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I.G. RIGHTS IN THE HYDROGENATION FIELD
E. SCHUTZRECHTE
BY O. GÖHRE

TRANSLATED BY
W.M. STERNBERG
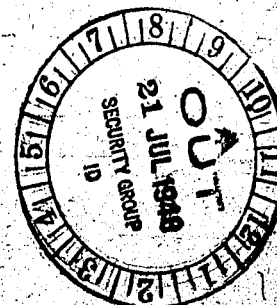
# I.G. RIGHTS IN THE HYDROGENATION FIELD

## By O. Göhre

### INDEX

The developments in the field of hydrogenation to their present stage is represented in over a 1,000 patent applications of the I. G. Farbenindustrie Aktiengesellschaft. These applications were made in Germany and, depending on their importance, also abroad. There are at present over 3,000 patents in the world on hydrogenation belonging to I. G. The Ruhr mining industry fought a bitter patent fight against the German hydrogenation applications, and as a result, before the patent peace of 1936 had been concluded no patents have been obtained on a number of German applications for purely formal reasons. This is the reason why only foreign patents exist on some of the inventions.

The basic patents date from the years 1925-1926. In the course of development especially of active catalysts many process improvements have been discovered, and have been applied in all the modern hydrogenation plants.

We will mention first the development work, in the years 1927-1928, when applications of pressure hydrogenation had been widened and many industrial advances made. E.g., the refining hydrogenation, the pre-hydrogenation, the use of several converters connected in series, operations with hydrogen in a gas circuit and the joint heating of the raw materials with hydrogen in gas heated tubular preheaters, all were developed at that time.

Next followed improvements in hydrogenation catalysts which were of deciding importance for the industrial realization of the process. First came the preparation of highly active sulfides, next the discovery of the so-called dilute catalyst which offer the advantages of increased yield, improved quality of the gasolines, combined with a considerable saving in valuable metals such as tungsten. The preparation and use of these catalysts is protected in almost all countries. These patents will remain for some time yet under the patent protection; patents on a number of special processes in the field of hydrogenation and related fields have been taken out, e.g. the TTH process, the DHD process, the preferential use of which is decided from consideration of the properties of raw material and of the required end products.

The text below gives the principal patents and their development. For this purpose the patents have been arranged in the following groups:

I. Catalysts

a) catalysts: general                        )
b) catalysts: halogens and acids    ) Treated
c) catalysts: iron – tungsten            ) together
d) catalysts: synthetic silicates      ) in the
e) catalysts: reactivation                 ) text

## II. Operating Methods

a₁) vapor phase (treated together with b and c in the text)
a₂) aromatization
a₃) dehydrogenation
a₄) DHD process
b ) liquid phase (treated together with a₁) and c))
c ) pressure range (treated together with a₁) and b))
d ) multi-stage processes
e ) pretreatment
f ) refining hydrogenation
g ) production of lubricating oil by hydrogenation
h ) TTH process
i ) pressure extraction
k ) the use of prehydrogenated coal for the production of coke

## III. Raw Materials and Finished Products

a) special starting materials
b) hydrogen and hydrogenation off-gas
c) the working-up of hydrogenation products
d) the use of hydrogenation products
e) the production of low-boiling aromatic hydrocarbons
f) the production of definite polynuclear compounds
g) production of phenols

## IV. Combination Processes

Hydrogenation and cracking

## V. Technical

a ) materials
a₁) equipment
a₂) Wickelofen
b ) heating

A list of German, French, English and American patents or patent applications arranged in these groups is to be found in the appendix, and their principal features are mentioned.

## I. Catalysts

A few basic patents of F. Bergius (Germ 301,231, 303,893 and others), had already been issued when the I. G. Farbenindustrie A. G., Ludwigshafen/ ~~Oppau became interested in the pressure hydrogenation of carbon-containing~~ materials, after the development of the ammonia and methanol syntheses. These patents have not been in industrial use, but were of importance to the I. G. in the operation of their processes. After taking over the EVAG (Erdöl- und Kohle-Verwertungs Aktiengesellschaft) the I.G. had at her disposal the German rights of the Bergius patents for the working-up of the brown coal, brown coal tar and petroleum; the I. G. could at all times obtain from the Kobergin (Steinkohlen-Bergin A. G.) a license for the hydrogenation of bituminous coal and bituminous coal tar, because they owned the majority of its stock.

No technically useful process of pressure hydrogenation could, however, be carried out with the patents of Bergius alone. The process could only be introduced industrially after the I.G.'s invention in the field of catalysts, which permitted a practically complete conversion of the starting materials into valuable high grade products.

Poisoning of catalysts with sulfur and other non-metals affected very adversely the study and the industrial application of catalytic processes with impure raw materials. E.g., extremely minute amounts of sulfur were sufficient to affect strongly the catalyst in the ammonia synthesis, or even to make it completely worthless. The catalyst used in other catalytic reactions, e.g. nickel in the hydrogenation of naphthalene, became impaired very quickly; even the purest commercial products could not be hydrogenated with platinum, because they still contain traces of sulfur. Industrial hydrogenation could be undertaken in such cases only after an extremely careful preliminary refining.

Bergius therefore believed that the industrial pressure hydrogenation of coal and heavy oils would be only practical without the use of catalysts. Klever worked on the preparation of lubricants from tar and oil residues etc by hydrogenation under high pressure, and he also considered sulfur to be one of the substances interfering with hydrogenation and recommended to have it eliminated from the raw materials (Germ 301,773).

Indeed, all that was known then about catalysts seemed to preclude the possibility of effecting the hydrogenation of coal, coal products and mineral oils with the aid of catalysts, because all these raw materials always contain varying amounts of sulfur.

The investigation of the use of catalyst in these processes without regard to any preconceived ideas was therefore unquestionably an exceptionally lucky and courageous act. The astounding fact for those days has been found for catalysis, that the conversion actually could be catalytically affected, and very effectively at that, by finding substances

which could act catalytically even when containing the most feared catalyst poison, sulfur.

The metallic compounds of the VI group of the periodic system, and particularly the metal sulfides have been found to be the most active among the different metals, non-metals and their compounds. The discovery of the particularly great catalytic efficiency of these metallic compounds has actually made possible the pressure hydrogenation on a large industrial scale.

These catalysts possess not merely the property of directing and accelerating the conversion of coal, tars and oils into lower boiling hydrocarbons, permitting higher thruputs and better yields under milder operating conditions than have been used formerly; these catalysts permit also to make it unnecessary to free the materials used from the elements which ordinarily act as catalyst poisons. Obviously, the application of catalysts would have been made immediately impossible if a complete sulfur removal and purification of raw materials were the necessary pre-requisites. The regular raw materials with their usual sulfur content, phenols and other impurities could be used without any damage to the catalysts, and the remarkable practical importance of catalysts for pressure hydrogenation reactions are based on this fact.

The catalyst patents applied for by Krauch and Pier in the year 1925 were pioneering patents, which formed great milestones in the history of inventions. These inventions form the foundation of the great installations in which hydrogenation gasoline has been prepared for many years (O.Z. 3067, 3073, 3121, 3068, 3072, 3128, 3166)[1].

The importance of this process explains the bitter fight begun inside the industry against these patent applications. In Germany the attack was led particularly vigorously by the Ruhrindustrie, in particular by the Aktiengesellschaft für Steinkohleverflüssigung and the HIAG (Holzverkohlungs-Industrie A.G.). In connection with Professor Varga of Budapest, their attacks were based on the published patents of Bergius and on cracking, as well as on the publications on catalytic hydrogenation of unsaturated compounds, and as a result the patent examination lasted over ten years.

We will discuss in somewhat greater detail the patent fight on the basic catalyst patents. The use of molybdenum in cracking and in hydrogenation under normal or under only slightly raised pressure was known from the work of Ellis and McComb (Brit 160,907, US 1,345,589). If investigators had indeed been directed by this literature to use moly-bdenum (O.Z. 3067, 3073, 3121), and had been moreover forced to assume on the strength of the data given by Bergius that molybdenum is an active catalyst this would have necessitated, that Bergius himself would have used molybdenum. We will therefore present the opinion of Bergius in which he admitted the success of the I. G. in developing the catalytic process.

1). The patents corresponding to these O.Z. numbers are listed in the appendix.

"I may say, that the Ellis and the Klever patents were known to me but I could not deduct from them any particular advantages in using molybdenum, which anyway, has not even been mentioned in the Klever patent.

We have not carried out systematic investigations on catalysts for coal liquefaction in our Mannheim-Rheinau laboratory, because we did not possess the organization required for it. However, even in the occasional chance experiments on the accelerating action of different materials upon hydrogenation reactions which have been carried out by us, and in which I tested a whole number of addition substances, I have never suggested the use of molybdenum in spite of my knowledge of this patent literature.

I wish to emphasize that I consider the use of molybdenum catalyst as a great step forward, which has helped to make the industrial applications of the process practical".

Ellis as well has taken a definite stand on the use of molybdenum catalyst in the pressure hydrogenation (translation of an extract from an opinion expressed in 1935).

"The only catalyst of greater importance known in 1925 was aluminum chloride. It permitted cracking and re-combining hydrocarbons at very low temperatures, and is the only catalyst of its kind. Cracking with this catalyst is entirely different from the purely thermal process and from cracking with other catalysts, because the former process operates at temperatures considerably below 400°C, while the latter are active only at higher temperatures. It appeared for a time as if aluminum chloride could enter in competition with the usual non-catalytic thermal cracking, but the non-catalytic cracking has made great progress and has kept aluminum chloride cracking far behind, so that the use of the aluminum chloride process was limited to a single plant in the United States, namely the Gulf Oil and Refining Company, which also practices on a large scale the usual non-catalytic cracking.

The development of the technique of petroleum cracking was but little affected prior to 1925 by the use of other catalysts then aluminum chloride......... The principal influence of such catalysts before 1925 in this field was of a negative nature. The activity of metals of the iron groups, such as nickel, cobalt and iron was in general recognized, but the principal effect of these substances consisted in setting free carbon which was undesirable, and as a result

this experience tended to frighten one away from the use of these substances for purpose of catalysis, or to reduce their use........

Recommendations have been made before 1925 to use other catalysts than aluminum chloride in order to increase the benzol formation, and that was done even in the earliest days of the development of the cracking technique. The effect of these materials is, however, doubtful in most cases, and almost so slight as to possess no true practical importance. In some cases materials of high commercial value were suggested, e.g. chromium oxide, but their effects had to be very great to justify their use, because of the cost of recovery of the catalysts from the carbonization residue, and these materials have according to my best knowledge found no practical application. There were proposals also to use cheap substances such as iron oxide, the recovery of which was unnecessary. I may illustrate the use of such materials in the early use of the so-called "Gyro-process", which operated at relatively high temperatures and made use of a mixture of iron oxide and cement as a filler in the cracking tubes, apparently for the purpose of catalysis. This process has not been nearly as much used as other processes which operate at lower temperatures without any catalysts.

Except for the above cases catalysts have played but a slight or no role in the United States gasoline production by cracking prior to 1925. Publications on the catalytic pressure hydrogenation, especially the patents issued in the United States to Carl Krauch and Mathias Pier became known at about that time. The process described by these inventors differs from the earlier cracking processes by preferentially working at much higher pressures than used in cracking, and by the use of free hydrogen. The pressure hydrogenation process of these inventors was the first practical communication of the application of catalysts in high temperature processes which were used to crack mineral oil by heat. This process is used in two plants in the United States, with which I am well acquainted, and is in my opinion unquestionably a catalytic process in that the results there obtained could not have been obtained in the absence of the catalysts."

The patent offices as well differentiates between the invention and the cracking technique prior to 1925.

"The cracking technique at first used raised pressure only to permit reaching and maintaining the decomposition

temperature, e.g. from about 650 to 720°C. No thought
was given at first to the possibility of affecting
catalytically the thermal decomposition of heavy hydro-
carbons. The cracking technique developed further in
the course of time, catalysts came into use, and hydrogen
was simultaneously added to decrease the gum forming
tendency of the cracked gasoline. It must, however, be
always borne in mind that the use of this relatively small
excess pressure during cracking was intended primarily for
reaching and maintaining the required cracking temperatures,
and not to increase the concentration of hydrogen for the
purpose of hydrogenation acting upon the raw materials or
the cracking products. This difference in the established
methods manifests itself in the products of the processes,
and can therefore be best established by comparing the
products formed. The formation of considerable amounts of
coke and asphalts is practically unavoidable during
cracking, while in the cracking pressure hydrogenation
almost no coke is formed and relatively little asphaltic
materials, because the hydrogen present in excess counteracts
the formation of these materials and in particular of coke
by saturating the unsaturated compounds............".

The catalytic pressure hydrogenation methods of the I. G. represents
therefore a new path in comparison with cracking and treating with
hydrogen under high pressures without catalysts.

Example I of the German patent 609,538 (O.Z. 3073) states that a
phenol-free almost water-clear product is obtained from brown coal tar
using a molybdenum catalyst, and that the product distills mostly below
350°C. Figure I and Figure II below show the improvement resulting from
the use of the molybdenum catalyst in comparison with the addition sub-
stances known before, such as fullers' earth, zinc oxide, zinc dust,
nickel oxide and alkalized bog-iron ore, with which high-boiling dark
colored tarry products are obtained containing greater or smaller
amounts of phenol.

The first catalysts to gain wide industrial application consisted
of molybdic acid mixed with zinc oxide and magnesia. It has been found
satisfactory in refining, hydrogenation and cracking reactions and excells
particularly in its resistance to mechanical stresses and to chemical
action, such as the asphalt contamination of raw materials.

## Figure 1

### Comparison of Efficiency of Mo Catalyst with other Substances in the Hydrogenation of Brown Coal Low Temperature Carbonization Tar



Specific Gravity of the Product at 15°C

Hours of Reaction

## Figure 2



Residue + 325°C
Phenols

Middle Oil 180-225°C

Gasoline - 180°C

I. $MoO_3$ + ZnO
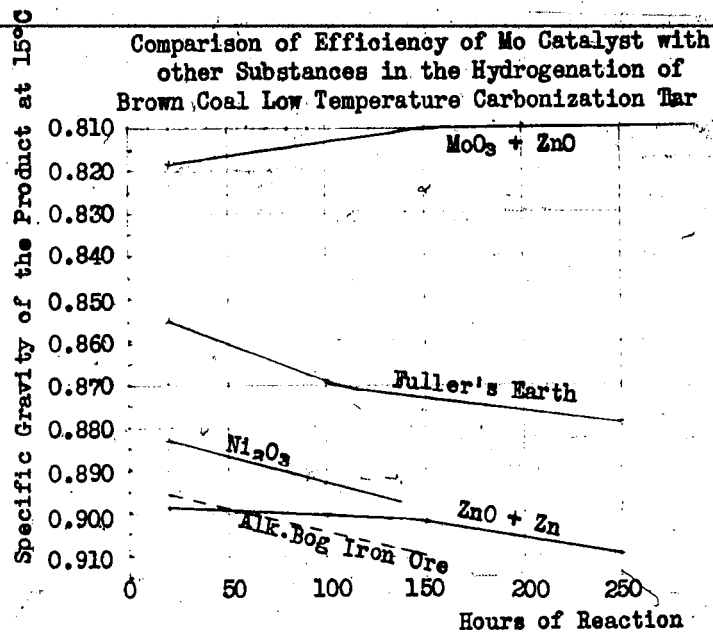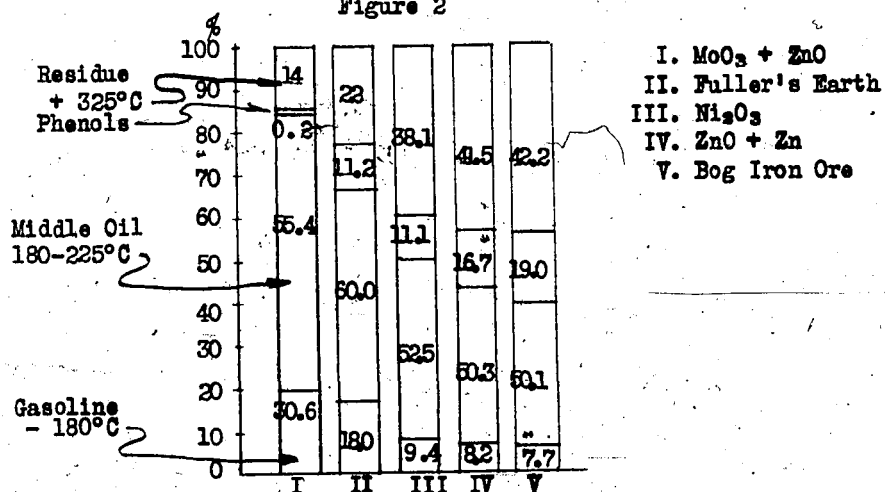II. Fuller's Earth
III. $Ni_2O_3$
IV. ZnO + Zn
V. Bog Iron Ore

The excellent catalytic activity of the heavy metal sulfides was recognized simultaneously with the catalytic effect of molybdenum (O.Z. 3068, 3072, 3120). The sulfides could be used alone or mixed with metals and non-metals, e.g. activated charcoal or oxides, hydroxides, carbonates, halides etc. Even ammonia sulfide can be used as a catalyst. Among the heavy metal sulfides the iron sulfides stand out by their strong activity.

A patent war has also been fought over the sulfide patents, which was successfully terminated by an exhibition test to representatives of the German industry by the "High Pressure Experiments" Ludwigshafen/Oppau. Pressure hydrogenation tests with iron sulfide and iron oxide showed the far greater effectiveness of the sulfides.

Crude cresol from coal tar and a de-hydrated brown coal tar (Producer tar) have been used as the starting materials in these demonstration tests. The iron sulfide catalyst was obtained by sulfurizing pure iron with hydrogen sulfide at 450°C. Pure iron oxide from the oxalate was used as the iron oxide catalyst. The tests with crude cresol were carried out in converters with 100 ml catalyst space. The catalysts were compressed to cylindrical pills about 5 mm in diameter and of about the same height. The reaction space was maintained at 450°C, with a pressure of 200 atm. The thruput was 30 ml/hr, and the hydrogen passed through simultaneously amounted to 150 and 600 ll respectively. The tar tests were run with the catalysts space of 500 ml, the reaction temperature was 475°C.

The specific gravity of the products from crude cresol obtained with the iron oxide was 0.918, while with iron sulfide it was 0.818. The initial boiling point with the iron oxide was 82.5°C, with iron sulfide 100.5°C. Accordingly the products obtained with iron oxide contained 12.6% gasoline boiling below 100°C, while the products obtained with iron sulfide contained no gasoline fractions boiling below 100°C. On the other hand the proportion of gasoline boiling to 120, 150, 180°C was very much lower with iron oxide than with the iron sulfide, and namely

|  | Iron Oxide | Iron Sulfide |
|---|---|---|
| Up to 120°C | 31.7% | 76.9% |
| " " 150°C | 43.5% | 80.1% |
| " " 180°C | 50.9% | 90.5% |
| " " 200°C | 62.8% | 92.8% |

The products obtained with iron oxide contained 50.7% of neutral oil, against 92.1% in the product obtained with iron sulfide.

Experiments with raw cresol have shown that the iron oxide was

preferable in the formation of gasolines boiling below 100°C than the iron sulfide. On the other hand, in all the other counts, such as specific gravity, neutral oil content, amounts boiling to 120, 150, 180 and 200°C, iron sulfide was preferable.

The specific gravity of the products made with iron sulfide proved superior also in the experiments with tar.

Specific gravity of products with iron oxide     0.894
"        "        "        "        "        "     sulfide   0.850

The initial boiling point with iron oxide was 74°C, while with iron sulfide it was 92.5°C. In these tests gasolines boiling below 100 and 120°C have not been determined as in the raw cresol tests. We may assume that the amounts of gasoline boiling below 100°C and 120°C were greater with iron oxide than with iron sulfide. On the other hand the fractions boiling to 150, 180, 200, 250, 300, and 325°C were greater with iron sulfide than with iron oxide, and namely:

|          | Iron Oxide | Iron Sulfide |
|----------|-----------|-------------|
| to 150°C | 4. % | 8.3% |
| " 180°C  | 9.2% | 18.2% |
| " 200°C  | 16.0% | 25.3% |
| " 250°C  | 36.5% | 47.2% |
| " 300°C  | 55.3% | 70.9% |
| " 325°C  | 68.1% | 79.8% |

The phenol content of gasolines boiling to 200°C amount to 15.5% with iron oxide, as against 1.35% with iron sulfide. The iodine number of the de-phenolated gasolines was 66.4% when produced with iron oxide and 9.6% with iron sulfide. The specific gravity of the middle oils boiling between 200 and 325°C, obtained with iron oxide was 0.922, with iron sulfide 0.881. The phenol content of these middle oils was 13.65 with the iron oxide and 0.92% with iron sulfide, the aniline point (a measure of the degree of hydrogenation) was + 19.7 with iron oxide and + 30.5 with iron sulfide. The corresponding iodine numbers are 32 and 15.1. No appreciable difference could be found in the sulfur content.

Comparative tests performed with tar have produced essentially the same kind of a picture favoring the iron sulfide catalyst, as was obtained in the experiments with raw cresol.

Tests with coal gave similar advantages to sulfides against the oxides. Autoclave tests with Brassert coal (pasted with bituminous coal-tar oil) at 150 atm initial pressure, 440°C, and the addition of 5% of either iron oxide or iron sulfide gave:

|  | kg oil from 1,000 kg bituminous coal | % asphalt in total oil | % utilization referred to pure coal |
|---|---|---|---|
| Iron oxide | 710 | 10.0 | 90 |
| Iron sulfide | 760 | 7.5 | 98 |

The favorable effect of higher pressures has also been established with the discovery of the sulfide catalysts.

Middle oil was hydrogenated under 15 and 75 atm total pressure and 477°C in 200 ml high pressure converters, filled either with chips of clay or with a catalyst composed of 80 parts cobalt sulfide and 20 parts manganese sulfide.

The composition of the original oil was,

| | | |
|---|---|---|
| specific gravity | 0.942 | |
| phenol content | 25.1 % | |
| boiling point curve: | | |
| 212 – 225°C | 8.6 % | |
| –250° C | 51.4 % | |
| –300° C | 92.8 % | |
| distillation end 312° C | 96.2 % | |

After phenol removal
specific gravity        0.893
unsaturated        abt 43. %
sulfur        1.35 %

The results of tests are shown in the table below

### Effects of Pressure During Hydrogenation With and Without A Catalyst

| Pressures | 15 atm H₂ | | 75 atm H₂ | |
|---|---|---|---|---|
| Catalysts or filling | Clay Chips | Cobalt + Manganese Sulfides | Clay Chips | Cobalt + Manganese Sulfides |
| **Final Products:** | | | | |
| Phenol content | 18.7 % | 16.0 % | 21.5 % | 4.46 % |
| de-phenolated end-products, sp.gr. | 0.892 | 0.872 | 0.883 | 0.825 |
| Unsaturated | 31.1 % | 19.8 % | 25.8 % | 2.1 % |
| Sulfur | 1.34 % | 0.78 % | 1.13 % | 0.005 % |
| Boiling curve: | | | | |
| –200°C | 13.1 % | 13.0 % | 15.4 % | 42.6 % |
| –250°C | 45.7 % | 46.6 % | 48.2 % | 77.5 % |

The catalytic activity of tungsten and molybdenum sulfides exceeds that of all the other sulfides.

One may start with the sulfites or sulfates instead of the ready made sulfides, because they are converted to sulfides during hydrogenation or by the addition of sulfur to the catalysts, e.g. the metals or metallic oxides.

The sulfides can be produced in a variety of ways, e. g. by treatment of metals, oxides, hydroxides or halides with hydrogen sulfide at an elevated temperature. It has also been suggested to carry out the hydrogen sulfide treatment at increased pressures (O.Z. 7017). The sulfurization may also be carried out at increased pressures and in the presence of hydrogen (O.Z. 5851). It has been found that sulfides prepared in different ways behave catalytically differently.

Treating the metallic sulfides produced in any way with sulfur or with oxygen-free volatile sulfur compounds increases their activity (O.Z. 6935, 10,870). These sulfides differ from compounds previously known in that they are saturated with sulfur and do not contain a trace of oxygen. With the usual methods of preparation of sulfides, small amounts of oxygen are still present, which reduces their catalytic activity in the pressure hydrogenation of coal, oils, etc. The Germ 686,456 (O.Z. 10,870) shows that the gasoline yield of the petroleum middle oil hydrogenation with oxygen-free re-sulfured tungsten sulfide increased by 58 to 65% against the commercial tungsten sulfide.

Sulfides prepared by way of the sulfo_salts (O.Z. 6935) have a particularily high catalytic efficiency. Tungsten sulfide catalysts prepared in this way have been used industrially on a large scale and are used whenever the hydrogenation reaction is the principal in importance, e.g. in the prehydrogenation, the lubricating oil refining, the TTH process, and has been used for a long time also in the splitting reaction (benzination).

-Sulfides of several metals can be conveniently prepared by a double decomposition of sulfo-salts with heavy metal compounds in solution or suspension in water or in organic solvents, such as acid amides, acid chlorides, amino acids, keto acids, amines etc. (O.Z. 8233).

Such sulfide mixture can also be prepared by heating mixtures of ammonium sulfo salts prepared in the dry way and containing the metals of the VI group in the acid radical, with finely divided metals of the iron group prepared from carbonyls, to temperatures in excess of 300°C (O.Z. 12,089).

According to this patent application the nickel-tungsten catalyst, frequently used in hydrogenation and dehydrogenation, is obtained by mixing nickel, obtained by a thermal decomposition of nickel carbonyl,

with ammonium sulfo tungstate in a molar proportion of 1 : 2, and treating the mixture at 400 to 450°C in a stream of hydrogen... Such a catalyst produced in a dehydrogenation test a gasoline..with 57% aromatic hydrocarbons from a coal liquid phase gasoline containing 7% aromatic hydrocarbons.

We may mention under the sulfide mixtures also the weakly hydrogenating sulfides in combination..with smaller amounts of strongly hydrogenating sulfides (O.Z. 9136, 9675, 9982).

Thus a catalyst has been used composed of 85% FeS and 15% WS2. A comparison of the activity of such a catalyst with tungsten sulfide and with molybdenum sulfide, and with a mixture of 85% WS2 and 15% FeS shows that the phenol reduction proceeds almost as well as with the tungsten sulfide, but that the hydrogenation is much weaker, so that the neutral oil was composed of 66% aromatic hydrocarbons.

| Catalysts | WS | FeS | 85% WS2 15% FeS | 15% WS2 85% FeS |
|---|---|---|---|---|
| % of neutral oil | 100 | 80 | 98 | 99 |
| % aromatic hydrocarbons in neutral oils | 3 | 27 | 5 | 66 |

Sulfides may also be deposited upon carriers such as bleaching earth, clay, activated charcoal etc. These carriers may be pretreated in certain ways e.g. sprayed or saturated with hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid or organic acids (O.Z. 7732) or else charged with halogens or hydrogen halides, (O.Z. 8231). The catalytically most active carrier consists of a siliceous mass, e.g. fullers' earth, pretreated with fluorine, hydrogen fluoride or hydrofluoric acids (O.Z. 8695). Such a pretreated fullers' earth mixed with about 10% tungsten sulfide has found industrial application as a catalyst for the splitting pressure hydrogenation.

A middle oil obtained by pressure hydrogenation of brown coal produces with such a catalyst at 425°C and 200 atm hydrogen pressure 60% of -185°C gasoline, while the same catalyst in which the fullers' earth had not been pretreated produces only 40% of -185°C gasoline.

It has been found that in the pressure hydrogenation with this catalyst the formation of methane is suppressed in favor of the higher gaseous hydrocarbons. This method of operation is therefore well suited for the production of large amounts of propane and butane (O.Z. 9496).

We may mention in addition that when sulfides are used the splitting is suppressed in favor of an increased yield of the products richer in hydrogen and a boiling range within the limits of the starting materials,

if pressure hydrogenation with the heavy metals sulfides be carried
out with the addition of small amounts of basic materials, in particular
of ammonia or of substances which produce ammonia (O.Z. 8490).

We may mention here briefly in connection with the sulfide patents
about the proportioning of the amounts of sulfur to be added. After
publication of the use of molybdenum and tungsten sulfides in the
pressure hydrogenation and the advantages of the presence of hydrogen
sulfide in the reaction converters, in amounts of 1-6% of the hydrogenating
material, J. Varga has applied for patents for a similar process two years
later. The German patents refer to our methods of operation in which the
hydrogen sulfide concentration in the reaction space is altered depending
on the improved activity of the molybdenum and tungsten catalysts with
every particular starting material, until the optimum efficiency is obtained
with regard to the yield of the desired reaction products. The hydrogen
sulfide content in the hydrogenation reactor is then set at the level
found to be the most advantageous (Germ 639,762, 761,884).

The I. G. possesses additional patents on sulfur concentration e.g.
the catalyst is added to the starting material for hydrogenation before
heating, and substances promoting the catalytic activity, such as sulfur
containing substances are added after heating (O.Z. 8425). The starting
materials such as coal may also be pretreated with sulfur (O. Z. 8620,
8621). A still further method of the I.G.'s consist in adding sulfur only
intermittently, and the time intervals when none or only very little sulfur
is added, are extended until the increased activity of the catalyst
resulting from previous additions of sulfur has begun to decrease (O.Z.
10,391).

The basic molybdenum and sulfide patents have been discussed in
somewhat greater details and the other catalyst patents will be only
briefly mentioned. Details can be obtained from the patent list in the
appendix.

Special patents similar to molybdenum have been obtained for the
other metals of the VI group of the periodic system, especially tungsten
and chromium (O.Z. 3166, 8863).

The compounds of chromium can be used jointly with the sulfides of
molybdenum or tungsten (O.Z. 12,632, 12,633, 12,986).

When using iron compounds it is advantageous to add to them alkali
metal compounds (O.Z. 8483, 8711, 8962), in contradiction to the metals
of VI group. These substances may be used as sulfides (O.Z. 10,735).

In addition to the highly active catalysts of the VI and VIII groups,
tests were also made with silver, copper, cadmium, zinc, lead, bismuth,
titanium and tin in the metallic or in the combined form, as well as with
the oxides and carbonates of zinc, manganese, compounds of vanadium alone

or mixed with other metals, e.g. of the VIII group, or their compounds (O.Z. 3283, 3701, 3712). Of these elements tin has acquired a greater importance (O.Z. 9124, 9278, 9179) and is introduced by the I.C.I. in the form of tin oxalate as a catalyst in the hydrogenation of bituminous coal at 300 atm pressure.

Methanol-forming catalysts are of importance when working with hydrogen, containing carbon monoxide (O.Z. 3266).

A number of applications cover the use of metallo-organic compounds, which may be used upon carriers (O.Z. 6442, 6633, 6636, 6792, 8554, 9222, 9179, 11,658).

Furthermore patents have been applied for combinations of different metallic compounds. Good results have been obtained in the use of combinations of metals of the IV to VIII group with compounds of metals of the II to VII group, which are usually used in smaller amounts than those mentioned first (O.Z. 3699). The use of catalysts consisting of three metals is very significant, with two of the catalysts belonging to groups higher than the IV (O.Z. 5102, 10,380).

Other substances in addition to the metals and sulfur are of importance. Hydrogen halides and organic halides increase the activity of the metal-containing catalysts (O.Z. 3700, 7384). Halogen-containing catalyst compositions have found greater application in the coal hydrogenation. Hydrogen halide was used at first in the form of hydrochloric acid to neutralize the basic constituents of the coal ash prior to pressure hydrogenation. Larger amounts of hydrogen chloride were later used (O.Z. 8162). Other acids such as the oxygen acids of sulfur and nitrogen may also be used (O.Z. 7493).

Difficulties with construction materials have been experienced when operating with halogen, in particular where the steam formed could condense during cooling after leaving the reaction space. The I.C.I. inserted a vessel containing alkaline compounds between the converter and the catchpot, where the hydrogen halides would be neutralized before reaching the critical temperature range. Similar processes have also been used by the I.G. (O.Z. 8447, 10,020). Some substances combining with the halogens can be added towards the end of the reaction (O.Z. 8555). It has further been attempted to passivate the walls of the vessel by the addition of arsenic compounds (O.Z. 8136).

The use of metal halides together with halogen and halogen halide was more significant (O.Z. 8170).

Not only the coal used in hydrogenation may be pretreated with halides, but activated charcoal and similar adsorption materials may be subjected to a similar pretreatment before being used as carriers (O.Z. 8231). Similarily, carriers may be pretreated with other acid

materials (O.Z. 7732) or with gases (O.Z. 7728, 7841).

The addition of halogen compounds in the form of hydrogen halide or organic halogen compounds is particularly advantageous when iron, zinc, tin, titanium, manganese and lead are used (O.Z. 8534, 8553, 9174, 9212), as well as with the metals of the V and VI groups (O.Z. 7398, 7400).

Boron, phosphorus, arsenic and the compounds of these non-metals have been successfully tested and patents applied for (O.Z. 3700).

Magnesia, chromium oxide and metals were used as carriers in addition to fullers' earth and activated charcoal (O.Z. 4096, 3701).

Fullers' earth has been found particularly advantageous as a catalyst carrier among the many substances tried, and its catalytic activity has been increased by pretreatment with halogens, in particular by fluorine, by swelling (O.Z. 9100) or by the addition of active silica (O.Z. 14,062), as well as by the addition of definite amounts of oxides of magnesium, zinc or beryllium to produce a suitable acidity (O.Z. 12,807); as a next step aluminum silicates have been produced synthetically. This was done by combining siliceous materials in the form of gels with solutions of salts of metals (O.Z. 10,157, 10,167). The silicate is preferably formed from the solution of silicate gel with a pH between 3 and 7 (O.Z. 11,079, 11,081, 11,226, 11,252, 11,316, 11,623). The finished silicate must be free from alkali metal compounds when used as a catalyst (O.Z. 11,196).

A silicate thus prepared can be used as a carrier for the compounds of metals, in particular of molybdenum, tungsten, vanadium or chromium.

Synthetically produced silicates containing compounds of the metals of the II, III and/or the VIII group of metals and pretreated with fluorine are also very well suited as catalysts, if the finished silicate contains less fluorine than is equivalent to the metals of the II, III and/or VIII group contained in them (O.Z. 14,782, 14,819).

Water soluble magnesium salts or metals of the II, III or VIII groups have been mixed with the known hydrogenation catalysts in order to increase their mechanical strength (O.Z. 4025, 4517). The much used molybdic acid is given the necessary mechanical strength by combining it with zinc oxide. The finely dispersed metallic compounds are mixed with water, the water evaporated from the paste, the mass ground with the addition of dry metal compounds to produce a very hard catalyst containing molybdic acid (O.Z. 8248) which is distinguished by being very little affected by the high molecular weight substances.

The catalysts may be used in a fixed bed arrangement in the reaction space or else in the finely divided state. In this case it is advisable to add the catalysts or some parts of it to different locations of the installation (O.Z. 7312).

The life of the catalyst in pressure hydrogenation is very long,
e. g. one to two years; the catalysts can then be again made ready for use
in a variety of ways (O.Z. 5898, 6403, 8056, 8843, 11,079).

II. **Methods of Operation**

a₁) **Vapor Phase**

The experience gained in the industrial synthesis of
ammonia and methanol, both of which are based on catalytic gas reactions,
determined the applications of the methods in the initial operations
with tars and oils. The vapors were led over fixed bed catalysts. In
case of higher boiling oils the feed was finely dispersed in the catalyst
space by pulverization, aromatization, etc (O.Z. 3161). It has been
found, however, that with the higher boiling feed only then low boiling
final products and a lasting activity of the catalysts could be
obtained if the thruput and the partial pressure of the feed were kept
low (O.Z. 3618).

Middle oils were therefore selected for the splitting reaction as
the starting material in order to permit performing the reaction in a
pure vapor phase (O.Z. 3636). It may be pointed out in this connection
that operations in the vapor phase in this field were fundamentally new.

The vapor phase reaction has been mastered to such an extent that
it became possible to systematically investigate catalysts in vapor phase
reactions and to arrange them according to their activity. The catalysts
in general were used in a fixed bed and in some cases their mechanical
strength improved by additional compounds (O.Z. 4025, 4517, 8248, 13,043).
Experiments have also been conducted with finely divided catalysts
fluidized by the gas, (O.Z. 3678, 6676). The causes of the drop of the
catalytic activity with higher concentration of the feed have become
recognized more clearly, and this has permitted operating with appreciably
higher partial pressures (O.Z. 5839), when the gasoline formed was removed
from the converters and all the other products were re-circulated by means
of pumps (O.Z. 4169, 4423). The thruput was increased in this way and
the quality of the product, in particular the anti-knock property of the
gasoline, was favorably affected (O.Z. 5084, 5839).

A suitable choice of the catalysts e.g. metal sulfides upon carriers,
permits the extensive conversion of the raw materials in the vapor phase
hydrogenation into valuable gaseous hydrocarbons such as propane (O.Z.
9157, 9496).

a₂) **Aromatization and** a₃) **Dehydrogenation**

Depending on the nature of the materials used in the vapor phase,
paraffinic and naphthenic hydrocarbons can be dehydrogenated or converted
into cyclic compounds in the vapor phase. In such a case there is a more
or less extensive new formation of aromatics, with the evolution of hydrogen.
The materials to be dehydrogenated may also be conducted over catalysts
in the presence of hydrogen, hydrogen-containing gas mixtures, or inert
gases. It has been shown that the presence of hydrogen during dehydro-
genation strongly depresses the formation of high molecular weight compounds

and increases thereby the activity of the catalysts, improving the
yield and the thruput. When operating in this way, temperatures were
selected of 450 - 600°C and at either normal or increased pressures.

The pressure hydrogenation of middle oils and gasolines, preferably
the higher boiling gasoline fractions (O.Z. 6082) has been carried out
in the vapor phase on the strength of the experience obtained at temperatures
at 500°C and above, with the production of final products enriched in
aromatic hydrocarbons. The formation of high molecular weight coke-like
substances was prevented during this "aromatizing pressure hydrogenation",
but the gasification is greater than during the cracking pressure hydro-
genation which is carried out at lower temperatures (O.Z. 3617, 3847).
Under such conditions it is recommended to form first from the initial
products the higher aromatic hydrocarbons in a more or less pure state,
and then crack these to the required low-boiling aromatic hydrocarbons.
The principal catalysts are the oxides of the metals of the VI group which
can be advantageously deposited upon carriers such as alumina, pumice,
or activated charcoal (O.Z. 3464, 3474, 3617, 3847). Later, a chromium-
vanadium catalyst deposited upon activated charcoal has acquired greater
importance for the aromatization under high pressures (O.Z. 11,328,
11,729).

The dehydrogenation process for gasoline has been developed from the
experiences gained in the dehydrogenation with hydrogen and the aromatization
under high hydrogen pressures. The feed is dehydrogenated at low hydrogen
pressures, e.g. 30 - 60 atm with a gasoline vapor partial pressure of
0.5 to 3 atm, using as catalysts a mixture of the oxides or sulfides of
the metals of the VI group with those of the VIII group (O.Z. 7950, 7952,
9987, 10,210, 11,578). When operating under such conditions and using as
feed a pressure hydrogenation product boiling below 256°C, safety fuel
could be obtained (O.Z. 10,210).

Work with the original catalysts deposited upon alumina, e.g. alumina
-chromium or alumina-molybdenum oxide, were then resumed at normal pressures
or at 3 - 50 atm to convert the paraffinic hydrocarbons into cyclic
compounds (O.Z. 10,062).

a₄) The DHD Process

The Standard Oil Company of New Jersey and the Kellogg Company
produced aromatics a few years later with the above mentioned catalysts
and at pressures of 2 - 40 atm. Unlike the aromatizing pressure hydro-
genation operations at high pressures, no attention was paid to the long
life of the catalysts, and intermittent operations commonly used in the
catalytic cracking were adapted with short operating cycles, followed by
the reactivation of the catalysts. The reactions are carried out in the
presence of hydrogen which is introduced at the beginning of the reaction
and is continuously circulated through-out the process; the reaction proceeds
without hydrogen consumption, because hydrogen is steadily formed as a
result of dehydrogenation. This so-called H.F. (hydro-forming) process

was mostly used by the Standard Oil Company and the Kellogg Company for the improvement of the octane number of more paraffinic gasolines.

This method of operations was studied by the "Division of High Pressure Experiments" of the I. G. They found that pressures in excess of 40 atm and up to about 90 atm were preferable when operating with the coal hydrogenation gasolines, in particular from bituminous coal. The process adjusted to the German conditions called the "DHD Process". Higher yields were obtained at higher pressures when working with naphthenic gasolines and their octane number was higher than during operations at lower pressures. In addition, the life of the catalysts was improved, and the cycles used could be lengthened. The partial pressure of hydrogen in the DHD process was 20 - 70% of the total pressure, but was kept below 30 atm. The gases leaving the reaction space were recycled in a proportion of 0.5 - 4 cbm per kg of the feed (O.Z. 11,888). Naphthenic middle oils could be worked up in the same way (O.Z. 11,808), while lower pressures had to be used with paraffinic middle oils (O.Z. 11,807). The most active alumina was obtained by precipitation from aluminum salt solutions at temperatures above 80°C and a pH of 7 - 10 and then heating (O.Z. 12,718, 12,694, 12,916, 15,032). The alumina obtained by peptization with nitric acid has been found to be particularly well adapted as a carrier substance (O.Z. 12,054, 14,183, 15,033). Small amounts of one or several of the oxides of molybdenum, chromium, tungsten, or vanadium were added to this alumina. Small amounts of other metal compounds added to the above catalysts have been found to be beneficial. Among these were the fluorides of metals, ammonium, or of non-metals free from alkalies, (O.Z. 12,743, 12,924); also the compounds of lithium, magnesium, beryllium, zinc, zirconium or titanium (O.Z. 12,657) have shown to possess good additional catalytic properties.

The catalyst in the reaction space may either be arranged in a fixed bed or else be in the fluidized state (O.Z. 12,897, 13,679, 12,926, 13,627).

The DHD process may also be used for the production of low boiling aromatic hydrocarbons by de-alkylation of the higher boiling aromatic hydrocarbons and in this case it has been found advisable to add up to 30% of silica or silicates to the catalyst (O.Z. 14,368, 12,207).

The high boiling hydrocarbons can be converted into middle oils under the DHD conditions, and the latter converted by cracking pressure hydrogenation into anti-knock fuels (O.Z. 12,180, 12,769).

The DHD products boiling above the end point of gasolines can be converted into anti-knock gasoline by cracking pressure hydrogenation in the presence of active silicates, (O.Z. 14,123). The silicates can be entirely or partly replaced with alumina and heated with fluorine compounds or combined with metallic fluorides (O.Z. 14,431).

DHD permits also carrying out a refining pressure hydrogenation of

contaminated crude hydrogenation middle oils and a catalyst consisting
of alumina, molybdenum and nickel has been found suitable for the
purpose (O.Z. 12,477, 12,478, 14,410).

The DHD process forms a connecting link between the catalytic
pressure hydrogenation and the catalytic cracking processes because of
the manyfold applications.

b) Liquid Phase

The liquid phase was used by Bergius without any catalysts
as a single stage process, but it was not successful in this form, since
it produced principally heavy products of little value and operations
could not be modified for the production of any definite final products.
The use of the liquid phase in combination with the vapor phase was of
deciding importance, as will be discussed below under "Multi Stage
Processes".

In the liquid phase the hydrogenation gases had to be brought into
intimate contact with the liquid. The mixing arrangement described in
the Bergius patents Germ 337,388, 289, 946 was insufficient to utilize
the hydrogen satisfactorily and to prevent a deposition of asphaltic
materials. Operations in thin layers was recommended to bring about a
good contact of the liquid with the gas (O.Z. 3590) and later on a good
distribution of the gas was produced by leading the hydrogenation gas
into the tars through porous plates, (O.Z. 3605). A good gas distribution
can also be secured by the use of orifices and by other methods (O.Z.
4420, 4933). On a large industrial scale the mixing of the two components
is done by conducting the liquids and the gases through several converters
connected in series (O.Z. 4445).

Catalysts are equally important in the liquid phase. Special catalysts
and means for keeping them in an intimate mixture with the feed are
described in patents O.Z. 4423, 5141. The use of finely divided catalysts
in the liquids leads to a circulation of the liquid with the suspended
catalyst. The catalysts are kept at a certain concentration, and enough
make-up feed must always be added to correspond to the amount of the lower
boiling products withdrawn, thus maintaining the original concentration
of the catalyst, (O.Z. 5141, 6136). Catalysts may be recovered under
certain conditions by withdrawing a certain proportion of the oil-catalyst-
recycle (O.Z. 5141).

Bergius operated only in the liquid phase and he mentioned in his
patents certain additions (alkalyzed iron, lux mass or red mud, alkali
metals); however, these additions were supposed to be effective only for
de-sulfurizing and for dispersion. Larger amounts of them are added to
the original feed and removed from it and they are not to be considered
as catalysts.

In the preparation of the paste a high boiling oil, a product of the reaction, is used in the hydrogenation of coal for the production of middle oil. Should, however, a heavy oil or a fuel oil be desired as the end product of the process, the coal is pasted with the hydrogenation middle oil produced with the residue (O.Z. 9187, 9817, 13,114, 13,555).

Coal can also be pressure hydrogenated in the powdered form without any pasting medium. In this case the solids can be separated from the vapors and gases without great drop in the temperature (O.Z. 13,988).

c) High Pressures

In 1925 the catalytic pressure hydrogenation of coal, tar, and mineral oil was carried out on a small scale at 200 atm and at 600 - 1,000 atm (Fr 616,237). Large scale operations in Leuna have shown that 300 atm are advisable for that purpose. Experiments with hydrogen dissolved at 500 atm and above were carried out in 1930 (Germ 669,049). At the same time operations were conducted with a finely divided catalyst passing continuously through the reaction space at 500 and 1,000 atm (Fr 718,956). Finally, higher boiling substances, such as brown coal tar and petroleum residues were hydrogenated with finely divided catalysts at 400 atm. Operations were conducted in 1932 at 300, 500 and 1,000 atm with diluted catalysts in which the carrier substance, such as bleaching earth was pretreated with hydrogen or with acids (Fr 747,459, 762,324, 44,183 supplement to 750,296).

When bleaching earth pretreated with hydrogen fluoride was found in the course of this work as a carrier for molybdenum and tungsten compounds, with this catalyst experiments were carried out under pressures of 300, 400, 500, 700 and 1,000 atm (Fr 800,972, 821, 792).

The direct hydrogenation of coal was also investigated at pressures of 250 - 500 atm, especially for the production of lubricating oils from brown coal.

The pressure hydrogenation of asphalts and pitches in the liquid phase at pressures of 300 - 700 atm was closely investigated in 1935, 1936. The use of catalysts of varying degrees of effectiveness were studied in large numbers of experiments with asphaltic substances and with coal of varying carbon content at pressures exceeding 300 atm (O.Z. 9274, 9397, 10,101, 10,562).

Vapor phase hydrogenation at 700 atm was studied systematically simultaneously with the experimental liquid phase hydrogenation at 700 atm (O.Z. 9366). Results showed that operations could be conducted at 700 atm with higher thruputs and with a simultaneous reduction in the amount of the molybdenum and tungsten deposited upon the carrier substances. It is even possible to operate at pressures of 400 to 800 atm with pretreated fullers' earth or synthetically prepared silicates without

the addition of oxides or sulfides of the metals of the VI group, when operating with refined products (Fr 841 898, O.Z. 11 056, 12 390).

### d) Multi Stage Processes

The great variety of the raw materials to be hydrogenated as well as of the finished products makes it preferable in many cases not to convert the raw materials in one stage to a definite finished product. Pressure hydrogenation is therefore carried out in several stages. The different stages of the processes may be carried out at different temperatures, pressures in different phases, catalysts and occasionally with the recovery of intermediates.

The multi stage processes have acquired the greatest industrial significance in the manufacture of gasoline from coal, tar, and high boiling oils. The first stage is carried out in the liquid phase and produces middle oil. This latter is split together with other similar products in the vapor phase in a second stage (O.Z. 3105).

The considerable differences in the mode of acting of catalysts brought about a staged treatment by catalysts, with alternating splitting and hydrogenating catalysts in the different stages, with a recovery of those products from every stage which were particularily valuable in that form, and which occasionally were treated further separately (O.Z. 3688, 4445, 4890). The removal of polymerization products which would harm the catalysts may be one particular purpose of the pretreatment, and this treatment raises the life of very valuable catalysts (O.Z. 4481). It may be worth while to separate products which can be but little improved at moderate temperatures and to treat them separately at higher temperatures (O.Z. 4444, 5037), to prevent a strong gasification of the previously formed lighter fractions. The different pressure stages (O.Z. 4334) are of particular importance when other products than motor fuels, e.g. lubricating oils, are required.

### e) Pretreatment

The refining effect of pressure hydrogenation catalysts can be utilized to have the first stage perform a refining pressure hydrogenation, and then treat the purified products obtained using very sensitive catalysts in a second stage (O.Z. 3288, 4434, 4809, 5256, 5621, 5768). Hydrogen -poor raw materials, which contain principally asphalts, are first hydrogenated under milder conditions, which removes any asphalts present. It is advisable to remove the lubricating oils and paraffins before the next cracking hydrogenation (O.Z. 4890). Asphalts and resins may also be removed by adsorbents or by liquefied methane hydrocarbons prior to the catalytic pressure hydrogenation (O.Z. 5322, 6679, 7106).

It is particularly advisable for the hydrogenation of oils and tars in the liquid phase with a fixed bed catalyst to remove the asphaltic

materials and resins with adsorbents, by chemical agents or by vacuum distillation, as it is done in the vapor phase (O.Z. 5955, 6106, 9752, 10,464).

Organic nitrogen bases frequently interfere with the catalyst activity especially of the dilute vapor phase catalysts. It is therefore advantageous to remove nitrogen bases with greatly diluted acids, which do not affect the olefins (O.Z. 8330, 14,733). Another pretreatment consists in the distillation at atmospheric or reduced pressures (O.Z. 6881), which permits one to select a high end point hydrogenation feed (O.Z. 8160). In connection with this process the pressure distillation of asphaltic raw materials and of pitch has been developed. The oil fractions thus obtained as vapors were catalytically hydrogenated under pressure (O.Z. 11 308, 11 665, 12 209).

To adapt the hydrogenation more efficiently to the desired products the raw materials may be selectively extracted, and to convert the hydrogen -poor fractions into anti-knock fuels, and the hydrogen-rich into diesel oils and lubricating oils (O.Z. 7494, 8436, 10 632).

It is at times necessary, at times preferable to dry the coal before hydrogenation (O.Z. 3343, 3676, 4477, 4631, 4771) by heating it under pressure (O.Z. 4168), or to deash it (O.Z. 9568, 8985), e.g. by treating with acids (O.Z. 7756, 8088, 9590, 10 053, 7962), or merely to neutralize with acids the basic constituents of ash.

f). Refining Hydrogenation

It already has been mentioned that the catalytic pressure hydrogenation may also be used for the refining of impure products. We thus can refine catalytically in the vapor phase crude benzol (O.Z. 3288, 5067, 5955), crude gasoline (O.Z. 4434, 7951, 11 960), crude phenols (O.Z. 7130) and oxygenated products of the reduction of carbon monoxide (O.Z. 8520, 8521), as well as other volatilizable hydrocarbons similar to middle oils (O.Z. 4434) or even lubricating oils (O.Z. 6084). Refining hydrogenation of high boiling products may also be carried out in the liquid phase. We can refine and improve the quality of heavy oils, fuel oils, and lubricating oils by catalytic pressure hydrogenation (O. Z. 4809, 9721), and improve their quality. Paraffins (O. Z. 4793, 6598), waxes (O.Z. 3731, 7149) and glycerine (O.Z. 14 550) can be freed from impurities in this manner. Finally the industrial production of a high grade vaseline was developed using the refining pressure hydrogenation (O.Z. 14 714, 14 810).

g) Production of Hydrogenation Lubricants

The quality of the lubricating oils produced can be also greatly improved by refining. By splitting one part of the lubricating oil results in the production of an oil which is greatly superior to the original oil, chiefly in the color, viscosity, and viscosity index (O.Z. 7234).

Processes have been developed in the course of time to obtain good
lubricating oils from coal and to separate them from other hydrogenation
products (O.Z. 8055, 8334, 8693, 9081, 9543).

## h) TTH Process

The TTH process falls into the range of pressure hydrogenation
under mild conditions. In this process oils and tars containing high
boiling asphalts and gums were pressure hydrogenated with fixed bed
catalysts at 270 - 380°C under such mild conditions that the asphalts and
gums were reduced with an increase of at most 10 to 20% in the proportion
of oils boiling below 350°C (O.Z. 9533, 9636). The temperature may be
raised above the above mentioned limit only towards the end of the reaction,
after the asphalts and gums have been converted (O.Z. 10 128).

## i) Pressure Extraction

Pressure extraction is also considered as a pressure hydrogenation
of coal under mild operating conditions, with the production of high boiling,
fusible materials. This method of separation was used in 1926 with a tar
middle oil fraction as the extraction medium, e.g. bituminous coal tar
distillation fractions boiling between 250 and 320°C, or lower boiling
fractions, 180 - 300°C, such as benzol derivatives, or the phenol-containing
brown coal LTC tar distillates. The process may be conducted also in the
presence of small amounts of hydrogen (O.Z. 3894, 3942). The extracts or
the residues can be later pressure hydrogenated. The yield can be increased
by heating the coal under pressure prior to extraction (O.Z. 4062). The
presence of catalysts is very advantageous during extraction especially
when small amounts of hydrogen are used (O.Z. 9168). The available
pressure hydrogenation catalysts favor these reactions also.

In addition to the extraction media mentioned above we may use the
80 - 150°C fraction of the pressure hydrogenation or cracking products
high in aromatics (O.Z. 4828), or the 170 - 260°C fraction of the pressure
hydrogenation product of the extraction, and the pressure hydrogenation
must be so conducted that the fraction would contain 5 - 40% of cresol
(O.Z. 9747).

Patents have also been issued to A. Pott and H. Broche on the
pressure extraction at higher temperatures (e.g. Germ 632 631). The I. G.
has concluded an agreement with Stinnes in 1936 which gave the I. G. a
license to use this method of operation.

There is a voluminous literature on extractions. The Rütgerswerke
(Germ 320 056) and E. Berl (Germ 411 540) have extracted coal under
pressure and at elevated temperatures as early as 1918 and 1922 respectively
with a high boiling bituminous coal tar oil and hydrogenated naphthalene,
and only the extraction with such middle oils and the use of hydrogen were
new. The I. G. has bridged the gap between ordinary pressure extraction
and pressure hydrogenation by the pressure extraction in presence of hydrogen

F. Uhde has applied in 1934 for a patent on a pressure extraction process with less hydrogen than calculated from the absorption capacity of the carbonaceous substance (O. Z. 10 708). H. C. Lander, F. S. Sinnatt, and I. G. King have converted coal in 1927 by an incomplete hydrogenation under pressure into a plastic and sticky mass, which was liquid at elevated temperatures and which solidified upon cooling into a pitch-like mass (Brit 301 720). The I.C.I. has obtained a patent in 1928 on a binder for coal briquettes obtained by pressure hydrogenation of a coal-oil paste under such conditions that the hydrogenation was incomplete. A hydrogen absorption of 2 - 3% by weight of hydrogen was understood to take place here (Brit 322 194).

In order to avoid any patent litigations, I. G. has decided to take over the patent application of F. Uhde. The agreement with the firm F. Uhde was made in 1936.

Experiments on pressure extraction with small absorption of hydrogen were resumed in 1938. Coal paste was pressure hydrogenated with such a high thruput, that only a preliminary hydrogenation to a fusible product could result.

### k) Use of Prehydrogenated Coal for the Production of Coke

The products obtained by pressure extraction in the presence of hydrogen can be used in briquetting in the same way as coke oven and LTC pitch. They may thus be pressed with coal to a solid mass which is then carbonized at a low temperature for the production of tar and coke (O. Z. 10 740). The pressed mass may also be used for firing or gasification. It is desirable that the prehydrogenated coal should have a softening point of 45 - 150°C, best 60 - 100°C. If this requirement is not met the product is pretreated by distillation, extraction, addition of pitch or organic solvents or by treatment with oxygen-containing gases (O.Z. 12 510 and supplements).

Such extracts are very well suited to the production of carbon electrodes (O.Z. 14 115/16).

## II Raw Materials and Finished Products

### a) Special Raw Materials

Pressure hydrogenation processes are not limited to the working up of coal, tar, and mineral oil, but may also be used for the treating of oil shale (O.Z. 12 785) lignite (O.Z. 8685, 10 154), gums (O.Z. 9452) fats and fatty acids (O.Z. 7809) thickened washing oils (O.Z. 9452), polymerization products (O.Z. 3541, 7677, 10 035), condensation products (O.Z. 5471, 13 386), aldehydes and ketones (O.Z. 12 277, 12 339, 14 190), organic acids (O.Z. 6599, 6865), with the recovery of valuable products from these raw materials.

### b) Hydrogen and Hydrogenation Off-Gas

The cost of hydrogen plays an important role in the process, and the production of cheap hydrogen, the proper treating of the circulation gas and a proper utilization of the hydrocarbon gases obtained are of importance.

Hydrogen from any source may be used for hydrogenation. Should electrolytic hydrogen be used it must be freed from oxygen before use (O.Z. 6631). Hydrogen must be freed from unsaturated hydrocarbons, oxygen and nitric oxide when obtained from solid fuels(O.Z. 6640).

Hydrogen is used industrially in a gas circuit. The circulation gas contains the gaseous hydrocarbons, hydrogen sulfide etc formed during the reaction.

The concentration of saturated hydrocarbons and hydrogen sulfide in the circulation gas is so much reduced by pressure scrubbing with low boiling oils, such as gasoline or middle oil, occasionally with higher boiling oils, that the gas can be returned to the reaction space (O.Z. 3604, 4601). Partial pressure release results in a separation into the hydrocarbon-richer and hydrocarbon-poorer fractions (O.Z. 3604, 4889).

A further recovery of hydrocarbons from the off-gases is done by recompression or by low cooling of the pressure released gases (O.Z. 5103, 6967).

The hydrocarbon gases may be used for the production of hydrogenation hydrogen by conversion with oxygen-containing gases, such as air, steam, carbon dioxide (O.Z. 3226, 3339, 3781, 7211, 6933, 6934, 7182). Olefins and oxygenated products are obtained from fractions in which such hydrocarbons as butane and propane have been enriched.

Some of the fractions are used separately, e.g. for a conversion with oxygenated gases for the production of olefins, which can be further converted into aromatics (O.Z. 3398, 3855, 4226).

Another method of production of hydrogen consists in a conversion of
a circulation gas in two stages at different temperatures. Methane is
converted with steam to hydrogen and carbon monoxide at a higher temperature,
carbon monoxide converted with water to carbon dioxide and hydrogen at
lower temperatures (Germ 435 588).

In addition to the above mentioned patents on hydrogen and hydrogenation
off-gases, based on the inventions by the "Hochdruckversuche" (High Pressure
Experiments Division), there exists a number of patents of other I. G.
concerns, which have not been mentioned here.

c) The Processing of Hydrogenation Residues

At first great difficulties have been met in the processing
of the solid carbonaceous residues obtained in the pressure hydrogenation.
At first extraction experiments were made, such as with methanol alone or
mixed with cyclohexane (O.Z. 3267, 3247). The residues were heated with
flushing gases in worm driven kilns in 1927 on a larger scale with a
partial recovery of the oil contained in the residues (O.Z. 4095). A
rotating furnace was developed in 1935 since the development of bituminous
coal hydrogenation (O.Z. 9165, 10 185), which was filled with balls or
with other tumbling shapes. The solids were first separated from the
oily constituents by centrifuging after the addition of solvents (O.Z.
4391, 7949, 7966, 11 234, 11 340). The residues were continuously
extracted with a variety of solvents such as liquefied sulfur dioxide,
aromatic hydrocarbons and their mixtures, or with pressure hydrogenation
products like middle oils (O.Z. 4394, 4484, 4756), this process was combined
with filtration (O.Z. 4591, 5399, 5432, 10 435).

Heating of the residue for a length of time or the addition of the
flocculation agents can facilitate the separation of oil from solid con-
stituents (O.Z. 4831, 5540, 5733, 5907, 6457, 7913, 8434, 8616).

d) Uses for Hydrogenation Products

The increasing requirements in the octane number of gasoline
as a motor fuel could be met e.g. by a choice of special starting materials
for the pressure hydrogenation processes, by a preliminary conversion of
unsuitable raw materials into suitable materials, by blending knocking
gasolines with aromatic gasoline fractions (O.Z. 3850, 4342, 4530, 4829,
5153, 5249).

The pressure hydrogenation gasolines can be blended with other low
boiling products, e.g. with gasolines from other sources (O.Z. 3306, 3321),
polymerization gasoline (O.Z. 6549, 7544), casing head gasoline (O.Z.
4707), or with alkylated benzols (O.Z. 12 422, 12 080, 14 153, 14 516).
Hydrogenation gasolines of different boiling ranges, or different anti-
knock gasolines, also could be blended (O.Z. 6623, 4829). It is rather
surprising that gasolines with a guming tendency can be improved by the

addition of gasolines refined by hydrogenation, (O.Z. 7894). The
addition of metallic anti-knock agents to bituminous coal hydrogenation
gasolines is particularly effective (O.Z. 8557).

The use of the hydrogenation products as scrubbing oil for benzol-
containing gases as well as solvents and cleansing agents is protected,
(O.Z. 3324, 8384). The conversion of coal hydrogenation residues into
industrially valuable materials, such as filter mass or activated charcoal
is covered in the O.Z. 5412, and 5530. The hydrogenation residues can
also be used as plasticizers, for impregnation or as fillers for rubber-
like masses (O.Z. 10 177, 12 345, 12 707). The resins from pressure
extraction or hydrogenation products are basic materials for lacquers and
insulators (O.Z. 13 187).

### e) The Production of Uniform Low Boiling Aromatic Hydrocarbons

The low boiling aromatic hydrocarbons, in particularly benzol
and its homologs can be obtained in a very simple way from the high boiling
cyclic compounds or from products containing the latter, e.g. heavy benzol.
The heavy benzol is for that purpose first refined by pressure hydrogenation,
then aromatized with the production of considerable amounts of benzol,
toluol, and xylol (O.Z. 8116). These products can also be obtained by
treating aromatics, hydroaromatics or heterocyclic compounds such as the
tar fractions and heavy benzol or by treating cresol and the like, with
steam at elevated temperatures (Fr 612 327, 32 260) or with hydrogen,
occasionally mixed with nitrogen, carbon dioxide or steam at either
normal or elevated pressures (Fr 612 908). Cyclo paraffins (O.Z. 3499),
naphthaline (Fr 629 838), may also be considered as starting materials
for the production of aromatics. There exists also a process to convert
phenols into benzol, toluol etc, in which the phenol reduction is only
partly complete during the first pass, and the unaltered phenols are
returned to the reaction space (O.Z. 7301). A reduction of phenols by
treating with hydrogen under pressure in the presence of molybdemum or
activated charcoal is claimed in O. Z. 7441.

The principal starting material for the production of low boiling
aromatics is gasoline. The latter is heated to 500°C with hydrogen in
the presence of catalysts either under pressure (O.Z. 3617, 3847), or at
atmospheric pressures (Fr 619 838). The dehydrogenation of gasoline is
best carried out with such catalysts, as nickel-tungsten with a total
pressure of about 50 atm (O.Z. 7950, 7952), or with finely divided catalysts
(O.Z. 7757). It also is advantageous not to work with the total gasoline
fraction, but only with a part of it, in particular that which boils above
100°C (O.Z. 5839, 6082). This fraction can be converted into aromatic
hydrocarbons even without the presence of hydrogen (O.Z. 8291, 6951).
Treating of gasolines with hydrogen, as well as without any additions is
mentioned in the Fr 629 838. It is occasionally advantageous to subject
the gasolines to a hydrogen refining prior to the cracking or aromatization
(O.Z. 7642, 7835). The anti-knock properties of gasoline may be improved
by isomerization with metal halides and then dehydrogenation (O.Z. 8208).

A suitable method to isolate aromatics from gasoline is the treatment with propane and sulfur dioxide at low temperatures (O.Z. 8907).

Low boiling aromatics can also be obtained from middle oils such as are obtained e.g. in the distillation, cracking or pressure hydrogenation of coals, tars, mineral oils etc. These are subjected to an aromatizing pressure hydrogenation (O.Z. 3617, 3847, 3636, 7453). The yield on the low boiling aromatics may be increased by aromatization of the middle oil in several stages (O.Z. 7152, 8591). The readily polymerizable substance present in the oil present the danger of affecting the activity of the catalysts, which makes it advisable to remove the harmful substances by distillation (O.Z. 8160), refining pressure hydrogenation (O.Z. 4333), preliminary hydrogenation to hydrogen-rich products (O.Z. 4880), by propane treatment (O.Z. 7106, 8436, 8160), mild hydrogenation below 300°C (O.Z. 7835), or by treating with chemicals (Fr 703 696). The aromatization can be carried out in the liquid phase with a finely divided catalyst if no refining is intended. Middle oil may also be treated with selective solvents and only the hydrogen-poor fraction pressure hydrogenated to particularly high anti-knock gasoline. The low boiling aromatics can be obtained by carrying out a cracking cyclization with steam or without any gaseous additions (Fr 628 838, 612 327, 32 260).

Heavy oils or residues can also be used for the production of low-boiling aromatics. The Fr 628,838 recommended producing the higher aromatics first and converting them by cracking or aromatization into low boiling aromatics.

### f) The Production of Pure Polynuclear Compounds

Polynuclear hydrocarbons like pyrene, phenanthrene etc have been obtained from the products of pressure hydrogenation or pressure extraction. The high boiling products of pressure hydrogenation are dehydrogenated and the polynuclear compounds separated by physical or chemical methods, (O.Z. 8165). 1,12 benzperylen and coronene can be obtained by the distillation of the hydrogenation residues and are separated from the distillate (O.Z. 9207, 9265, 9894, 10 456, 10 533).

### g) Production of Phenols

Large amounts of phenols are formed in the liquid phase coal hydrogenation together with hydrocarbons. The phenols are separated from the pressure hydrogenation products by treatment with water under pressure (O.Z. 11 025), using low-boiling hydrogen-rich hydrocarbons at definite temperatures (O.Z. 11 027) with liquid ammonia, or with selective solvents which dissolve well the neutral oils, but are poor solvents for phenols (O.Z. 14 004). Phenols can also be obtained from bituminous coal tars by a protective pressure hydrogenation, which causes the high molecular weight phenols to be converted into low molecular weight phenols (O.Z. 13 151, 14 241, 15 000).

## IV Combination Processes

### Hydrogenation and Cracking

The processing of oils and work on problems of the refining industry in countries with large oil supplies have led to processes combining pressure hydrogenation and cracking. By pressure hydrogenation difficult-to-crack-oil rich in sulfur and asphalt can be converted into oils easy to crack (O.Z. 4333). The introduction of sufficient hydrogen has permitted the cracking of products which have been formerly considered entirely unsuited for cracking, as bituminous coal tars or oils produced by extensive cracking (O.Z. 4880). A variety of combinations has been tested by experiments and the processes developed have been protected by patents (O.Z. 4337, 4940, 10 364, 11 371, 11 543).

One particularly fortunate complementary process to the cracking processes is the hydrogenation of asphalt-containing oils and residues. In this way the distillation and cracking residues of these oils could be largely converted into valuable oils (O.Z. 6894, 10 059). Particularly high grade gasolines could be produced by aromatizing pressure hydrogenation of cracked middle oils (O.Z. 7718).

## V. Industrial

### a) Materials of Construction and Special Equipment

~~Pressure hydrogenation requires better construction materials~~
than do the ammonia and methanol synthesis because of the composition
of the raw materials, especially with regard to erosion, resistance to
sulfur and strength at high temperatures.

But also the construction materials have a certain effect upon the
hydrogenation products by decomposition of these products to coke and
methane this is principally the case on metal surfaces which are increased
by the attack by hydrogen.

All these requirements upon the materials forced the development
of special new materials.

About the same precautions as used in methanol synthesis must be
observed when working with water gas or gases in which carbon dioxide and
carbon monoxide are in part formed during synthesis (O.Z. 3104). Because
of the high sulfur content in the feed stocks of the pressure hydrogenation,
copper is excluded at these temperatures. Aluminum can be used if phenol
and water content are low up to temperatures of about 500°C (O.Z. 3323).
The plating of equipment with silver has also been found satisfactory
(O.Z. 3892). Chromium steels have been found very satisfactory for the
purpose (O.Z. 3277, 3279, 6186). When carbon monoxide-free gas is used
it is recommended to work with the exclusion of iron, and the more so the
carbon-richer the starting materials are. It is necessary for that purpose
to have the reaction space and the parts of the apparatus which come in
contact with the hot reaction materials to be built with corrosion
resisting materials, or else have them clad with them (O.Z. 3698, 3892).
Alloys containing chromium, molybdenum, tungsten, vanadium, and mangenese
have been found very suitable here.

The simultaneous attack by hydrogen and sulfur under high pressure
led to the use of double wall reaction vessels. A special steel of high
chemical corrosion resistance was used for the inner vessel, and the outer
vessel was made of mechanically strong special steel (O.Z. 4328). Later
on, in order to spare the use of the expensive special steels in the double
wall high pressure converters, the converter jacket was made of ordinary
S2 material (carbon steel) and provided with ventilation holes. Subsequent
experiments showed brass to be permissible because of its resistance to
corrosion by hydrogen, sulfur and hydrocarbons (O.Z. 5688, 5689). It
found applications in particular for the lining of the high pressure
converters. This permits the use of a single instead of a double wall
converter which is covered with a hydrogen and sulfur-resisting coating
(O.Z. 6015, 5688, 7618, 8420). In more recent times the high pressure
converters were provided with an inside heat insulation which supports a
chemically resisting basket, which need not be pressure resistant.

To facilitate the manufacture of the high pressure equipment the "wickel" high pressure converters have been created, which consist of an inner tube, on which steel bands were spirally wound in several layers (O.Z. 10 392, 10 519). It has been found here advisable to provide one side of the steel bands with grooves, and have ridges on the other side which would correspond in shape and position to the grooves (O.Z. 10 554, 10 812, 10 733).

Alloys with less than 10% chromium, e.g. with 6% chromium have been found satisfactory for preheaters and heat exchangers, if the usually harmful nickel is replaced, e.g. with molybdenum (O.Z. 6186).

Special steels are familiar from the cracking literature. It is, however, impossible to predict suitable construction materials for the pressure hydrogenation from experience with construction materials in cracking. This can be seen from the fact that the literature on cracking recommends materials which can be used in high pressure hydrogenation together with those which are not suited for pressure hydrogenation.

b) Heating

The method of heating used by F. Bergius and St. Löffler (Germ 303 332)with high pressure heating media e.g. with circulating nitrogen or hot water, were initially used but they are too complicated. At that time no sufficiently hydrogen and sulfur-resisting material was known and the heat had to be supplied by super heating hydrogen in an electric heater, corresponding to the method used in the ammonia synthesis (O.Z. 3682). The feed was then preheated in a molten bath or by hot water to somewhat lower temperatures, as by F. Bergius. This method of heating was no longer applicable with larger thruputs, and was therefore abandoned and a different form of preheaters was selected (Brit 192 849, 192 850, US 1.592 772).

One such form of preheaters for the feed stocks was the construction of the tubes themselves as electrical resistance heaters (O.Z. 3805). In this case a major part of heat was recovered by heat exchange inside the reaction vessel (O.Z. 4085).

A realization of the fact that a layer of liquid provided a certain protection against hydrogen and sulfur upon the pressure-resistant wall, permitted the joint heating of the feed and of hydrogen in the preheaters. This permitted an increase in the preheat temperature of the reaction feed (O.Z. 4871).

The use of hydrogen and sulfur-resistant materials permitted finally the joint heating of the participants of the reaction up to the reaction temperature in the preheater by direct heating with combustion gases (O.Z. 5133, 5830).

The danger of crust formation and of the decomposition or damage to
the product made it necessary to operate with low excess temperatures
and led to a special construction with a controlled heat supply and the
use of finned tubes provided with return bends (O.Z. 5897, 6743). When
materials high in ash such as coal were used, the return pieces had to be
made of particularily resisting materials and readily replaceable (O.Z.
9968, 13 332). In that connection such processes have been developed for
internal heating by the addition of carbon monoxide or of oxygen-containing
materials, such as phenols (O.Z. 5883).

The hydrogenation reaction is exothermal, and control of the reaction
temperature is of the utmost importance. In practice this is accomplished
by the addition of part of the hydrogenation gas in the cold state
(O.Z. 8424, 9100). This makes it also unnecessary to preheat all the
participants of the reaction to the reaction temperature. In many cases
it is sufficient to preheat the greater part of the starting materials
with hydrogen in the heat exchangers and preheat only a small part with
hydrogen in a preheater to the reaction temperature.

Coal paste may also be preheated in heat exchangers, with the larger
proportion of the coal paste prepared with a small coal content and heated
in heat exchangers, while the rest of the paste is prepared with a larger
proportion of coal and is preheated in a tubular preheater. It is also
possible to by-pass the preheater (O.Z. 10 473).

When several heat exchangers are used, it is advantageous to preheat
only the hydrogenation gas in the colder heat exchanger and lead it
together with the feed to be hydrogenated through the remaining hotter
heat exchangers (O.Z. 14 538).

The heat required in the reaction could be supplied without incurring
large losses of energy by equipping the introduction of the gas heated
tubular preheaters with finned tubes, the use of heat exchangers in the
preheating zone the distribution of the feed among the different heating
aggregates depending on its consistency, and an extensive heat recovery
from the reaction products made it possible to supply the heat required
in the process without great losses.