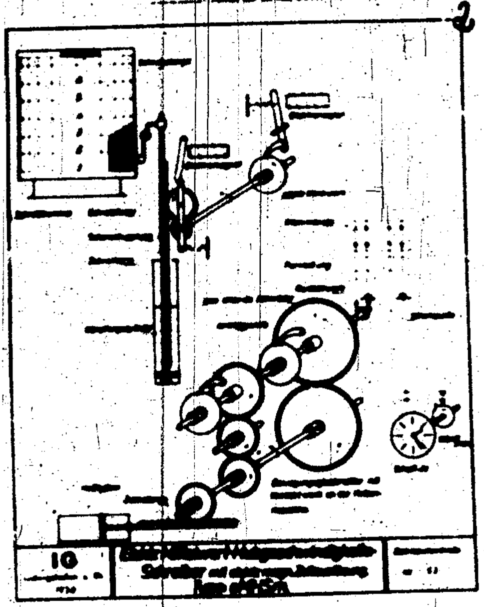
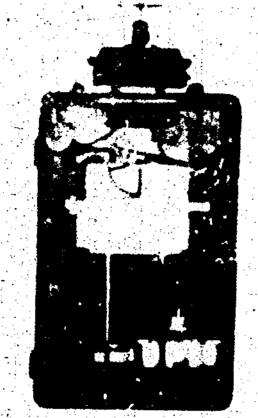


Fig. 2



Kolben-Differenzdruck-Schreiber

JG | Anordnung von JG Dosierbandwaagen

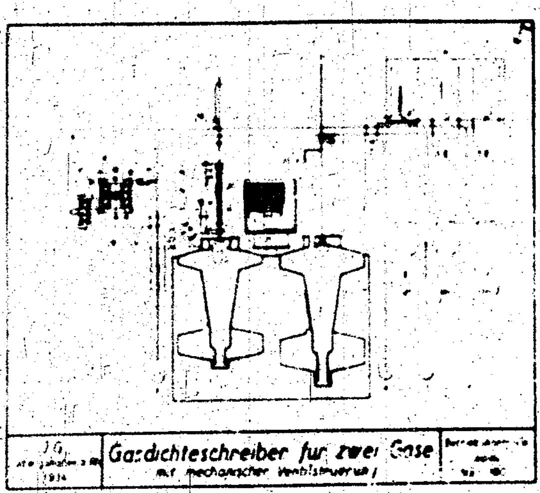
the same chart. It was usually applied to the inlet and outlet gas from the reaction chamber, thus giving the operator a picture of the condition of the process. A similar instrument was usually installed on all important metered gas flows where change in density might occur. These data are necessary for accurate measurements.

A combustion apparatus (Fig. 6) could be used for various purposes, such as determination of oxygen in the gas or combustible gas in the air. It contained a catalyst which caused oxidation and the amount of combustion is indicated by the recorded temperature of the outlet gas from the reaction.

A newer type of magnetic oxygen recorder (Fig. 7) has been developed which will indicate 0.01 percent oxygen in the gases. It makes use of the great magnetic susceptibility of oxygen by passing the gas mixture between the poles of a powerful electromagnet, then over a resistance differential thermometer which shows a temperature effect if oxygen is present. The only gas which has a magnetic susceptibility comparable to oxygen is NO, therefore this gas must be absent or the quantity must be accurately known. Further development envisions a permanent magnet instead of the 100 watt D.C. electromagnet.

An H_2S recorder (Fig 8) is operated on the conductivity change of a cell containing a solution of bromine or cadmium chloride. The scale could be made for any concentration of H_2S down to 10^{-5} or 10^{-6} volume percent. The reactions involved are shown on the figure. The second reactant ($CdCl_2$) is usable in the presence of unsaturated hydrocarbons, as the first (Br) is disturbed by the presence of HCN, NO, NH_3 or unsaturates. This instrument was used mostly in the gas separation units.

Ultra red absorption instruments(41) (Fig 9, 10) used to analyze for methane, CO, etc, operated on the small temperature difference between the methane-containing gas and pure methane when they were exposed to ultra red rays from the same source. This instrument is known in the U.S., and according to the I.G. staff the American type is [illegible]


I.G.
1934
Gasdichteschreiber für zwei Gase
mit mechanischer Ventilsteuerung

[illegible]

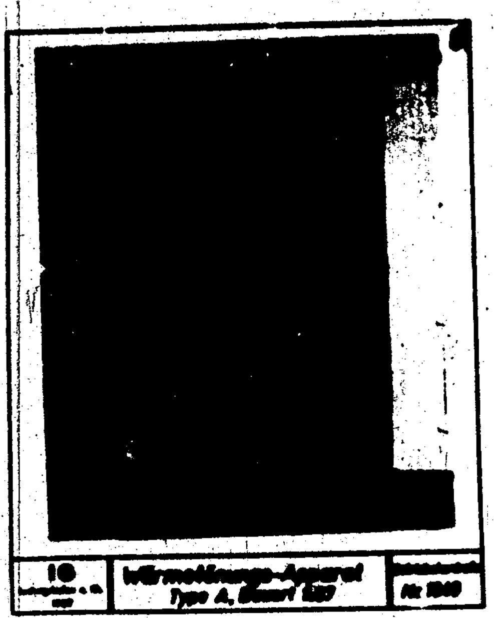

IG
Wärmetönungs-Apparat
Type A, Bauart [illegible]
Nr [illegible]

Fig. 6

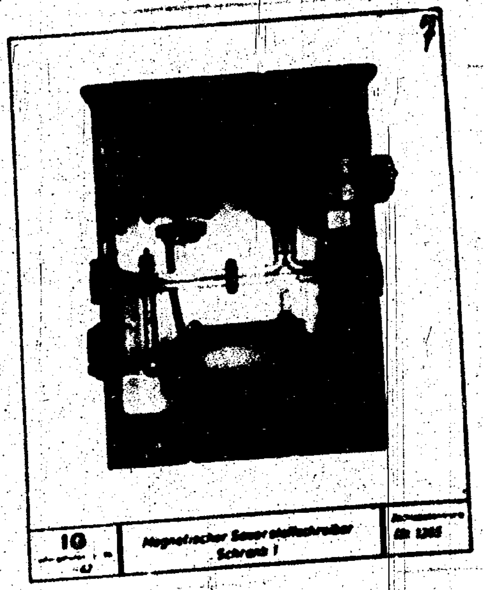

IG
Magnetischer Sauerstoffschreiber
Schrank I

Fig. 7

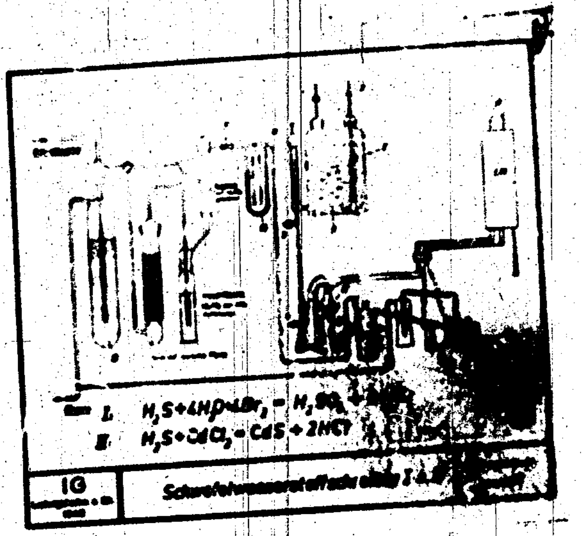

I. $H_2S + 4H_2O + 4Br_2 = H_2SO_4$ …
II. $H_2S + CdCl_2 = CdS + 2HCl$
IG
Schwefelwasserstoffschreiber

Fig. 8

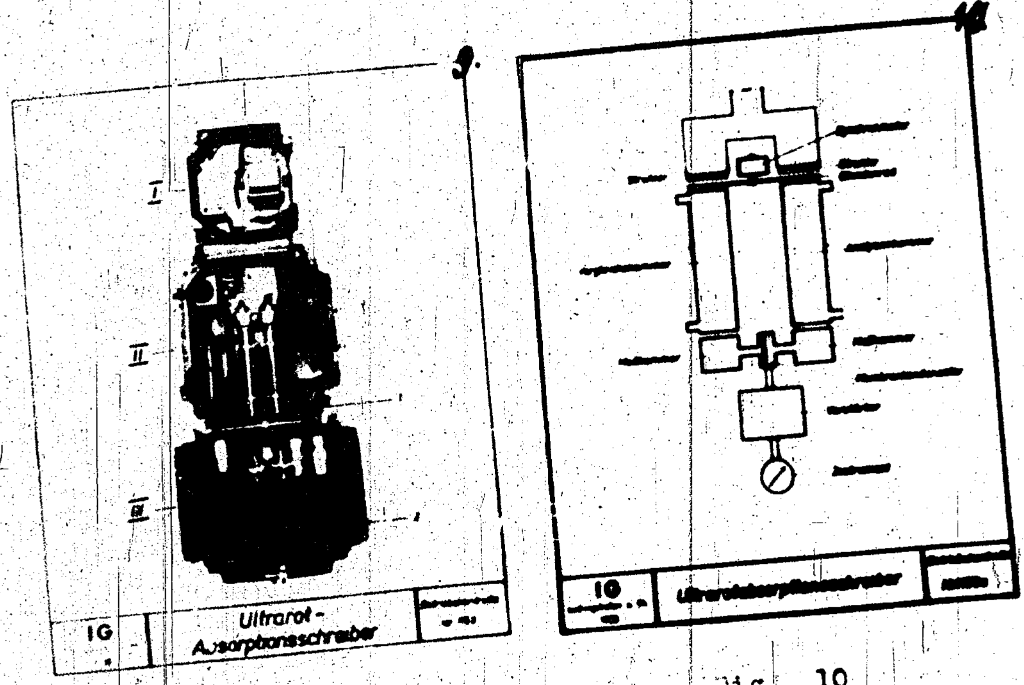


Fig. 10

better than their own.

The most important class of instruments was probably that for indicating, recording or controlling temperature, and very free use was made of this type in the hydrogenation plant. The extent of this use can best be demonstrated by the following photostats of drawings 1675 and 1677 which show the pressure and temperature points of the chamber and the preheater, respectively, of Sump Phase Chamber 5 of the I. G. Leuna Plant.(42) In the coal chamber the elements were iron constantin thermocouples, and because the temperatures are often given in millivolts for this couple in the literature and documents, a conversion chart is shown here. The type of each preheater element depends on the temperature at the point of installation. The report entitled "Fortschritte auf dem Gebiete der Messung, Regelung und selbsttätigen Betriebüberwachung von Hochdruckanlagen" in the appendix describes briefly some of the German methods and experiments for increasing accuracy and speed of thermometric instruments. They claim an accuracy of ± 1 or 2°C in their measurements at 400° to 500°C, using photoelectric cell compensators.

The Pölitz and Gelsenberg plants use a temperature alarm instrument that covers 60 points in less than two minutes, but the older plants rely primarily on indicating instruments which are switched from one point to the other, with only a few points of major importance recorded automatically.

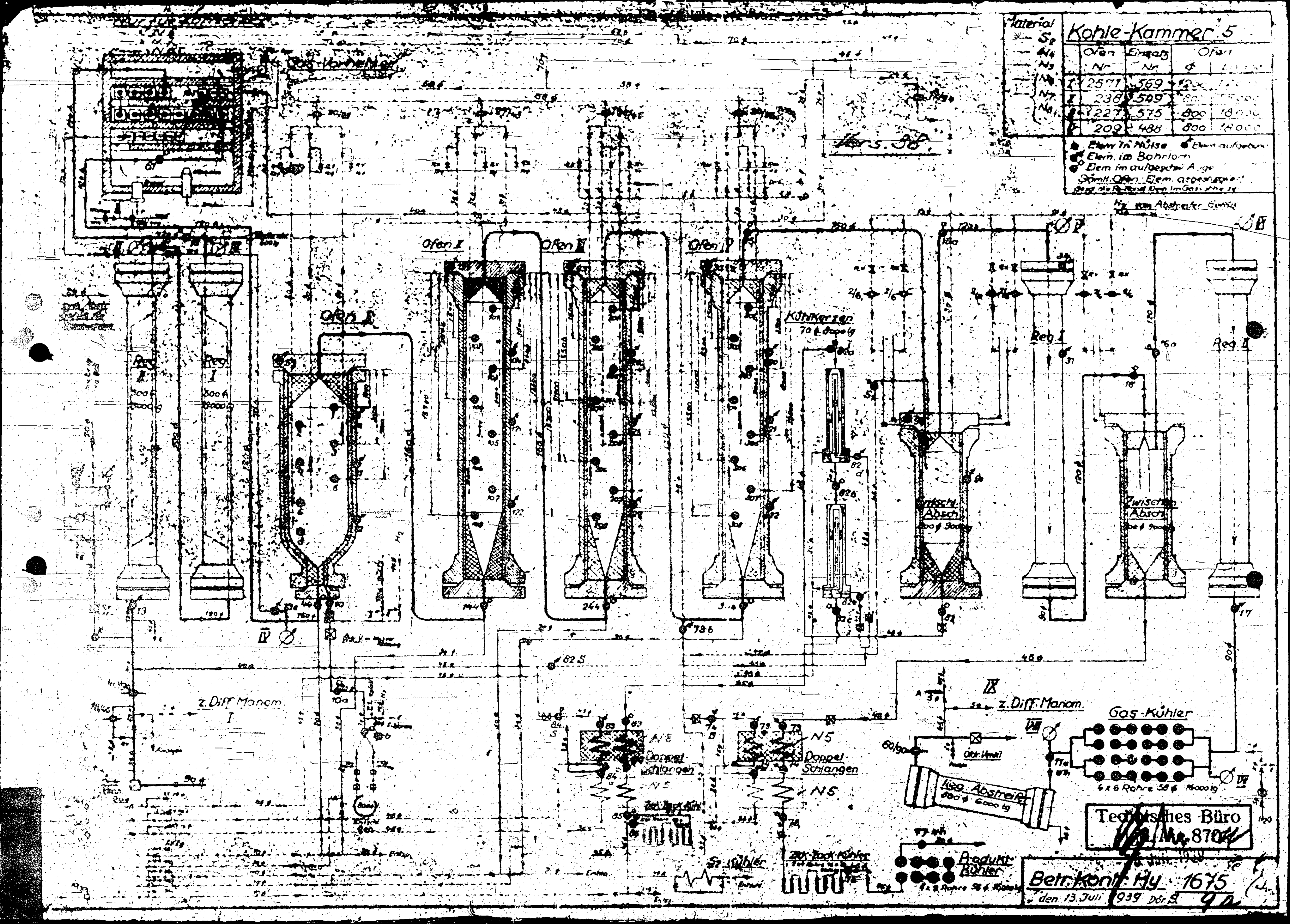
Liquid level instruments(43) are of two types, both of which are used in the U. S. One uses the differential pressure, recorded on a "Ringwaage", due to the hydrostatic pressure when very small flows of gas are bled into two tubes, one of which opens above the liquid surface and the other of which extends to a point near the bottom. This instrument was used for the hot separator of the sump phase, and for other services where heavy or dirty products were handled.

The second is the well-known displacement type where the buoyant effect of the rising level decreases the apparent

Tabelle für Eisen-Konstantan-Thermoelemente bezogen auf 40° C Klemmentemperat

C°	Millivolt	C°	Millivolt	C°	Millivolt	C°	Millivolt	C°	Millivolt
— 195,8	— 9,78	58	0,94	120	4,37	182	7,86	244	11,49
— 78,5	— 5,77	60	1,04	122	4,48	184	7,98	246	11,61
0	— 2,07	62	1,15	124	4,60	186	8,10	248	[illegible]
2	— 1,97	64	1,25	126	4,71	188	8,21	250	[illegible]
4	— 1,87	66	1,36	128	4,82	190	8,33	252	[illegible]
6	— 1,77	68	1,47	130	4,93	192	8,45	254	12,08
8	— 1,66	70	1,58	132	5,05	194	8,57	256	12,20
10	— 1,56	72	1,69	134	5,16	196	8,68	258	12,31
12	— 1,46	74	1,80	136	5,27	198	8,80	260	12,43
14	— 1,36	76	1,91	138	5,38	200	8,92	262	12,55
16	— 1,25	78	2,02	140	5,50	202	9,03	264	12,67
18	— 1,15	80	2,13	142	5,61	204	9,15	266	12,78
20	— 1,05	82	2,25	144	5,72	206	9,27	268	12,90
22	— 0,95	84	2,36	146	5,83	208	9,38	270	13,01
24	— 0,84	86	2,47	148	5,95	210	9,50	272	13,12
26	— 0,74	88	2,58	150	6,06	212	9,62	274	13,24
28	— 0,63	90	2,69	152	6,17	214	9,73	276	13,35
30	— 0,53	92	2,80	154	6,28	216	9,85	278	13,47
32	— 0,42	94	2,91	156	6,40	218	9,97	280	13,58
34	— 0,32	96	3,03	158	6,51	220	10,09	282	13,70
36	— 0,21	98	3,14	160	6,62	222	10,21	284	13,82
38	— 0,11	100	3,25	162	6,73	224	10,32	286	13,93
40	0,00	102	3,36	164	6,84	226	10,44	288	14,05
42	+ 0,10	104	3,47	166	6,96	228	10,56	290	14,16
44	0,20	106	3,59	168	7,07	230	10,67	292	14,28
46	0,31	108	3,70	170	7,18	232	10,79	294	14,39
48	0,41	110	3,81	172	7,29	234	10,91	296	14,51
50	0,52	112	3,92	174	7,40	236	11,02	298	14,62
52	0,62	114	4,04	176	7,52	238	11,14	300	14,74
54	0,73	116	4,15	178	7,63	240	11,26	302	[illegible]
56	0,83	118	4,26	180	7,75	242	11,38	304	[illegible]

C°	Millivolt	C°	Millivolt	C°	Millivolt	C°	Millivolt	C°	Millivolt
306	15,08	368	18,67	430	22,29	492	25,94	554	29,64
308	15,20	370	18,78	432	22,40	494	26,06	556	29,76
310	15,31	372	18,90	434	22,52	496	26,18	558	29,88
312	15,43	374	19,02	436	22,64	498	26,30	560	30,00
314	15,54	376	19,13	438	22,75	500	26,42	562	30,12
316	15,66	378	19,25	440	22,87	502	26,54	564	30,24
318	15,77	380	19,37	442	22,99	504	26,65	566	30,36
320	15,89	382	19,48	444	23,10	506	26,77	568	30,48
322	16,00	384	19,60	446	23,22	508	26,89	570	30,60
324	16,12	386	19,72	448	23,34	510	27,01	572	30,73
326	16,23	388	19,83	450	23,46	512	27,13	574	30,86
328	16,34	390	19,95	452	23,57	514	27,25	576	30,99
330	16,46	392	20,07	454	23,69	516	27,37	578	31,11
332	16,57	394	20,18	456	24,81	518	27,48	580	31,24
334	16,69	396	20,30	458	23,93	520	27,60	582	31,36
336	16,81	398	20,42	460	24,05	522	27,72	584	31,49
338	16,92	400	20,53	462	24,17	524	27,84	586	31,61
340	17,04	402	20,65	464	24,28	526	27,96	588	31,74
342	17,15	404	20,77	466	24,40	528	28,08	590	31,86
344	17,27	406	20,88	468	24,52	530	28,20	592	31,99
346	17,39	408	21,00	470	24,64	532	28,32	594	32,11
348	17,50	410	21,12	472	24,76	534	28,44	596	32,24
350	17,62	412	21,24	474	24,88	536	28,56	598	32,36
352	17,74	414	21,35	476	25,00	538	28,68	600	32,49
354	17,85	416	21,47	478	25,11	540	28,80	602	32,61
356	17,97	418	21,59	480	25,23	542	28,92	604	32,74
358	18,08	420	21,70	482	25,35	544	29,04	606	32,87
360	18,20	422	21,82	484	25,47	546	29,16	608	32,99
362	18,32	424	21,94	486	25,59	548	29,28	610	33,12
364	18,43	426	22,05	488	25,70	550	29,40		
366	18,55	428	22,17	490	25,82	552	29,52		



Material
Sa
N4
N9
N6
N7
N8

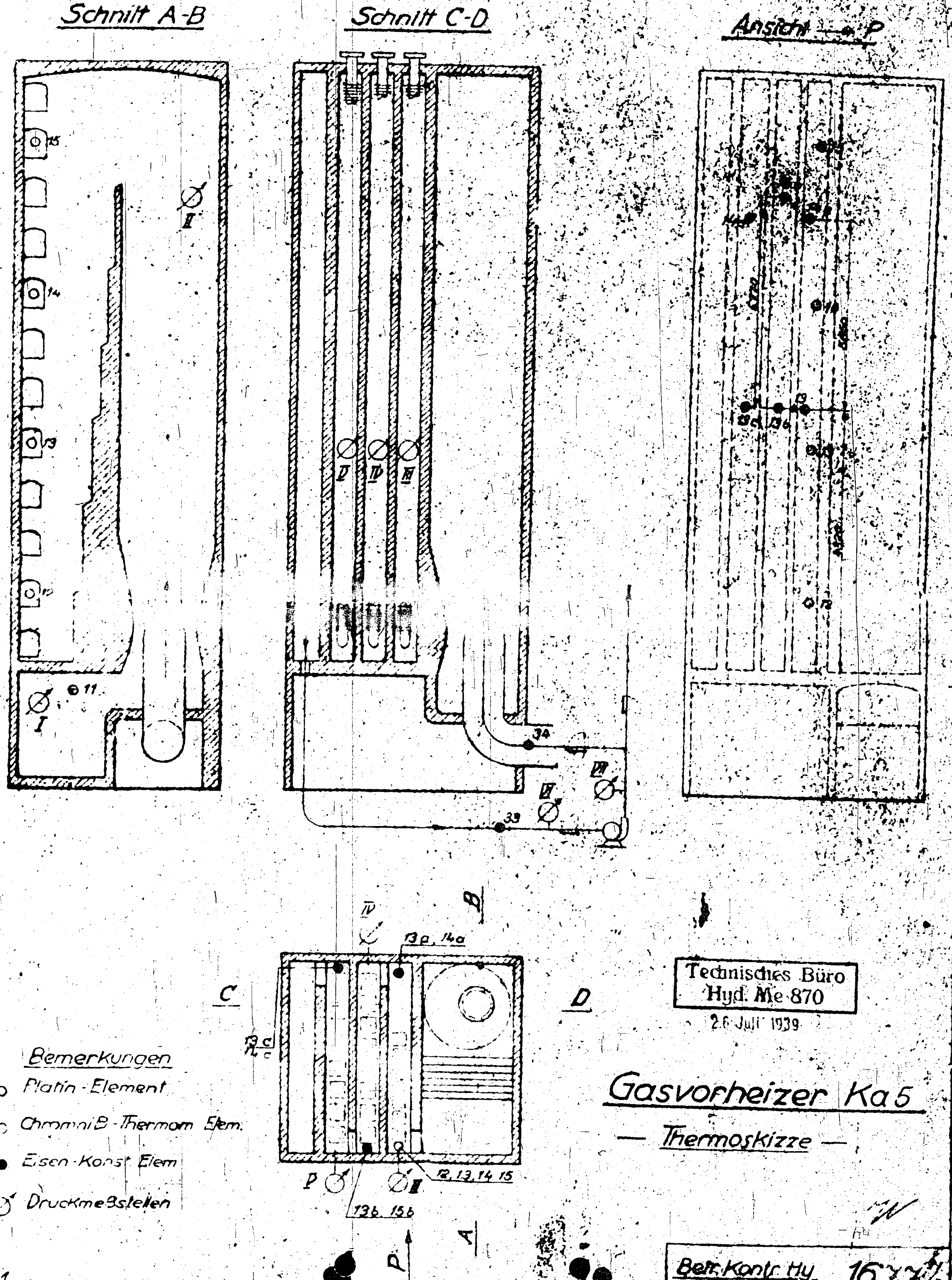
Kohle-Kammer 5

	Ofen Nr	Einsatz Nr	Ofen ф	
I	2571	569	1200	[illegible]
II	238	549	800	[illegible]
III	227	575	800	18000
IV	209	488	800	18000

● Elem. in Hülse ● Elem. aufgebaut
● Elem. im Bohrloch
● Elem. im aufgeschw. Auge
Sämtl. Ofen-Elem. abgesteckt

Technisches Büro
Nr. 870

Betr. Kontr. Hy 1675
den 13. Juli 1939 Dör.



Bemerkungen
- ○ Platin - Element
- ○ ChromniB - Thermom. Elem.
- ● Eisen - Konst. Elem.
- Ø Druckmeßstellen

Technisches Büro
Hyd. Me 870
26. Juli 1939

Gasvorheizer Ka 5

— Thermoskizze —

Betr. Kontr. Hy.
den 15. Juli 39. S

1677

N 1

11. Operation and Control of the Units (h)(cont'd.)

weight of a suspended cylinder.(44) The Germans supported the cylinder on a coil spring so that an iron rod attached to the top of the cylinder rises into an induction coil with rising level. The increasing insertion of the iron rod changes the inductance of the coil which can be determined and recorded as proportional to the liquid level. The Brown electric flow meter in the U. S. uses a similar principle, one advantage of which is the complete absence of any packing or stuffing box. This instrument was used for cold separators, column kettles, etc. where the liquid was fluid at atmospheric temperature and was comparatively free from sediment or suspended matter.

Automatic control of variables in the high pressure coal hydrogenation plants is in its infancy in Germany, and as mentioned before, the design of the instruments is somewhat crude when compared to American practice. Electric, pneumatic, and combinations of the two types of control are utilized. The controlled valves are usually of the diaphragm type, often using balanced pressures on both sides of the diaphragm rather than spring loading in one direction. A crude form of valve positioner was developed to overcome the stuffing box friction which is invariably present in high pressure control valves. Some hydraulic valves were observed, but these were usually remote manual control valves rather than automatic. Solenoid valves were also built, but their use in large sizes was not frequent.

The automatic controls in the Leuna plant were as follows:

(1) Liquid level, cold separator.
(2) Temperature into first converter.
(3) Temperature into second converter.
(4) Liquid level, intermediate separator.
(5) Temperature control of desanding first sump phase converter.
(6) Liquid level, hot separator.
(7) Liquid level, oil feed storage.

Not all of these instruments were used on all units.

and they are arranged in order of decreasing numbers. A description of the controls and their applications is included in the appendix in a report "Selbsttätige Regelung der Sumpf-und Gas phase Kammern in der Hydrierung des Leunawerkes."

(i) High Pressure Joints and Closures.

There are no indications that any novel or improved joints or closures for high pressure vessels or piping have been used in the German High Pressure Coal Hydrogenation Industry. The flanged piping joints used screwed, through-bolted flanges, and the gaskets were lens rings very similar to standard American high pressure practice. The lens rings were usually made of the same material as the pipe, and the joint was a line contact between the ring and the ground end of the pipe itself.

No self-sealing gasket designs were found. The large vessel closures all had the bolts in tension, and the entire gasket load was taken by the bolting. The bolts and nuts were usually made from one of the S steels for 325 atm. service, and from one of the K steels for 700 atm. service. Bolts were studded into the end of the vessel and passed through drilled holes in the forged head, with the nuts on top of the head.

Two general types of large vessel closures were found. The simpler type had no separate gasket, but the tapered end of the head entered the vessel and wedged the stainless steel liner of the vessel against the vessel wall. This design is shown on drawings C-1, C-5, and C-10 in the appendix to this report. The second type of closure uses a separate steel ring which has a facing of 1mm thick pure aluminum on the seating surfaces. The seating surfaces are bevelled at a 30° angle so that the aluminum is wedged into a recess in the head on the head seating surface and between the head and the vessel wall on the other surface. A detail of this construction is shown on drawing C-4 in the appendix, and the equipment shown on drawings C-7, C-11, and C-14 uses the same general design. Apparently

11. Operation and Control of the Units (i)(cont'd.)

the separate gasket is used only when the vessel has no stainless steel liner.

12. Materials of Construction.

One of the great problems in high pressure high temperature processes of any kind is the development or selection of construction materials that will stand up under the operating conditions. For coal hydrogenation the primary requirements of materials for the high pressure equipment are:

(1) Hydrogen resistance at high temperature and with high hydrogen partial pressure.
(2) High tensile and creep strength at the operating temperature.
(3) Resistance to H_2S and Cl_2 corrosion.

A great amount of experimental and development work has been done in Germany in an effort to produce suitable steels, but at best a compromise must be made between the various properties listed above. Their problems were multiplied by wartime shortages of molybdenum, tungsten, and chromium. Austenitic 18-8 Cr-Ni steel was fairly satisfactory, but the tonnage were so great that Germany could not supply the high chromium and nickel requirements.

The early experimental work on the hydrogenation process was done with vessels of various carbon steels, but hydrogen attack was severe and the vessels failed in a very short time.(31) Low alloy chrome nickel steels were then used, but nickel appeared to decrease the hydrogen and H_2S resistance of the alloy. Molybdenum was then substituted for nickel, and gave better alloys with less alloying metal. About 0.5 percent Mo gave high temperature strength properties equivalent to 2.0 percent Nickel. Krupp P469 (N6) was the first steel of this type. In chronological order, steels N6, N8, V 2AED, and N10 were developed, each being an improvement over previous material for high temperature high pressure hydrogen service. Then, during the war, N 8V and N9 were used to save critical alloys, but were not nearly so resistant to corrosion as the earlier steels.

12. Materials of Construction. (cont'd.)

Attached diagram 652 from the IG Farbenindustrie Ludwigshafen Works presents some of the characteristics of the materials mentioned. The "Dauerstandfestigkeit" is the maximum load at which the elongation does not exceed 0.001 percent per hour in a period of 25-35 hours after the beginning of the test, and the total elongation does not exceed 0.2 percent after 45 hours.

The steels used in the hydrogenation plant were classified according to general type and the purpose for which each was used.

Table I, at end of this report, lists the manufacturers, chemical analyses, physical properties, heat treatment and field of usefulness of the various steels of each group.

"S" steels are ordinary carbon steels. They do not withstand high temperature or hydrogen attack, but they are useful for flanges, bolts, cold piping and fittings, lens rings, gaskets, and structural supports. There appears to be little new in the "S" steels either in manufacture or in application.

"N" steels are the high temperature steels and are the most important group. The structural steels, NO, NOS, NO4, N2, CV, are characterized by about 1 percent Cr content and are used for stressed pieces which are not directly in contact with hydrogen or corrosive materials.

The N1 and N5 to N10 alloys contain more Cr, usually 5 or 6 percent and are the hydrogen resistant group of the low alloys. The heat treatment of this group is quite critical, and consists of heating to the austenitic region, quenching, and annealing. These steels have great mechanical strength at high temperature and are resistant (but by no means immune) to chemical attack.

N-1 steel is used almost exclusively for pressure vessels containing hydrogen, but it is not suitable for use at temperature above 250° C, because above this range hydrogen does attack the carbon and weaken the grain boundaries. For this reason all high pressure, high temperature vessels

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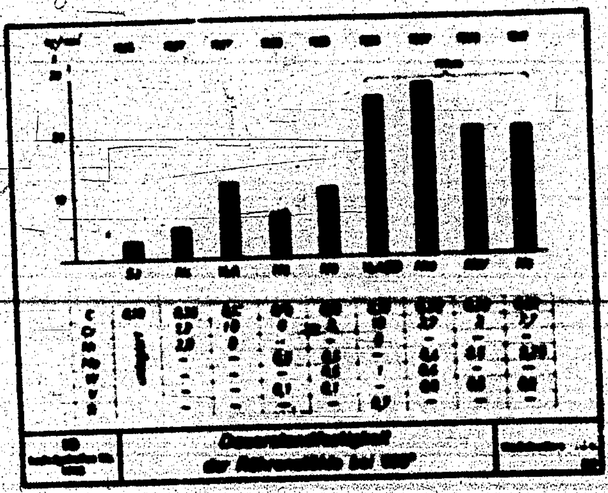

I. G. Diagram 652. "Dauerstand-Festigkeit."

HIGH PRESSURE 325 Atm

Applications of the Working Materials

Temp. Stage	Operating Temp. C	Nominal Range	Applicable Material for Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
I	0-200	6-16 16-160 200	St.45.29 St.35.29	S2	S2	S1	S3 K4Ms K1,K1MS	S3	S2
II Now 200 - 400°C	200-400	6-200	N8A	N8A	N8A	K4MS,K1, K1MS	K4MS,K1, K1V,K1CV K1MS	S3	N8A
II Previously 200-480°C	200-480	6-200	N8	N8	N8	K3,K3CV	K3,K3CV	S3	N8
III Now 400-510°C	400-510	6-200	N9	N9	N9	K3CV K3	K3CV K3	S3	N8A N8
III Previously 48 -510°C	480-510	6-45 58-200	N8 N8V,N10	N8 N8V,N10	N8 N8V,N10	K3,K3CV K3,K3CV, K5,K5V	K3,K3CV K5,K5V	S3 K1MS,K3 K1V,K1CV	N8 N8A

-102

HIGH PRESSURE 7[illegible]

Applications of the Working Materials

	Operating Temp. °C	Nominal Range	Applicable Working Materials for						
			Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
I	0-200	6-16 24-160 except 135 135	K2M K2	S3 S3	S3 K4MS K1 K1MS	S1 K1 K1MS	S3 K4MS K4MS K6	S3 S3,K1, K1V,K1CV	S2 S3
II New 200-400°C	200-400	6-45 58-160 except 135 135	K8A	K8A	K8A	K4MS,K1 K1MS K4MS,K1 K1,K3 K3CV	K4MS,K1 K1V,K1MS K4MS,K1,K1V K4MS K6	S3 S3,K1,K1V K1CV	K5A K6 K8A
II Previously 200-420°C	200-420	6-160	K8	K8	K8	K3,K3CV	K3,K3CV	S3	
III New 400-510°C	400-510	6-16 24-45 58-160	K9 K10,K8V K9	K9,K8V K8V	K9,K8V K8V	K3CV K5,K6V K7	K3CV K5,K6V K7	S3 K3,K1V K1CV K1MS	K8A K9
III Previously 420-510°C	420-510	6-160	K10W	K10	K10	K7 K5,K6V	K7 K5,K6V	K1MS K3,K1CV	K9A

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of this material contain internal insulation or cooling surfaces to maintain the shell at a lower temperature than the process materials.

N6 was the first preheater tube material that could be used to replace 18-8 Cr-Ni steel.(34) It was not entirely satisfactory due to low creep strength and a low resistance to hydrogen attack, but some N6 preheater tubes were still in service in Leuna during the war.

N8 was first used about 1935. It is a 3 percent Cr alloy with ½ percent tungsten, and is cheaper as well as stronger than N6 at the preheater operating temperature. N8 has somewhat lower high temperature strength than 18-8 Cr-Ni steel, and requires particularly careful heat treatment, but it is still considered satisfactory for 325 atm. preheater tubes.

N10 steel(35) is the best low alloy material that has been found for high temperature hydrogen service, and all preheater tubes and fittings for 700 atm. service were made from it. Exceptionally high hydrogen resistance and creep strength were claimed. It has more vanadium and less chromium, molybdenum, and tungsten than N8, thus a saving was made of the most critical metals during the war. Most of the newer installations had N10 preheater tubes whether they operated at 325 atm. or at 700 atm. except where wartime necessity required the use of substitutes. If N10 is properly heat treated (heated to 1050°, cooled in air stream, annealed at 700°) the cold tensile strength can be 90-100 Kg/mm^2. Faulty heat treatment can produce a material brittle at room temperature but still satisfactory at 500-600° C. Air stream cooling in the quench gives a Brinell hardness of 220-260 compared to 240-280 by oil quench, but the Germans state that the air-cooled steel has almost twice the strength at 500-600° C of oil quenched steel in that temperature range.

N10 steel preheater tubes were in service for five years before a failure occurred that could not be traced to some manufacturing flaw. Up to that time they had considered the metal immune to hydrogen attack, but they found that

12. Materials of Construction. (cont'd.)

a very slow removal of carbon from between the grains did occur. It has been claimed that a heat treatment of the tubes after each period of not more than 10,000 hours service will prolong the tube life indefinitely. This heat treatment is presumably the same as the initial treatment.

N steels can be arc or resistance welded but gas welding is risky. The design of most large vessels avoids welding but resistance welding of preheater tubes and piping is regular practice. The welding procedure most be followed by heat treatment.

"K" steels were made primarily for 700 atm work where the "S" steels were not sufficiently strong. The "K" steels contain about 1 percent Cr, and have lower Mo and higher C than the S steels.

The remainder of the steels shown have counterparts in American practice. The "RA" steels are 18-8 Cr-Ni alloys for acid and chemical resistance. The "RM" steels are 12-14 Cr steels for hardened pieces such as valve parts. 25Cr 20 Ni alloys are the non-oxidizing, flame-resistant steels. Alloys containing 1-5 percent nickel are used for heavy duty forgings such as piston rods, and for low temperature service. The final groups are the surface hardening and nitriding steels.

Hydrogen sulfide corrosion becomes progressively more severe as the temperature rises. Under the pressure and temperature conditions of coal (or tar) hydrogenation H_2S attack on ordinary carbon or low chrome steels is quite rapid. For instance, the Pillingham plant of I.C.I. uses 1½" thick low chrome steel liners in the converters and they estimate their life at about 5 years. The hydrogen sulfide cannot be eliminated because it forms during the conversion and because it is necessary to have some of this gas present to preserve the sulfide catalyst used in gas phase operation. A 14 percent chrome alloy withstande the conditions imposed, but due to the difficulty involved in fabricating large pieces from this material the Germans sometimes made their liners for converters and hot separators from 18-8 Cr-Ni steel.

12. Materials of Construction. (cont'd.)

It was found that brass containing at least 37-42 percent zinc has very high H_2S resistance, but of course brasses cannot be used at the high temperatures involved. In one set of German experiments they made a series of iron-zinc and nickel-zinc alloys containing up to 50 percent zinc to see if such alloys would be H_2S resistant. (It is interesting to note that these alloys were made under 60 atmospheres nitrogen pressure because of the high vapor pressure of zinc at the melting point of iron or nickel.) Alloys containing as much at 15 percent zinc were not attacked by H_2S but, as might be expected, the alloys were too brittle to be of any practical use. However, these experiments led to the vapor galvanizing of parts such as heat exchanger tubes and liners, a procedure that apparently proved to be satisfactory and is still used. They also galvanized 13 percent Cr converter internal parts. The vapor galvanizing is accomplished by holding the parts in zinc vapor for 25 hours at 670°C., thus forming a very thin crust of Fe-Zn protective alloy.

Chlorine and chlorine compounds form some hydrochloric acid under the conditions of hydrogenation. No practical construction material will withstand this attack, therefore when chlorine is present in the feed, soda ash is added to neutralize the acid.

Erosion is a serious problem in much of the equipment and piping. It can be traced to one or the other of two sources in most instance. One source is abrasive material in suspension in the fluids being processed, such as ash, sand and catalyst in the coal paste, the sump phase liquids, and in the sludge recovery system. Wear in the paste pumps is combatted by using surface hardened metals and nitrided plungers and valves, and by low plunger velocity. The return bends of the sump phase preheaters suffer much damage and hardened inserts, usually of 12-14 percent chrome steel, are often placed inside the outer wall of the fitting. Valves have hardened seats and discs, and are designed so that the flow is streamlined as much as possible. Heat exchanger tube sheets are approached with long conical sections which reduce solid deposition as well as erosion on the ends of the tubes. Stuffing boxes are equipped with

12. Materials of Construction. (cont'd.)

flushing oil connections, and are flushed continually while in service.

The second type of erosion is due to high flow velocities of fluids, especially mixtures of vapor and liquid, through pressure release points. This condition is partially combatted by the design of the unit and the equipment. Expansion is carried out through expansion engines or in several stages. Expansion valves have turbulence chambers with slightly restricted openings on the outlet. Piping is installed undersized in order to take part of the pressure drop. Where it is necessary that a considerable pressure drop be taken across a valve, the seat and disc are made replaceable and of some abrasion resisting material such as tungsten carbide or tungsten-titanium carbide. Two pressure reducing stations are always installed in parallel, with shutoff valves one each side of each expansion valve so that it can be removed from service for replacement or repairs.

Hydrogen attack on steels(37) is a particular type of corrosion, causing decarburization at the grain boundary, and it is of such great importance in high temperature high pressure operation that it is considered separately. The mechanism of the attack is the slow hydrogenation of the carbon in the steel to methane. This takes place primarily in the matrix rather then in the crystals, and greatly diminishes the strength of the steel. The reaction velocity for any given steel increases with the temperature and with the hydrogen partial pressure. The resistance of steels to hydrogen attack varies from that of carbon steel, which is quite sensitive even at 200°C, up to stabilized 18-8 Cr Ni austenitic alloys which are practically immune over the entire range of temperature used in the process.

Due to the great cost of austenitic stainless steel, low alloys were developed which would have sufficient hydrogen resistance for particular purposes. These are the "N" steels. N4 could be used for 325 atm H_2 up to 400°C and N6 and N8 up to 600°C. The use of 700 atm pressure dropped these permissible temperature ranges and forced the development of N10.

12. Materials of Construction.(cont'd.)

The first report of tests published by F.K. Nauman in 1938 (Stahl und Eisen, pg 1239) stated that N10 was unaffected by 200 atm hydrogen at 600°C in 100 hours. The failure by hydrogen attack of N10 preheater tubes after several years of service caused additional study of the effect. It was found that chemical analysis alone did not mean much with regard to hydrogen susceptibility, but fabricating and operating conditions played a considerable part. Many steels showed evidences of attack only after 400-600 hours and some only after 1000 or more hours. Heat treatment was an important factor, and in general, air quenched steels were found to be more resistant than oil quenched. These tests indicated that resistance increased with a decrease in unstable carbides in the matrix and with less dissolved carbon in the ferrite, also, that complete immunity is not attained by ferritic-pearlitic steel containing as high as 6.5 percent Cr., but that grain boundary failure will occur in time.

The following four figures show micrographs of N10 tubes which failed in 700 atm. service in the hot section of a preheater after approximately 11,000 hours service. The two photographs with a magnification of 12 diameters show the fissures caused by hydrogen attack which ultimately result in failure of the tube. These fissures are typical of hydrogen attack on any steel. The two micrographs with a magnification of 125 diameters emphasize the deterioration at the surface in contact with the hydrogen. The etched sample in particular shows the effect of the decarburization on the steel grain structure.

The following figure shows bend tests of samples taken from one of the tubes which failed. The samples from left to right are taken: from the inner tube surface, with the immediate surface removed, 0.2 mm removed, 1 mm removed, middle of tube, outside of tube. It can be seen that the attack penetrated less than one millimeter over the tube as a whole.

Results of experiments led the Germans to believe that the life of N10 steel preheater tubes could be prolonged indefinitely by giving them a heat treatment after each

Micrographs (x12) of N10 Tube [illegible]
Due to Hydrogen Attack in 700 Atm. High
Temperature Service.

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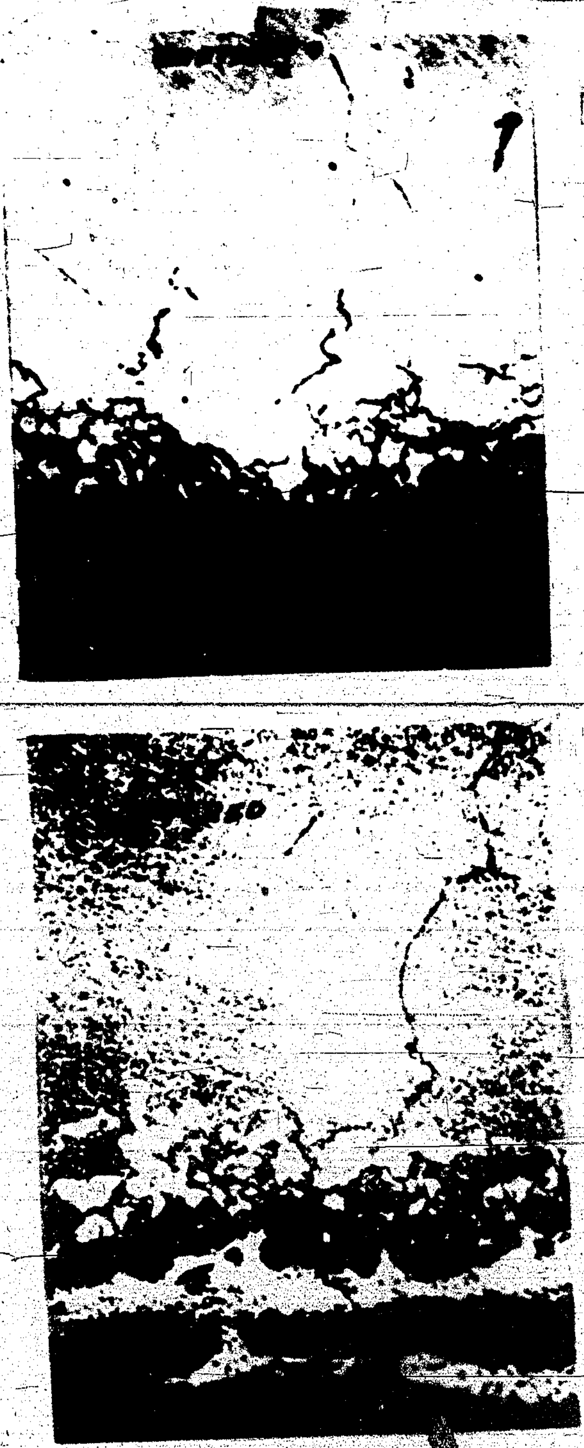

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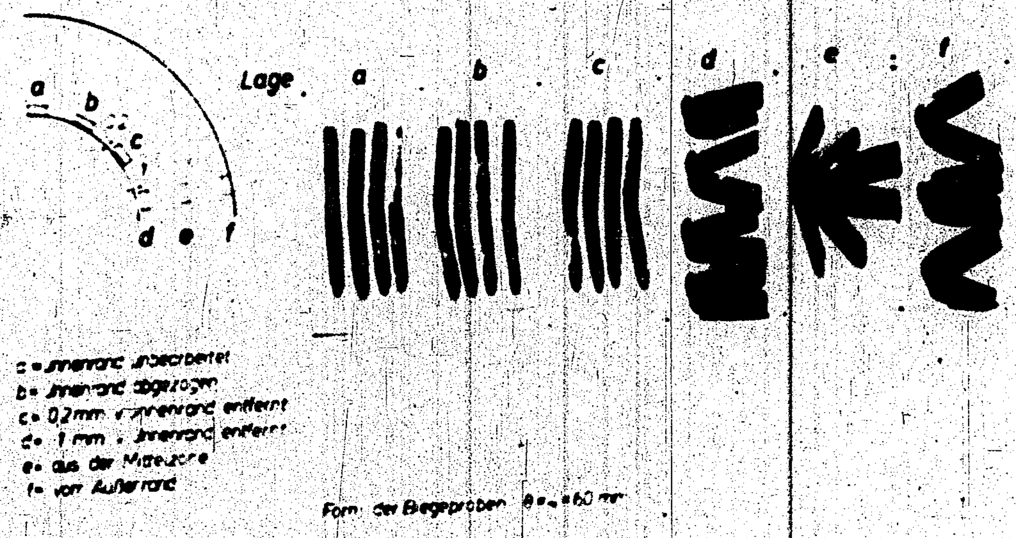


Bend Tests on Samples from N10 Tube Which Failed

In 700 Atm. High Temperature Hydrogen Service.

12. Materials of Construction.(cont'd.)

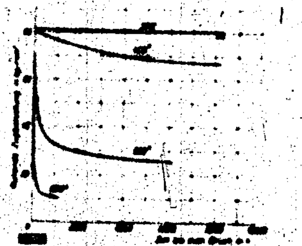
10,000 hours service. Apparently the heat treatment re-established the carbon equilibrium in the steel of the inner tube surface, but it is not clear just how this was accomplished.

A thorough study of the use of columbium to replace the carbon for blocking grain slippage in the steel was proposed as a possible method of developing a completely hydrogen resistant low alloy steel. These experiments were not carried out due to wartime shortage of manpower.

The German creep strength test consists of putting a series of constant loads on test pieces held at the specified temperature for periods of 45 hours each. The creep strength (Dauerstandfestigkeit) is the greatest load in Kg/mm^2 at which the creep velocity does not exceed 1/1000 percent per hour during the 25-35 hour period and the total extension in the 45 hours does not exceed 0.2 percent. It is claimed that this test is reproducible and extremely useful as a method of evaluating creep strength in a short term test.

A second method of evaluating high temperature strength is a plot of different constant loadings at constant temperature against the number of hours elapsing before the fracture of a given material occurs. This is known as the load-time curve (Belastungs-Standzeitlinien), and is usually plotted on both rectangular and log-log coordinates. Two types of these plots are shown in the attached figures. The first two (marked Abb. 4 and 5) show curves for a 0.91 percent Ni, 0.78 percent Cr, 0.94 percent Mo steel at 300°, 400°, 500°, and 600° C., plotted with the two types of coordinates. The second pair shows the curves for 500° C of five different chrome steels, including V2AE, N9, a 20 percent Cr. steel and two low alloy Cr-Ni steels.

The following figure (Abb. 18) shows the loading, time to fracture, elongation, and reduction in area beneath photographs of test pieces of a steel corresponding to N10 composition which were broken under the various loads. It is interesting to observe the changing appearance of the



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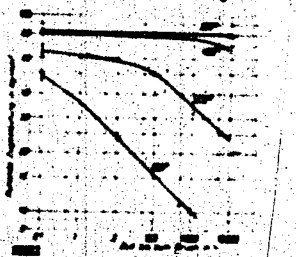

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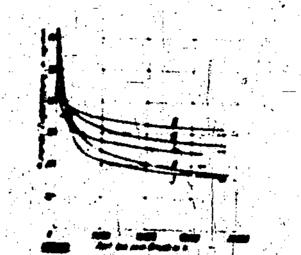
bb. 4 and 5



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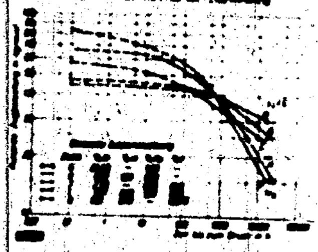

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bb. 6 and 7

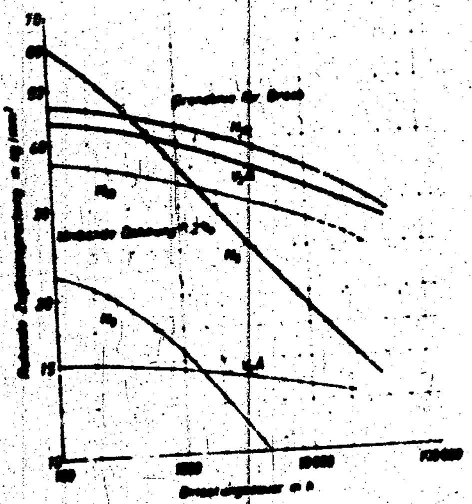

Abb. 18. N10 Test Pieces.

Break and Creep Tests on High Temperature Steels.

18a

12. Materials of Construction. (cont'd.)

fracture after increased periods of time. The next figure shows the relation between the break point and the loading which produces an elongation of 0.2 percent after various periods under tension at 500°C. The poor qualities of war-time substitute N9 as compared to N10 are plainly shown.

The following tables are taken from Technical Report No. 87-45 of the U. S. Naval Technical Mission in Europe, and shows the uses of the principal materials in high pressure equipment.

It should be noted that N8 and N9 would both be replaced by N10 for new construction when alloying metals are available in the necessary quantities.

Internal parts and liners for the vessels are not listed above, but austenitic 18-8 Cr-Ni still is the preferred material, with 13 percent Cr steel as the best substitute.

Austenitic stainless steel is also preferable for pressure shells, but N1 is satisfactory when precautions are taken to avoid metal temperatures of over about 250° C. It can be noted that no cases of failure of pressure shells have been found, although on a few occasions vessels have been blown out of the cells by gas explosions in the cell space.

On the whole, the German development and selection of steels appear to be satisfactory in conjunction with their equipment design.

(b) Insulation(39)

There were three principal classes of service where insulation was required in the high pressure hydrogenation units. The first consisted of coverings for pipe lines and fittings; the second was the internal insulation employed inside of the pressure vessels to maintain the shell temperature below 250° C; and the last was the protection of steel work to prevent buckling in case of fire.

12. Materials of Construction (b)(cont'd.)

For pipe coverings in the range of 100 to 250° C, an insulation called Diamag, which was a Magnesium carbonate, Kieselguhr, asbestos mixture in a 60 - 25 - 15 ratio, was employed. This material was used for low pressure steam lines and pipes which were not carrying very hot fluids. In the temperature range of 400 - 450° C. glass wool or rock wool was commonly used on hot gas and high pressure steam lines. A sheet metal housing outside of the pipe was packed with the wool to a density of about 180 kg/m^3 for glass wool and 240 kg/m^3 for rock wool. At these densities the respective thermal conductivities at 200° C were 0.063 and 0.956 KCal./meter (hr)(°C.).

At temperatures over 450° and up to 300° C a diatomit insulation was used. This material was a kieselguhr produced by a low temperature burning. It had a compression strength of 6-8 kg/cm^2, a density of 450 kg/m^3 and a thermal conductivity of 0.08 Kcalories/meter(hr)(°C) at 100° C. An asbestos cement of 4 percent asbestos, 90 percent kieselguhr and 6 percent alumina plus a binder was commonly used to fill in the cracks and produce a smooth surface. When the lines were to be protected against possible fires, a thin iron sheath was placed on the outside of the insulation and held in place by galvanized iron bands.

As has been previously described, the inside of the hot, high pressure vessels such as the converters, heat exchangers, and hot separators were insulated in order to keep the external wall temperature below 250° C., and thereby prevent hydrogen embrittlement. A harder grade of Diatomit made by burning kieselguhr at a higher temperature was used for this purpose. The compression strength of the Diatomit blocks was 25 kg/m^3, and the thermal conductivity was 0.12 K. Cal/meter(hr)(°C.) at 100° C. At 200-300 atmospheres pressure the conductivity of the oil saturated Diatomit rose to 0.4 - 0.8 k.Cal/meter(hr.)(°C.). In practice the vessels were lined with blocks of the insulation about 65 m/m thick, and asbestos cement was employed to fill up the cracks. The cement had a thermal conductivity essentially the same as that of the Diatomit.

In order to protect the structural steel work in the

12. Materials of Construction (b)(cont'd.)

stalls from buckling in the case of fire, the supports for the converters and connecting girders were insulated. A layer of Diatomit blocks about 65 m/m thick was laid around the outside of the structural steel and held in place by a wire mesh. A coating of 15-20 m/m of cement was applied over the top to protect against weather and to make a smooth finished surface. Other structural steel members were also covered with either brick or Diatomit and finished with a cement coat. These precautions helped to prevent more serious accidents in the case of fires, since the steel could stand intense heat for 30 minutes or longer when so protected.

The following table No. IV shows the I.G. Farbenindustrie application of various types of insulating materials for different applications. The ordinates show the temperature ranges and the services, while the blocks show the type of material and the thickness for different diameters.

13. Conclusions.

In a planned economy and in anticipation of war, a nation may artifically stimulate the production of potentially strategic materials. In this light the chronological development in Germany of the high pressure hydrogenation processes are of interest. The earliest commercial plants were the Haber units for the hydrogenation of nitrogen to ammonia. Developed prior to 1913, this process made Germany independent of Chile saltpeter imports for explosives production during World War I.

The experience gained in design and operation of these units proved helpful when the Germans expanded their search for materials and started in the early 1920's to hydrogenate carbon monoxide to methanol. The designs of auxiliaries, safety precautions, and materials of construction could be applied directly, and the designs of the converters, heat exchangers, and separators, could, with suitable modification, be used. Thus the Germans had two large scale high pressure processes in operation prior to the next expansion

TABLE IV

Isoliertabelle

Temperaturen °C	Art der Leitungen.	Äußerer Rohrdurchmesser in mm. bis 40	bis 133	bis 216	bis 200	bis 355	bis 420	bis 520	bis 620	bis 720	bis 900	bis 1100	bis 1[illegible]
—80	Cold Service Kälteleitungen	150/180		200/210						250/260			
—60		100/110		150/160						200/210			
—40		50/60	100/110							150/160			
—30			50/60						100/110				
—20				50/60							100/110		
20-100	Warm Water and Condensate Warmwasser- u. Kondensatleitung.	20/25	40/50 bis 80		50/60					60/70			
			50/60		60/60								
100-200	Low Press. Steam Niederdruckdampfleitungen.	30/35	50/60		60/70					[illegible]			
					90/110			110/120					
200-300	High Pressure Steam Hochdruckdampfleitungen.	40/45	60/80	70/90	90/110		110/130		130/150				
300-400	Very High Press. Steam Höchstdruckdampfleitungen.	70/80	90/110		110/130		130/150		150/170				
400-450	Very High Press. Steam Höchstdruckdampf- und Heißgasleitg. and Hot Gas.		110/130	130/150		150/170		180/200					
450-500			120/140 (2 Lagen [illegible])	140/160 (2 Lagen [illegible])		160/180 (2 Lagen [illegible])		190/210 (2 Lagen [illegible])					
500-600	Hot Gas Heißgasleitungen.			160/180 (2 Lagen [illegible])		180/200 (2 Lagen [illegible])		210/230 (2 Lagen [illegible])					
600-700	Hot Gas Heißgasleitungen.			180/200 (2 Lagen [illegible])		210/230 (2 Lagen [illegible])		230/250 (2 Lagen [illegible])					

[illegible] Isolierung gegen Feuergefahr ist Isolierstärke u. Art von Fall zu Fall zu bestimmen.

▭	Eiskork
▭	Wärmekork ([illegible])
▬	Diamag
▭	Schlackenwolle-Stopfverfahren.
▬	gebr. [illegible]
▭	Glasgespinst

Kleine Zahl = Schalen- bzw. Stopfdicke.
Große Zahl = Gesamtisolierstärke.

Leunawerke den 7. März 1936

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13. Conclusions.(cont'd.)

in 1926 when the first coal hydrogenation plant was started at Leuna. Here again much of the early work on ammonia and methanol was applied directly; however, this operation, involved the handling of solids, and it was necessary to gradually evolve specialized equipment such as converters, preheaters, and heat exchangers. This latter operation was much more difficult than the straight handling of gases and clean liquids as in the ammonia and methanol systems. New techniques were developed and the high pressure stage changed so that either coal or tar could be handled in the same equipment. A second, gas phase hydrogenation was developed that could process middle oil from any of several sources to produce a variety of motor fuels. Thus in the two stage hydrogenation process the Germans had a fairly flexible process capable of handling a wide variety of raw materials to produce end products of nearly the same characteristics or widely different, as desired.

Mention has been made of the enormous size of these plants in relation to their throughputs. The largest plants were Leuna and Bruex each of which produced approximately 600,000 tons of motor fuel per year. Each used ten to twelve high pressure stalls with all of the auxiliaries, such as gas manufacture, gas purification, power and steam production, gas compression and recycle units, product treatment, and covered an area of roughly fifteen square kilometers. It is difficult to evaluate the cost of these German plants on account of an arbitray relationship between the reich mark and the dollar. An indication may be obtained from a proposal made by the I.G. Farbenindustrie to the U.S.S.R. in 1939 giving the cost of a plant to produce 180,000 annual tons of aviation gasoline by the hydrogenation of brown coal.(28) The total cost of the high pressure plant and all auxiliaries was estimated at 47,800,000 R.M. Since this production corresponds to only 4,000 barrels a day, the cost per barrel per day is 12,000 R.M. At a 40 cent R.M. this corresponds to an investment of approximately $5,000 per barrel of aviation gasoline per day. This investment is high, and the operating cost would also be quite high on account of the large amount of labor required. Automatic controls were virtually unknown, as compared with

13. Conclusions. (cont'd.)

American practice, and instead manual operation was used in all but the simplest positions. Undoubtedly American engineering and instrumentation could materially cut the labor requirement, but it would still be a major item. The utilities also formed a large fraction of the operating cost. For every ton of bituminous coal processed, it required approximately four or five tons to supply the power, steam, and hydrogen.

In anticipation of and during the course of war, the present Germany again resorted to high pressure hydrogenation to produce certain materials regardless of cost. With little petroleum accessable, Germany planned to use other raw materials, such as coal, to supplement the meager supplies of crude oil obtainable from outside sources. Altogether eleven large installations were constructed for processing coal and tar with a total production of aviation gasoline (the principal product) in 1942 of about 3,900,000 tons or 32,000,000 barrels per year. While relatively large and a tribute to German engineering this output was entirely too small to support the war needs of Germany and was further diminished by strategic bombing during the later war years.

The high pressure hydrogenation of hydrogen-poor materials as developed by the Germans was a very interesting process from the scientific viewpoint. The possibilities of altering the compositions and/or quantities of various materials by changes in operating conditions or catalyst naturally attracted the interest of technical men. The economy of the process, however, was not so easily determined. The huge investment cost and the large number of men required to operate a plant that would produce 13,000 barrels per day (output of the largest units) made for high production costs. For a country that did not have any appreciable supply of petroleum, a high pressure plant could possibly compete in a protected home market. In the United States with its still large reserves of low-cost petroleum, the process at present could not hope to make headway without a subsidy. Outside of small scale experiments in government supported laboratories such as the Bureau of Mines, and certain research institutions like Armour Research Foundation and Battelle Memorial Institute, there are

13. Conclusions. (cont'd.)

no known applications of coal hydrogenation to produce gasoline or liquid fuels in the United States.

Certain phases of the hydrogenation process might be considered to advantage, since it is highly probably that they might soon become economically feasible. The Standard Oil Company of New Jersey is conducting a limited hydrogenation of lube oils in order to saturate them and improve the viscosity index, but this is practiced only on a very small and limited scale. This company at its Baton Rouge refinery has also conducted many tests on the hydrogenation of cracked residues to obtain an additional yield of gasoline. This work is still in progress, and has reached the point where an increase in the price of either crude or gasoline will make the process economically attractive. The Standard Oil Company has followed the development of high pressure hydrogenation for many years, learning much of the technique from the I.G. Farbenindustrie. It is now in a position to exploit the process as soon as the economics are favorable.

Another point in favor of hydrogenating residues is the conservation of crude reserves. For every barrel of gasoline obtained from residuum about two barrels of crude may be left in the ground. Obviously the marketing of residues as fuel oil is only done because of the low selling cost of gasoline. Therefore, the further investigation of the advisability of processing these heavy hydrogen-poor materials in stages such as the Germans used for tars might well be considered.

Along the same line it might be economically feasible to process the heavy ends of crude petroleum in order to increase the hydrogen content before cracking. Such measures would raise the yields of gasoline per barrel of crude and at the same time decrease the amount of residue to be either reworked or sold. Undoubtedly the two processes could be advantageously worked together so that a heavy fraction from the crude petroleum would be blended with the cracking recycle stocks and hydrogenated, the ultimate products being only gasoline and gas.

13. Conclusions. (cont'd.)

In conclusion it does not appear that coal hydrogenation as practiced by the Germans offers any immediate prospect of competing with petroleum in the United States. It is quite possible, however, that certain features of the process may soon become justified from both a conservation and economic standpoint. The work of the Germans should be carefully studied by any industry undertaking to exploit any phases of high pressure operation. Such a study should be of considerable help in the design and operation of high pressure plants.

Prepared by:

JOHN H. HOWELL
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Technician.

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APPENDIX A

TABLES OF OPERATING DATA

TABLE NO. 4

Analysis of German Coals Used For Hydrogenation.

Type of Coal	Brown Coal		Bituminous Coal	
Plant	Leuna	Wesseling	Gelsenberg	Pölitz
% Ash in dry coal	12.8	5.9	3.0	6.6
Element Analysis on dry, ash-free basis				
% C	71.9	68.7	83.8	81.9
% H	5.7	5.0	5.3	4.9
% O	17.9	24.9	8.0	11.5
% N	1.0	1.3	1.75	1.1
% S	5.8	0.40	1.0	0.8
% Cl	----	0.11	0.09	0.05
% available H	4.1	2.4	4.6	3.9
Volatile Matter	57.9	53.5	37.5	37.2

TABLE NO. 5

Summary of Operation Data for Sump Phase Hydrogenation

Material Treated	Brown Coal	Brown Coal Tar	Bituminous Coal	Pitch
Temperature, °C	470-480	450-460	485	485
Pressure, atm.	300&700	300	700	700
Catalyst	Iron Oxide	Iron sulfide	Sodium Sulfide Iron Oxide Iron Sulfide	Iron Sulfide
Total reaction volume per stall, in M^3	27	27	36	36

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TABLE NO. 5 (cont'd.)

Material Treated	Brown Coal	Brown Coal Tar	Bituminous Coal	Pitch
Specific feed rate tons/m3 hr	1.1 - 1.3	0.75	0.9 - 1.0	0.7
Total feed rate, tons/hr	30 - 35	20	33 - 37	25
Concentration of material in feed, wt. %	36 - 40	75	40	60
Total gas flow, M/hr	35-45,000	27,000	50,000	40,000
Gas Circulated with paste, M^3/hr.	25-30,000	20,000	30,000	25,000
Gas used for cooling, M^3/hr	10-15,000	7000	20,000	15,000
Water added to product, M3/hr.	1	1	1	0.7
% Conversion of Coal	97	-	95	----
Tons of middle oil/ton feed	0.48	0.38	0.62	0.29
Tons of C3 plus C4/ton feed	0.06	0.03	0.12	0.02
Hydrogen Consumed /ton middle oil, M3	1500	250	1600	700-800

TABLE NO. 6

Analysis of Sump Phase Oils

Middle Oil From	Brown Coal	Bitminous Coal
Specific Gravity 20°C	0.962	0.974
Aniline point Phenol-free oil, °C.	-10	-20
% Phenolics	20	15
Element Analysis		
% C	86.05	87.28

[illegible]

[illegible]	[illegible] Coal	Bituminous Coal
Element Analysis		
% H	9.37	9.54
% O	3.90	3.08
% N	0.55	1.06
% S	0.13	0.04
gms H / 100 gms. C	10.90	10.93
Heavy Oil from		
Specific gravity, 50°C.	1.030	1.038
Element Analysis		
% C	88.62	89.27
% H	8.40	8.26
% O	2.62	1.64
% N	0.28	0.77
% S	0.08	0.06
gms H/100 gms C.	9.46	9.25

TABLE NO. 7

Summary of Operating Data for Gas Phase Hydrogenation

Stage -	Prehydrogenation	Gasoline Production Coal & Tar	 Pitch
Temperature, °C	390-410	400-420	500
Pressure, Atm.	300	300	700
Catalyst	Tungsten Disulfide	Tungsten Dissulfide & Act. Clay	Chrome-Zinc Malybdenum Act. Clay
Total Catalyst volume per stall, M3	28	23	32
Specific feed rate, tons/M3 hr.	0.6-0.8	1.2	0.45

TABLE NO. 7 (cont'd.)

Stage	Prehydrogenation	Gasoline Production Coal & Tar	Gasoline Production Pitch
Total feed rate, tons/hr	20	35	14
Total gas flow M3/hr	55,000	27,000	38,000
Gas circulated with oil, M3/hr	35,000	20,000	30,000
Gas used for cooling M3/hr	20,000	7,000	8,000
Tons gasoline produced /ton feed/pass*	0.20	0.60	0.50
Tons C3 plus C4/ 1 ton feed/pass*	0.08	0.075	0.12
Hydrogen consumed/ton middle oil, M3	500	200	950

TABLE NO. 8

Comparison of Screw Type with Ball Type Sludge Coking Ovens

Type of Oven	Screw		Ball	
Plant	Wesseling	Leuna	Wesseling	Gelsenberg
Steam Consumption tons/ton feed	6.5	19.5	15.5	20.0
% solids in moisture free product	75.5	81.0	99.5	96.2
% ash in solids	86.2	83.0	64.2	41.1
% Benzol soluble oil in discharge product	24.5	19.0	0.5	3.8
Coke analysis of moisture free product				
% tar	6.1	8.7	0.5	1.3
% Coke	93.2	91.3	99.4	95.0
Ash content of the coke	70.8	75.2	64.4	42.0

*Single pass through the Converters Yields.

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TABLE NO. 9

Element Balance for Sump Operation with Brown Coal

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons	Residue Tons
Dry Brown Coal	1000.00	619.12	48.06	181.93	5.81	53.72	91.36
Catalyst	89.48			61.53			27.95
Fresh Gas H_2	52.95		52.95				
N_2	13.94				13.94		
CO	3.03	1.30		1.73			
CO_2	2.48	0.68		1.80			
CH_4	5.76	4.31	1.45				
Total Fresh Gas	78.16	6.29	54.40	3.53	13.94		
Total Inlet	1167.64	625.41	102.46	246.99	19.75	53.72	119.31
Middle Oil	417.17	353.98	44.24	14.84	1.68	2.43	
High Volatile Gasoline	19.73	16.42	3.31				
Total Liquid Product	436.90	370.40	47.55	14.84	1.68	2.43	
Outlet Gas H_2	7.29		7.29				
N_2	13.94				13.94		
CO	13.27	5.69		7.58			
CO_2	91.26	24.90		66.36			
CH_4	37.68	28.20	9.48				
C_2	31.80	25.40	6.40				
C_3	36.41	29.75	6.66				
C_4	19.39	16.02	3.37				
C_5	2.90	2.41	0.49				
H_2S	34.66		2.05				
Total outlet Gas	288.60	132.37	35.74	73.94	13.94		
Miscellaneous Solids in Sludge	214.13	18.01	0.72	38.99	0.67	21.00	134.74

TABLE NO. 9 (cont'd.)

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons	Residue Tons
Water of Reaction	148.25		16.59	131.66			
Phenols	2.18	1.67	0.14	0.37			
H_2S in Disch. H_2O	1.21		0.07			1.14	
NH_3 in Disch. H_2O	3.21		0.57		2.64		
CO_2 in Disch. H_2O	4.49	1.22		3.27			
Oil Lost in Coking	75.05	70.50	4.18	0.27	0.05	0.05	
Total Miscellaneous	448.52	91.40	22.27	174.56	3.36	22.19	134.74
Total Outlet	1174.02	594.17	105.56	263.34	18.98	57.23	134.74
Balance Difference	+ 6.38	-31.24	+3.10	+16.35	-0.77	+3.51	+15.93
Balance Difference in % of Inlet	+ 0.54	-5.00	+3.02	+ 6.62	-3.90	+6.53	+12.93

TABLE NO. 10

Element Balance for Sump Phase Operation with Bituminous Coal

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons	Residue Tons
Dry Coal	1000	769	45.0	11.3	5.2	107.7	61.8
Catalyst	44.8		1.4		2.7	20.8	19.9
Pasting Oil	1363	1239.3	99.5	10.6		13.6	
Solids in Pasting Oil	117.4	72.5	2.6	0.8	2.9	0.7	37.9
Heavy Oil Added	63.9	57.7	5.2	0.4		0.6	
Flushing Oil	52.0	46.8	4.3	0.4		0.5	
Fresh Gas(1,150,000M^3)	140.0	14.6	95.7	29.3		0.4	
Total Inlet	2781.1	2199.9	253.7	52.8	10.8	144.3	119.6

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TABLE NO. 10 (cont'd.)

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons	Residue Tons
Middle Oil	526						
Cold Separator Oil		965.3	91.4	8.0	0.3	24.0	
Heavy Oil	563						
Phenol Oil	3.7	2.8	0.3			0.6	
Oil in Slurry	922	844	62.5	8.1		7.4	
Solids in Slurry	294	138.3	5.9	1.2	7.6	1.7	139.3
Slurry Gas	30.1	14.6	8.0	5.5		2.0	
Lean Gas	146	79.7	34.4	21.8	0.5	9.6	
Rich Gas	166.7	123.5	31.4	4.8	0.8	6.2	
Reaction Water	96		10.7			85.3	
NH_3 in Water	6.8		1.2	5.6			
H_2S in Water	0.2		0.0		0.2		
CO_2 in Water	8.9	2.4				6.5	
TOTAL OUTLET	2763.4	2170.6	245.8	55.0	9.4	143.3	139.3
Balance Difference	-17.7	-29.3	-7.9	+2.2	-1.4	-1.0	+19.7
Balance Difference in % of inlet	-0.64	-1.34	-3.12	+4.16	-13.0	-0.70	+16.5

TABLE NO. 11

Element Balance for 5058 Gas Phase Operation with Brown Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons
Middle Oil	1102.98	935.8	116.92	39.26	4.52	6.40
High Volatile Gasoline	27.04	22.51	4.53			
H_2S	3.36		0.20			3.16

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TABLE NO. 11 (cont'd.)

		Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons
Fresh Gas	H_2	52.34		52.34	--		
	N_2	13.70				13.70	
	CO	3.14	1.35		1.79		
	CO_2	2.61	0.71		1.90		
	CH_4	5.62	4.21	1.41			
Total Fresh Gas		77.41	6.27	53.75	3.69	13.70	
Total Inlet		1210.79	964.66	175.40	42.95	18.22	9.56
Gasoline		1000.00	858.32	139.46	0.94	1.14	0.14
Outlet Gas	H_2	3.25		3.25			
	N_2	11.84				11.84	
	CO	0.22	0.09		0.13		
	CO_2	0.92	0.25		0.67		
	CH_4	9.21	6.89	2.32			
	C_2	2.92	2.33	0.59			
	C_3	27.38	22.37	5.01			
	C_4	81.82	67.62	14.20			
	C_5	0.89	0.74	0.15			
	H_2S	2.44		0.14			2.30
Total Outlet Gas		140.89	100.29	25.66	0.80	11.84	2.30
Miscellaneous							
Water of Reaction		45.13		5.05	40.08		
Phenol		2.13	1.63	0.14	0.36		
NH_3 in Disch. H_2O		5.78		1.03		4.75	
H_2S in Disch. H_2O		6.45		0.38			6.07
CO_2 in Disch. H_2O		1.06	0.29		0.77		
Total Miscellaneous		60.55	1.92	6.60	41.21	4.75	6.07
Total Outlet		1201.44	960.53	171.72	42.95	17.73	8.51
Balance Difference		-9.35	-4.13	-3.68	--	-0.49	-1.05
Balance Difference in % of Inlet		-0.76	-0.43	-2.10	--	-2.69	-10.98

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TABLE NO. 12

Element Balance for 5058 Gas Phase Operation

with Bituminous Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons
Middle Oil	1000	863.8	108	4.9	4.3	19.0
Fresh Gas 489,000 M^3	59.4	6.2	40.5	12.5		0.2
Total Inlet	1059.4	870.0	148.5	17.4	4.3	19.2
Gasoline	360					
Cold Separator Oil		852	131.9	0.1		
Middle Oil	624					
Phenol Oil	0.4	0.3				0.1
Lean Gas	31.4	8.5	12.6	9.8		0.5
Rich Gas	7.8	5.6	1.5	0.5	0.1	0.1
Reaction Water	18.1		2.1			16.0
NH_3 in Disch Water	7.7		1.4	6.3		
H_2S in Disch Water	6.2		0.4		5.8	
CO_2 in Disch Water	0.4	0.1				0.3
Total Outlet	1056.0	866.5	149.9	16.7	5.9	17.0
Balance Difference	-3.4	-3.5	+1.4	-0.7	+1.6	-2.2
Balance Difference in % of Inlet	-0.32	-0.40	+0.95	-4.0	+37.3	-11.5

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TABLE NO. 13

Element Balance for 6434 Gas Phase Operation with Bituminous Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons
Middle Oil	1000	865.5	134		0.5	0.1
Fresh Gas 192,000 M^3	23.3	2.4	15.9	4.9		
Total Feed	1023.3	867.9	149.9	4.9	0.5	0.1
Cold Separator Oil Gasoline	565	801	136			
Cold Separator Oil Middle Oil	372					
Lean Gas	19.0	7.2	4.9	6.2	0.5	0.2
Rich Gas	63.0	49.4	10,8	1.0	1.6	0.2
NH_3 in Disch H_2O	0.04		0.1	0.03		
H_2S in Disch H_2O	< 0.01					
CO_2 in Disch H_2O	0.02	< 0.01				0.02
Total Outlet	1019.0	857.6	151.7	7.2	2.1	0.4
Balance Difference	-4.3	-10.3	+1.8	+2.3	+1.6	+0.3
Balance Difference in % of Feed	-0.42	-1.12	-1.06	+47	+320	+300

APPENDIX B

CATALYST PREPARATION

Preparation of 5058 Catalyst.

Old catalyst was roasted in air at 300°C. to convert the tungsten to the oxide.

$$WS_2 + 3\tfrac{1}{2}O_2 \rightarrow WO_3 + 2SO_2$$

The tungsten oxide produced by roasting was either treated alone or combined with an impure tungsten oxide called "gelberde" which contained 92 percent WO_3. These oxides were then treated with filtrate from previous catalyst batches. The filtrate was an aqueous solution of ammonium polysulfide and ammonium thiotungstate, and to this added 10 percent make-up ammonia and hydrogen sulfide. After heating to 50°C. and stirring for about 3 hours most of the oxide was converted into ammonium thiotungstate.

$$WO_3 + (NH_4)_2S_x \rightarrow (NH_4)_2WS_4$$

The solution was filtered to remove undissolved material, and the filtrate was heated up to 70°C. Then the ammonium thiotungstate was allowed to slowly crystallize out with continual stirring for 8 hours, during which time the temperature was lowered to 20°C. The slurry was filtered with nitrogen pressure, and the filtrate was recycled to dissolve more tungsten oxide.

The crystals of $(NH_4)_2WS_4$ were not washed, but dried in a nitrogen atmosphere at 100°C for about 3 hours. Great care was taken to prevent access of air to the salt on account of oxidation to the oxysulfide which would result in loss of activity.

$$(NH_4)_2WS_4 + 3O_2 \longrightarrow (NH_4)_2WO_2S_2 + 2SO_2$$

The dry salt was next heated to 400°C in a stream of hydrogen to convert it into tungsten disulfide.

Preparation of 5058 Catalyst (cont'd.)

$$(NH_4)_2WS_4 + H_2 \longrightarrow WS_2 + 2NH_3 + 2H_2S$$

This operation was conducted in a four pass heated kiln with internal screws. The top two passes were heated and had hydrogen introduced to decompose the salt, while the lower two were unheated and used nitrogen for cooling of the tungsten disulfide.

The WS_2 was dry ground so that the average particle size was about 0.5-1 millimeter. Too fine a powder reduced the mechanical strength of the finished pellets. The powder was then pelleted in a regular pellet press to make pills 10 millimeters in diameter by 10 millimeters high. During the operation it was necessary to maintain an inert atmosphere with nitrogen or carbon dioxide around the dies to present oxidation. The pellets were tumbled around in a mill to remove sharp edges and produce smooth uniform cylinders. The finished catalyst was stored under a nitrogen atmosphere until ready for use.

Some of the important data about 5058 catalyst are given in the following table:

Diameter	10 mm
Height	10 mm
Volume	0.785 cm^3
Weight	3.15 grams
Outer surface/pellet	4.7 cm^2
Weight of 1 liter pellets	2600 grams
Pellet surface/ 1 liter of pellets	0.39 M^2
Compression strength	300 kg/cm^2
Compression strength after 1½ years service	270 kg/cm^2

Preparation of 6434 Catalyst.

Fullers earth was activated by treatment with 8-10 percent of 10 percent HF solution by adding the acid slowly and stirring for about 20 minutes. Then sufficient ammonium thiotungstate was dissolved in the mother liquor from which

Preparation of 6434 Catalyst (cont'd.)

it crystallized to give a 10 percent WS_2 content in the finished catalyst. The ammonium thiotungstate was prepared in exactly the same manner as was done for the 5058 catalyst. The mixture was then heated to about 120° C maximum and stirred for about 8 hours until approximately dry.

The mass was then cooled in nitrogen and ground to about 1 to 3 millimeter size before passing through a kiln at 400°C. similar to that used for the pure tungsten sulfide. A 1 to 1 mixture of hydrogen to hydrogen sulfide was used in the heating process instead of pure hydrogen sulfide and nitrogen. After cooling, about 28-30 percent water was added while stirring to the material to give it good cohesive properties in pelleting. The addition of this water did not make the catalyst mass appear wet, since the Fullers earth absorbed it. The lumpy mass was screened to remove pieces over 3 millimeters, the oversize being reground, and then the power was pelleted in the same manner as was done with 5058.

After pelleting the pills were allowed to dry 3 to 4 hours to improve their hardness, and then tumbelled slightly in the mill. After final drying at 100-120°C, the catalyst was stored in a nitrogen atmosphere until used. Before use an initial heat treatment of 8 - 10 hours in hydrogen at 400-450°C improved the strength.

Some of the important facts about 6434 catalyst are given in the following table:

Diameter	10 mm
Height	10 mm
Volume	0.785 cm^3
Weight	1.24 grams
Outer surface/pellet	4.7 cm^2
Weight 1 liter pellets	800 grams
Pellet surface/liter	0.39 m^2
Compression strength	about 200 kg/cm^2

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Preparation of Welheim Gas Phese Catalyst No. K536.

Approximately 90 kilos of crude kieselguhr paste having a water content of 60 percent were mixed carefully for 30 minutes with 4 kilos of 70-72 percent hydrofluoric acid solution. Then 10 kilos of Fullers earth were added and mixed thoroughly. Next 3.7 kilos of zinc oxide plus 3 kilos of flowers of sulfur were added together with 4.6 kilos 50 percent aqueous solution of chromic acid. After 10 kilos more of Fullers earth had been added and the whole charge thoroughly mixed, it was neutralized with about 9 kilos of 0.916 density ammonia solution. Then 1.4 kilos of ammonium thiomolybdate dissolved in 7 kilos of ammonia solution were added together with 4 kilos of Fullers earth and the whole mass thoroughly mixed.

The catalyst was dried to a water content of 30-33 percent and then pelleted into cylinders 10 millimeters in diameter by 10 millimeters high. These pills were dried 3 to 4 days at 75°C before storing. In order to activate the catalyst, it was necessary to heat it for 12 hours in hydrogen at 350°C. After activation the catalyst contained 0.7 percent Mo, 2.0 percent Cr, and 4.0 percent Zn as the active metallic consituents.

APPENDIX C

DRAWINGS

No. C-1 Heat Exchanger, 500 mm. diameter, Assembly
C-2 Gas-Fired Preheater, Section
C-3 Gas-Fired Preheater, Thermocouple Location.
C-4 Sump Phase Converter, 1000 mm diameter, Assembly
C-5 Hot Separator, 800 mm. diameter, Top & Bottom Cooling, Assembly
C-6 Hot Separator, 800 mm. diameter, Gas Injection, Assembly
C-7 Cold Separator, 1000 mm. diameter, Assembly
C-8 Expansion Valve, Assembly and Parts.
C-9 Electric Preheater, Assembly
C-10 Gas Phase Converter, 800 mm. diameter, Assembly.
C-11 Gas Phase Converter, 1000 mm. diameter, Assembly.
C-12 Coking Oven, Screw type, Section and Flowsheet.
C-13 Coking Oven, Ball Type, Flowsheet.
C-14 T.T.H. Converter, 1000 mm. diameter, Assembly.

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