The results are shown graphically in the Curves I
and II.

Table I and the Curves I show that starting with the
benzene-cyclohexane mixture within the temperature interval of
about 440-500°C, the dehydrogenation equilibria become very accu-
rately established. At temperatures below 475°C, the mixture of
1:1 is hydrogenated to higher cyclohexane concentrations, at tem-
peratures over 475°C to higher benzene concentrations. At tem-
peratures below 400°C, the time of residence used in the test is
not sufficient for the production of equilibria. At temperatures
above 500°C one could observe a splitting of the naphthene ring
in addition to the dehydrogenation reaction, and at 550°C 8% gasi-
fication is already produced. The aliphatic hydrocarbons produced
during this splitting lower the index of refraction of the pro-
ducts, and the benzol contents calculated at higher temperatures
from the indices of refraction are too low.

Table Ia

Tests with Benzene, Benzene-Cyclohexane Mixture, 1:1 and Cyclohexane

Test conditions as in Table I.
Temperature   485°C
Theor. benzene concentration   78%

Feed	Operating Days	Sp.Gr.	Aniline Point	Refr. Index	% C_6H_6 by Wt.
Benzene	3	0.856	-43	1.4878	85
	4	0.856	-45	1.4900	87.5
Cyclohexane	5	0.856	-45.5	1.4895	87
	8	0.850	-42.5	1.4838	81
Mixture Benzene:	10	0.850	-43	1.4835	80.5
Cyclohexane 1:1	13	0.842	-43.5	1.4811	78

Table II (Curves II)

Experiments with Toluene, Methyl Cyclohexane
and Their 1:1 Mixture

| Feed	Days of Operat.	°C	Sp.Gr.	Refr. Index	% Toluene from Refr. Index	Aniline Point	% Toluene from A.P.	% Toluene Theor.
Toluene	320	340	0.766	1.4202	0	+40	0	-
	3	365	0.766	1.4230	2	+40	0	-
	6	391	0.760			+36	0.5	9
	9	416	0.782	1.4355	24	+17	20.2	23
	11	434	0.798	1.4522	50	- 8	44.8	42
	14	451	0.824	1.4740	78	-31	67.5	61
	16	468	0.842	1.4810	90	-40	76.3	84
	18	485	0.850	1.4860	96	-48	84.2	89
Methyl	19	485	0.850	1.4870	97.5	-48.5	84.7	89
Cyclohexane	20	485	0.842	1.4835	93	-42.6	78.9	89
	21	485	0.840	1.4798	83	-43	79.3	89
Toluene	23	501	0.848	1.4840	94	-43.5	79.8	93.5
Methyl	26	518	0.852			-48.5	87.7	96.5
Cyclohexane 1:1	29	544	0.850	1.4900	100	-50.5	89.8	98.5

Table Ia shows that the experimental results are the same whether one starts with pure benzene, pure cyclohexane, or their mixture. This means that the equilibrium is strictly reversible (disregarding the small amount of side reactions which take place). Table II and Curves II show that the toluene-methyl cyclohexane equilibrium becomes established on the nickel-tungsten catalyst. The splitting, which forms a side reaction at higher temperatures, results in an increase in the index of refraction to be attributed to the formation of benzene, and the toluene concentrations calculated from it appear too high. On the other hand, the splitting reaction products result in a rise of the aniline point, and the toluene concentrations calculated from the aniline point appear too low.

It is immaterial for the toluene-methyl cyclohexane equilibrium whether one starts with pure toluene, pure cyclohexane, or their mixture.

The diagram shows also that the concentration of aromatics obtained at the same temperature is higher with toluene than with benzene, which is to be attributed to the fact that with the higher aromatics the equilibrium is located further on the aromatics side than with benzene.

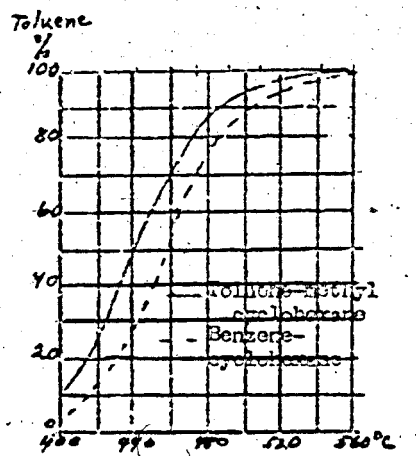Curve I shows the effect of the hydrogen partial pressure upon the equilibrium concentration of the aromatics.
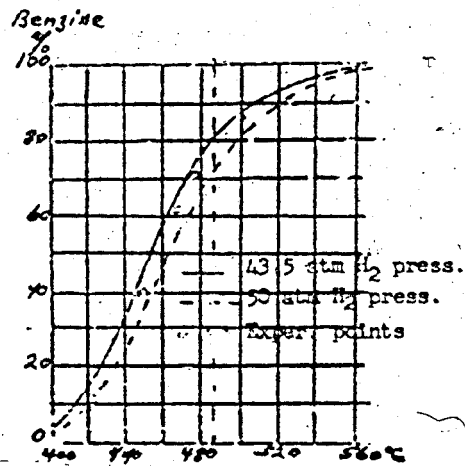
/s/ Peters
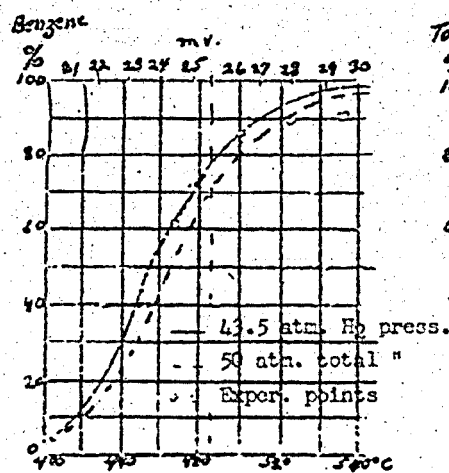
Benzene-cyclohexane
Equil.
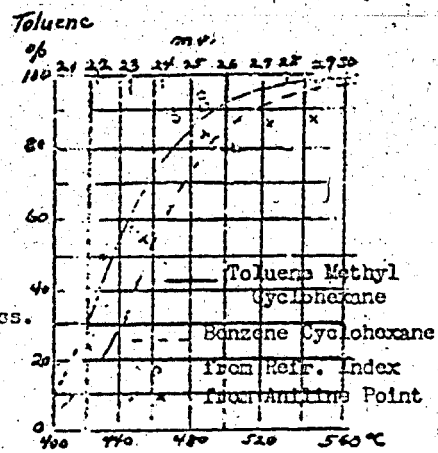
Theoretical Equil.
50 atm. total pressure
5.5 H$_2$ partial pressure

Theoretical Equilibrium

50 atm total pressure
5.5 atm H$_2$ partial pressure

Benzene-cyclohexane
Equilibrium

50 atm total pressure
6.5 atm H$_2$ partial pressure

III

THE AROMATICS-NAPHTHENES EQUILIBRIUM ON
THE TUNGSTEN SULFIDE CATALYST 5058

It has been shown in a summary of February 1940, that
the tungsten nickel catalyst 6718 produces rather exact equili-
brium between benzene cyclohexane and toluene-methyl cyclohexane
at 50 atm pressure and a thruput of 0.5.

New tests have shown that the tungsten sulfide catalyst
5058 causes a hydrogenation of benzene or toluene to strong approxi-
mation of the theoretical equilibrium at 50 atm and a thruput of
0.5 only when the temperature reaches 480°C. At lower tempera-
tures the equilibrium is not even approximately reached, with the
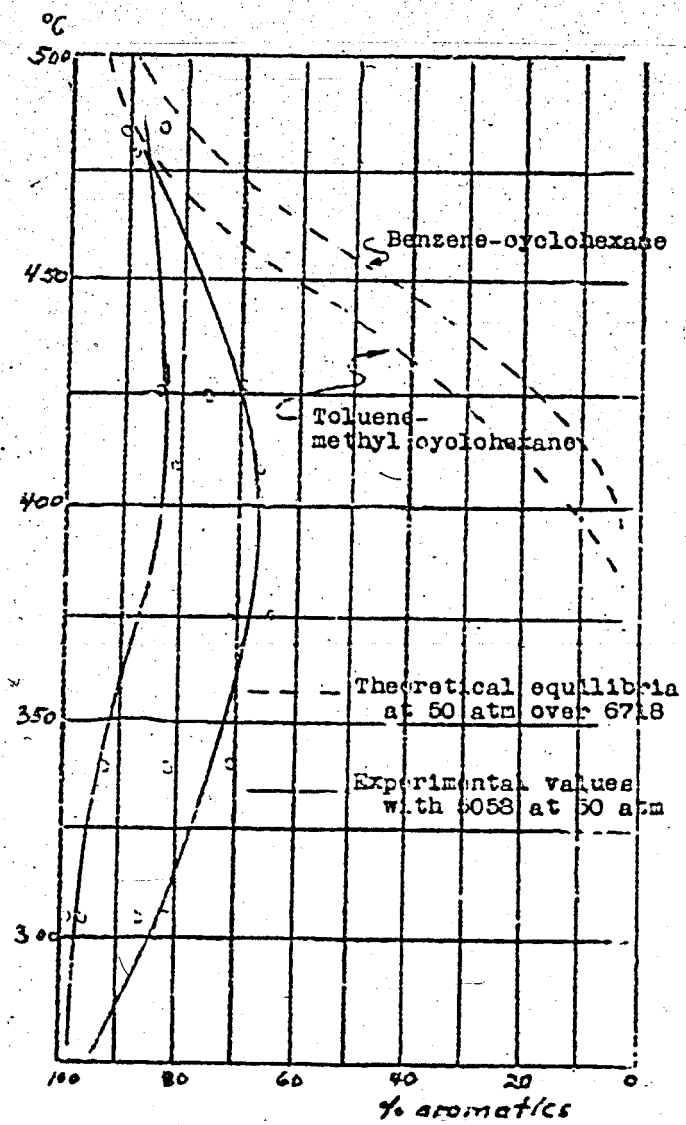toluene nevertheless somewhat more hydrogenated than benzene.

When changing over a 5058 catalyst operated for several
days at 50 atm to a pressure of 250 atm, the hydrogenation activity
is largely reduced even at higher pressures. Cyclohexane is not
at all dehydrogenated on such a 5058 catalyst at 50 atm and 485°C.

The curves appended show graphically the results of the
test. The results of the older tests with the nickel-tungsten
catalyst may be seen from Figures 2 and 3. See above.

/s/ Peters and Trofimow

°C

500

450   Benzene-cyclohexane

Toluene-
methyl cyclohexane

400

Theoretical equilibria
350   at 50 atm over 6718

Experimental values
with 6058 at 50 atm

300

100   80   60   40   20   0

% aromatics

0133

BRIEF SUMMARIES OF THREE PAPERS ON SPLITTING HYDROGENATION

I

SPLITTING HYDROGENATION CATALYSTS WITH HF TREATED ALUMINA AS CARRIERS

Summary

1. Catalytic cracking has shown that alumina acti-
vated by HF treatment possesses good splitting acti-
vity. It was therefore tested as a carrier for
splitting hydrogenation catalysts by making two cata-
lysts: 8160 (light alumina + 10 HF + 10 WS$_2$) and 8208
(light alumina + 10 HF + 10 Fe saturated with ferric
nitrate and precipitated with NH$_4$F).

2.) The two catalysts reach only at 22 mv (426°C)
approximately the splitting activity of the 6434 cata-
lyst at 19.0-19.5 mv (374-382°C). Obviously there is
more gasification with these alumina catalysts at an
operating temperature appreciably higher than used
with 6434.

3.) Earlier tests with an alumina molybdenum catalyst
(7360) showed that when alumina has not been treated
with HF there is practically no splitting up to the
temperatures here studied.

4.)   The gasoline from the alumina FeF_3 catalyst
contains a somewhat higher proportion of aromatics
(10-11%) against the 6434 gasoline (6-7%).

5.)   The nitrogen sensitivity of the alumina WS_2
catalyst appears to be somewhat smaller than of the
6434.

/s/ Rotter

II

TUNGSTEN-FREE SPLITTING CATALYSTS OF THE SiO_3-Al_2O_3-Fe_3O_3 MIXTURES TREATED WITH HF

Summary

1.)   The catalysts of the composition SiO_3-Al_2O_3-Fe_2O_3 in different proportions were treated with different amounts of hydrofluoric acid and tested for their splitting activity (splitting hydrogenation of Bruch- sal petroleum).

2.)   It was found that very active splitting cata- lysts were obtained with 20-90% SiO_2 when treated with 80% HF referred to Al + Fe if the concentration of Al_2O_3 was higher than of Fe_2O_3. The results are shown in the triangular diagram.

3.)   The most active splitting SiO_3-Al_2O_3-Fe_3O_3 mix- ture (80-15-5) was used in these tests to show the effect of the hydrofluoric acid treatment. The maxi- mum splitting activity was reached when treating with 80% HF, and presumably 5-80% equivalence HF referred to Al + Fe (splitting activity about 135-140, compared to 100 with the 6434 catalyst).

4.)   Long time experiments were conducted with the two best catalysts with 50% HF/Al + Fe (splitting activity 100 and 90) using petroleum a middle oil and with bi- tuminous B middle oil. The splitting was better than
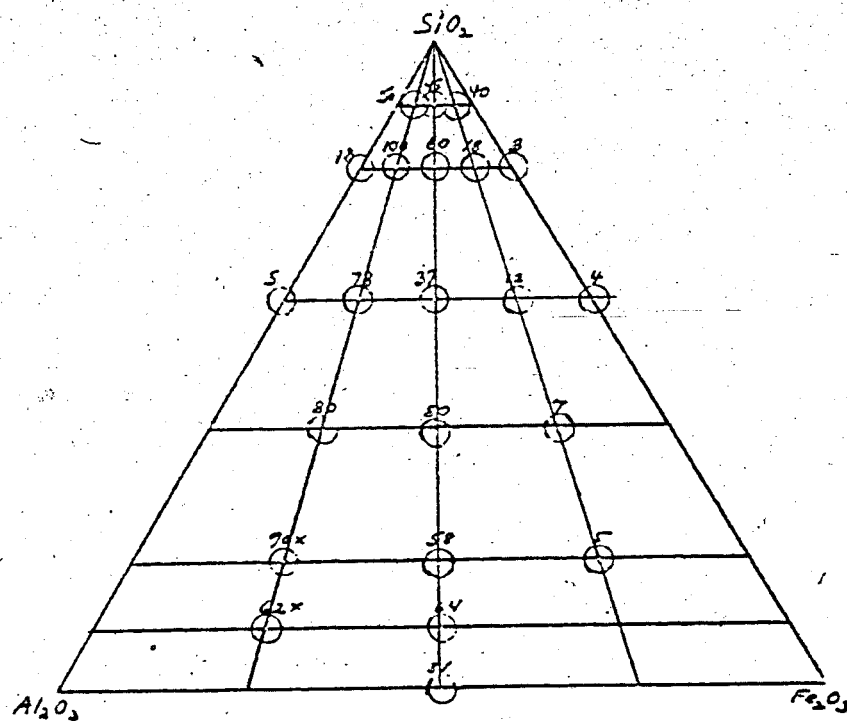
with 6434, the other results were about the same.
No loss in activity has been observed in spite of
the frequent interruptions due to the aerial war-
fare acts. The nitrogen sensitivity is somewhat
higher than the 6434.

/s/ Günther

SPLITTING ACTIVITY OF SiO_2-Al_2O_3-Fe_2O_3 CATALYSTS
TREATED WITH 50% HF/(Al + Fe)

ᵡThese two catalysts were prepared with 35% HF/Al + Fe.
The values would have been lower with 50% HF.

III

THE SPLITTING HYDROGENATION OF DHD RESIDUES

A large number of tables is presented on the results of splitting hydrogenation of the residues from the DHD catchpots, boiling +165°C, redistilled to the end point of about 300°C, either with previous prehydrogenation, or converted to gasoline directly with 6434, which was returned to the DHD feed. In the first case the residue (aniline point -48°C) was hydrogenated over catalyst 8376 at temperatures of 333-343°C, 180-270 atm pressure and a thruput of about 0.9 kg/l1 catalyst/h to an aniline point of +8 to +10°C. The -170°C gasoline was distilled off from the catchpot products, and the b-middle oil with an aniline point of about +9°C was subjected to splitting hydrogenation over 6434 with an H_2 partial pressure of 240 atm at 392-400°C and a thruput of 1.36 kg/l1 catalyst/h. The space/time yield of gasoline production of the second stage amounted to 0.82 kg/l1 catalyst/h, the space/time yield of both stages amounted to 0.48 with 9-11% gasification. In the second case the residue was converted at 403°C over 6434 catalyst to gasoline -170°C after mixing with a recirculation middle oil. The feed thruput was 0.75 kg/l1 catalyst/h and the gasoline space/time yield of 0.48 was reached.

The gasolines from the single stage and two stage methods differ principally in the following points:

1.) The single stage splitting hydrogenation pro-
duces gasolines containing larger proportions of
low boiling constituents.

2.) The aromatics content in the single stage gaso-
line amounts to 29% as against the 34% in the two
stage gasoline.

3.) The basic octane number was about the same (74-
75, M.M.), but the lead sensitivity of the single
stage gasoline is higher.

The overload curve is between B_4 and CV_2b gasolines, and
is parallel to the B_4 curve.

Both gasolines are well adapted according to their com-
position for DHD.

/s/ Gieg and Simon

T-476
W. M. Sternberg

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TOM Reel 173
Frames 642-641

December 17, 1940

UPPER LIMITS OF N AND PHENOL CONTENTS AND LOWER LIMITS FOR THE ANILINE POINT OF 6434 INJECTION 1/

Generally valid figures cannot be given, because different limiting values have been found depending on the raw material (bituminous coal, brown coal, brown coal tar, petroleum products, etc.). We may say about the splitting hydrogenation of middle oils with an e.p. of 325°C at 250 atm about as follows:

A. N Content

It has been generally assumed up to now that the prehydrogenation B middle oil permits an N content of up to 0.010%; this figure has been confirmed by the poisoning tests of 6434 during the splitting hydrogenation of petroleum gasoil with the addition of 0.1% aniline (= 0.015% N) to the gasoil 2/. On the other hand, many feeds containing up to 0.020% N could be very well worked over 6434, provided they were well refined from phenol (less than 0.02%).

1/ Information collected at the request from Pölitz.

2/ With the addition of 0.1% aniline to gasoil for four days, the yield was reduced to one-half at the same temperature. The damage was completely reversible.

B. Phenol Content

0.1% phenol in prehydrogenated middle oil is usually
assumed as the upper limit for bituminous coal, for brown coal -
0.5%. No deviations from this rule have been obtained within the
last years for bituminous coals, individual prehydrogenation brown
coal liquefaction middle oils containing 1.0% phenol could also be
very well worked with 6434.

C. Aniline Point

Exact information is most difficult to give in this case.
As a general rule an a.p. of +40°C in B middle oil is considered ──
sufficient for bituminous coal in order to permit operations with
6434 with good results. However, difficulties have arisen in diff-
erent works with an a.p. of +40°C. On the other hand, well O-and
N-refined feed could be well split at times with an a.p. of below
0°C. At present, the a.p. limit of 55°C is used for brown coals.

With petroleum distillates and feeds obtained from petro-
leum by splitting pressure hydrogenation, the a.p. is always so
high and the phenol content so low that the N content alone is
important.

The gasoil cracking residues usually follow the rules es-
tablished for bituminous coals, while the crude oil cracking resi-
dues follow the rule given for the brown coal.

Exceeding the above N or phenol values, or lower a.p.,
cause an increasingly reduced yield with 6434 at the same tempera-
ture, which can to a certain extent be equalized by raising the
temperature.

When the question is considered, the three factors - N,
phenols, and a.p., must be remembered to be mutually counteract-
ing each other in their effect, and that not only the amount but
also the kind of N and O compounds appear to be important, as well
as the constitution of the hydrocarbons to be split.

It must also be mentioned that 6434 is sensitive to H_2O
and NH_3, and that the harmful effects may be in part compensated
by sulfur in the injection feed and H_2S in the circulating gas.

The b.p. is of particular importance for the splitting
hydrogenation ability of middle oils over 6434. Even small addi-
tions of higher boiling substances, in particular if olefinic in
nature, can strongly reduce the catalyst efficiency. Such damage
is supposedly not completely reversible.

The better refined and prehydrogenated the feed, the higher
may also be the b.p. of the 6434 injection.

                        /s/ Peters and Günther

High Pressure Experiments
Ludwigshafen 558

T-478
W. M. Sternberg

TOM Reel 173
Frames 633-641

0203

March 23, 1942

CONNECTION BETWEEN NITROGEN CONTENT OF OILS AND THEIR SPLITTING HYDROGENATION ABILITY (SPLITABILITY)

I

Summary

1). No connection could be derived from the results of 28 tests on the splitting hydrogenation of middle oils between their splitability and the nitrogen content of the oils determined by the Kjeldahl method. On the other hand, a clear connection has been found between their splitability and the basicity (Merseburg method).

2). Properly prehydrogenated and not too high cut oils with basicity numbers up to 5 mg NH_3/ll can be properly split. Higher cuts or lower hydrogen oils require basicity numbers of less than 3 mg NH_3/ll.

/s/ Günther

1. Foundation for a Numerical Expression for the Splitability of an Oil

The splitability of an oil can in general be expressed numerically by:

a.) The concentration of gasoline in the catchpot obtained under standard conditions (type of converter, catalyst, pressure, temperature, thruput, gas:oil proportion, sulfur addition).

b.)   The temperature required to obtain a definite gasoline
concentration in the catchpot under otherwise constant conditions.

The method a) has the advantage of producing values for
splitability even in tests of short duration.

The method b) has the advantage of supplying data for
the working up of the oils on an industrial scale.

The splitting hydrogenation tests have been generally
made by us using the method b) and a gasoline concentration of
around 50% -150°C was produced in the catchpot. In most cases,
exactly 50% have however not been obtained and the characteriza-
tion of splitability could be made only by indicating both tempera-
ture and concentration.

The results of splitting hydrogenation in the paper below
have been recalculated to 19.5 mv = 382°C in order to characterize
the splitability by a single number. This was done by using an
empirical factor which claims that raising the temperature by
0.5 mv increases the gasoline concentration -150°C in the catch-
pot by 1.2 times. The calculated gasoline concentration for 19.5
mv is then used directly as a measure for the splitability of the
corresponding oil.

2. The Previous Knowledge About Connection Between the Properties of the Oils and Their Splitability

Up to now the following analytical data on oils were
supposed to be decisive for its splitability.

a.) The Boiling Behavior of an Oil

Heavy gasolines up to about 225°C can be converted
into gasoline relatively difficultly. Good splitting is pro-
duced with well refined oils having an end point up to 300-325°C.
Oils with an end point of about 350°C frequently split much less
well. Feed cut higher than 350°C cannot be converted into gaso-
line at 250 atm over catalyst 6434 without harming them.

b.) The Aniline Point of the Oil

The splitability is better for an oil with the higher
aniline point than of another oil of the same origin, with approxi-
mately the same boiling curve and of the same grade of refining.

c.) The Phenol Content of the Oils

Of two similar oils having different phenol content (or
oxygen-containing compounds) the oil with the higher phenol con-
tent is less well splitable.

d.) The Nitrogen Content of Oils

Of two otherwise similar oils having a different nitrogen
content, the oil with the higher nitrogen content is less well
splitable.

e.) The Sulfur Content of Oils

The sulfur content does act favorably upon the splitabi-
lity of oils, at least within certain limits.

f.) The Unsaturated in the Oils

The di-olefine content of the oils has a harmful effect
on the splitability. Mono-olefines have apparently no noticeable
effect, as can be seen from tests with cracked B middle oils.

g.)   The above results have been in part reported in Report
17889-I by Günther of December 17, 1940.

3.   The Previously Used Methods of Determination of Nitrogen

Up to the beginning of 1941 the high pressure section
of Ludwigshafen determined nitrogen essentially by the methods
of Dumas and Kjeldahl, and occasionally also by the method of
ter Meulen. The Dumas determinations are known to produce in
general too high values. Even substances free from nitrogen
show greater or smaller amounts of nitrogen when the determina-
tion is made by this method. The table below shows results of
analyses of several oils by the methods of Dumas, Kjeldahl and
ter Meulen.

Oil No.	N (Du) %	N (Kj) %	N (tM) %	$(N (Du) - N (Kj)) /N (Kj)$	
1	8.20	7.55	-	+	8.6 %
2	0.96	0.84	0.80	+	14.3 %
3	0.97	0.75	0.69	+	29.4 %
4	0.45	0.28	0.26	+	60.7 %

Of the three determinations the Kjeldahl analyses deserves
the greatest confidence.

A.   The Dumas Determinations

The percentage error of results obtained by the Dumas
analyses were calculated on the assumption that the results of the
Kjeldahl analyses are correct, and introduced in the last column
of the above table. The percentage error increases greatly with
dropping nitrogen content of the samples tested. The deviations

are higher than should be obtained in careful (and correspond-
ingly time consuming) work, but with not too great amount of
care the Dumas method produces results which are no longer accu-
rate in the second decimal. The nitrogen determination in the
splitting hydrogenation feed should be accurate in the third
decimal within at most two units ($\pm$ 0.002%) because the critical
limit is below 0.1%. The Dumas method must therefore be completely
abandoned.

    B.   The Kjeldahl Analyses

        The laboratories which make our analyses claim an accu-
racy of $\pm$ 0.001% by the Kjeldahl method. This would be entirely
satisfactory to us. This claim must, however, be taken with re-
servations as a result of the many hundreds of determinations made
in the course of several years.

        We have found only a very loose connection between the
nitrogen content and the splitability of the oils (with the scat-
tering of results of up to 0.025% N = about 3 times the critical
limit). We have found the following extreme cases:

a.)   The nitrogen content of two samples of an oil was found
to vary between 0.005 and 0.015 or between 0.007 and 0.024, and
between 0.002 and 0.012%.

b.)   About 30 oil samples which should have had similar nitro-
gen content resulting from their previous history were reported
with individual results varying between 0.003 and 0.025% (with the
probable correct average value of 0.008%).

c.)   An oil, the nitrogen content of which had been found to
be 0.009%, was extracted with 50% sulfuric acid. 0.013% nitrogen

was found in the extracted oil. A large number of such cases have been found during pressure refining.

4. The New Merseburg (Leuna) Basicity Determination

We have learned in the beginning of 1941 of a determination of the basic compounds in oil as done in Leuna. Their results were used for an evaluation of the splitability of oils, similarly to our nitrogen determinations. Because of the above mentioned deficiencies of the Kjeldahl nitrogen determination, their method was immediately introduced here to be run parallel to the Kjeldahl determinations. Their method involves the extraction of the basic constituents (or at least a part thereof) from the oil in about 10% acid. The acid solution is then made strongly alkaline and the volatile bases were distilled over into standard acid. The acid consumption was found by titration and the results expressed as "basicity" in mg NH_3/li oil. The following observations have been made on the basicity:

a.) Very good agreement of duplicate determinations.

b.) Rather good agreement in oils which should have had similar nitrogen content from their previous history.

c.) A uniform strong lowering of basicity by refining of oils with dilute acids.

Leuna has called oils with a basicity in excess of 20 as being unsuited for splitting hydrogenation (an exception was a test with 6434 B middle oil from Magdeburg (brown coal tar) with a splitability of 32 (poor, but still useable) while the basicity was 48). Oils with basicity between 3 and 5 are defined as very well refined.

5. Our Present Experience with the Connection Between
Splitability and Nitrogen Content or Basicity of Oils

In the course of the last year 28 oils of different
origin were split in 50 ml converters, and their nitrogen con-
tent was determined by the Kjeldahl method and the basicity were
determined. The results are presented in a table. The split-
ability value determined as in Section 1 is given in the last
column of the table. We may consider this value to mean:

Below 20	Unuseable
20-35	Poor
35-50	Moderate
50-55	Good (normal)
55-65	Very Good
Over 65	Exceptional

In the Diagrams I and II the splitability is plotted on
the ordinates. The Kjeldahl nitrogen contents are plotted along
the abscissa in the Diagram I and the basicity on the Diagram II.
One should have expected a similar course of the curves from left
to right on the two diagrams.

No such relationship can be found in the Diagram I. Two
oils with nitrogen values of 0.001 and 0.21% showed practically
the same splitability; on the other hand greatly differing values
for splitability (17 and 78) were found for oils with almost ident-
ical nitrogen content (0.008% N). Nor could any kind of regularity
be observed in the distribution of the points in the diagram.

The Diagram II shows a distinct connection between the
splitability and the expected basicity, even if the results were

quite strongly scattered. Exceptional splitability was only observed with a basicity of less than 2; poor splitability only for basicity in excess of 8. All middle oils with basicity values up to 2.5 were at least well splitable, while no oils with basicity in excess of 5 were better than moderately well splitable. The location of the points in the diagram permits the characterization of the relationship of splitability from the basicity by average value lines and a certain distance above and below it. With a given nitrogen content the location of the points above or below the line is caused by the scattering of the results on the one hand, and on the other by some other factors which are of determining value on the aplitability of an oil (b.p. range, a.p., phenol content). The results show that with properly prehydrogenated oils with a b.p. not in excess of 325°C, the splitability must be considered satisfactory with a basicity of up to 4-5 mg NH$_3$/ll, while oils with a lower aniline point, which possibly also have been cut higher, the basicity of less than 3 mg NH$_3$/ll is desirable. This could be reached by sulfuric acid washing if needed as has already been showed repeatedly by Dr. Donath.

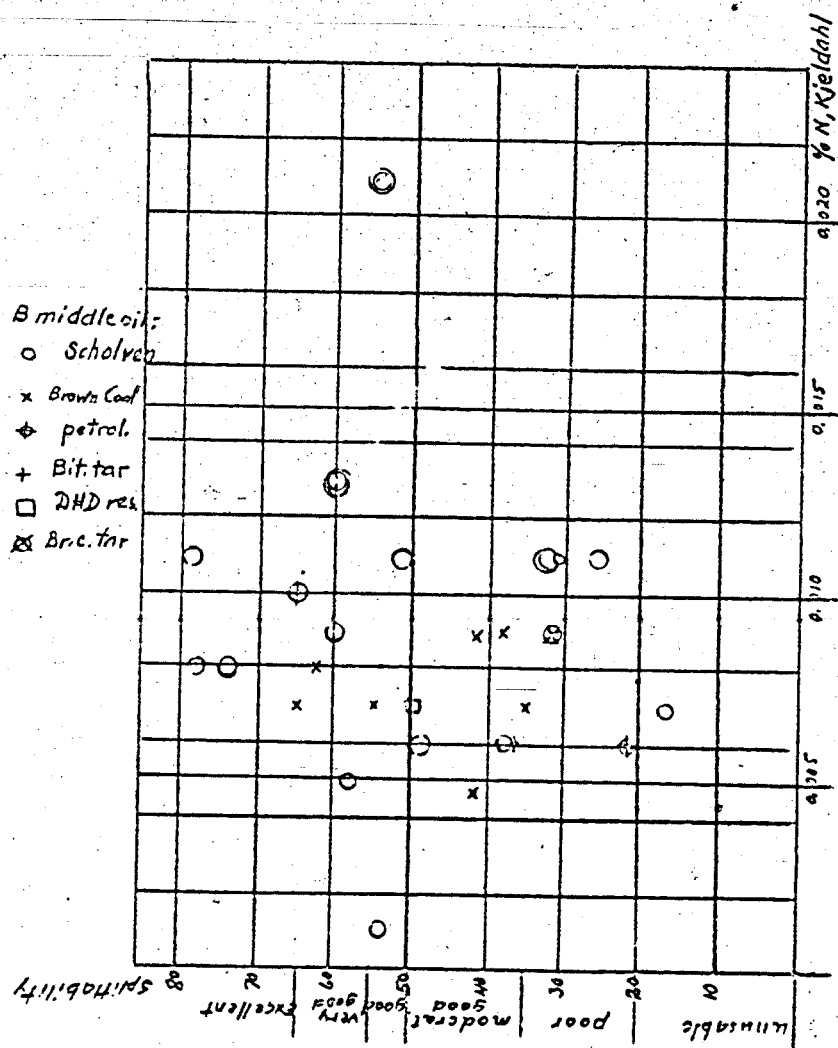   /s/ Gunther

Diagram I. Relation Between Splitability
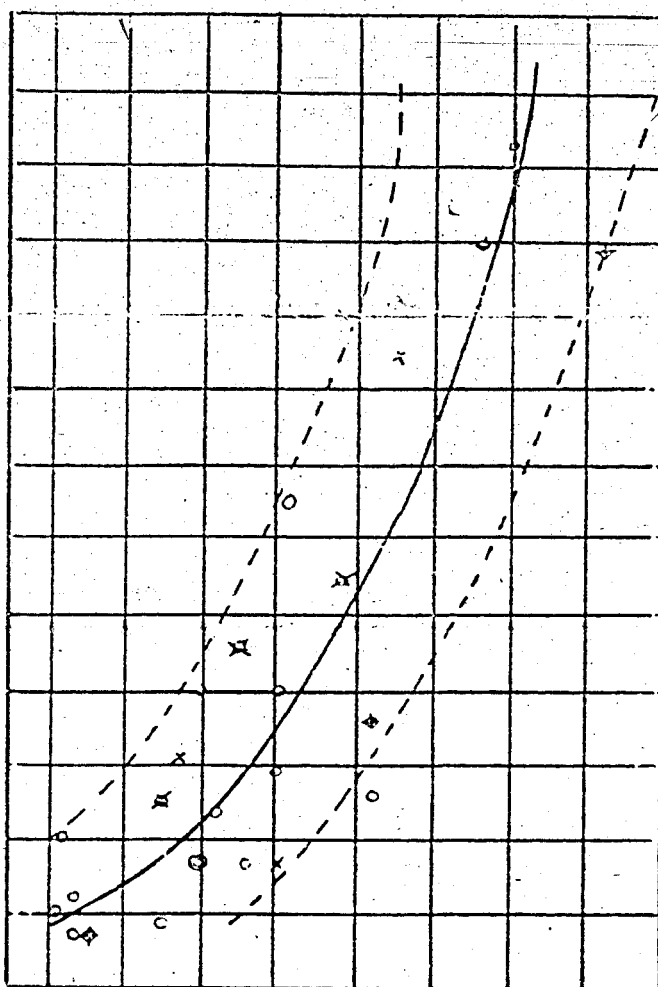and N Content (Kjeldahl)

Diagram II.   Splitting Hydrogenation of Oils and Its
Relationship to Basicity (Nitrogen)

+   B-m.o. from bitum. coal tar
o   " " " "   " liquefaction
⊙   " " "   Rhenish brown coal
x   " " " "   "   " liquefaction
✦ Petroleum A or B middle oil

The Influence of Nature of Feed, Boiling Point, Aniline Point, Phenol and Nitrogen Contents and Basicity on the Splitability of Oils

C213

No.	Feed	Prehydrogenation		B-middle oil						Splitting Hydrogenation (6434)			
		Catal.	T(mv)/Du	End. P.	A.P.	Phenol Content	% N Kjeld.	Basic. mg NH$_3$ Ltr.	T(mv)/Du	Gasoline Conc. -150°C Not Stab.	Gasoline Conc. Calcul. to 19.5 mv	Loss in Activ.	Evaluat.
1	DHD res.	8376	21.5/0.8	316	33	0.01	0.007	2.9	19.8/1.5	55	50	None	Good
2	Bitum.o. Tar	8376	22.5/0.8	338	29	0.02	0.009	10.9	22.5/1.5	15	5	?	No Good
3	Bitum.o. Liquef.	8376	22.5/0.8	315	52	0.02	0.011	1.0	19.0/1.5	66	79	None	Excell.
4	"	8689	22.5/0.8	312	43	0.03	–	1.2	19.3/1.5	69	76	None	Excell.
5	"	8376		310	40	0.13	0.001	1.7	20.0/1.5	65	54	None	Good
6	"	8149	22.5/0.8	312	47	0.02	0.008	2.0	19.0/1.5	65	78	None	Excell.
7	"	8376	22.5/0.8	320	51	0.02	0.005	2.4	19.5/1.5	58	58	None	Very Good
8	"	8238	22.5/0.8	300	39	0.02	0.006	2.6	20.5/1.5	55	38	None	Moderate
9	"	8376	22.5/0.8	306	46	0.02	0.009	4.0	19.5/1.5	60	60	None	Very Good
10	"	8376		313	33	0.24	0.011	4.0	20.0/1.5	60	50	None	Good
11	"	8376		308	44	0.13	0.006	6.5	19.5/1.5	49	49	Moderate	Moderate
12	"	8502	22.5/0.8	315	39	0.31	0.011	41.0	21.0/1.5	45	26	? None	Poor
13	Brown o.	8376	22.5/0.8	352	48	0.03	0.021	?	19.5/1.5	55	55	None	Very Good
14	"	8376	22.5/0.8	324	50	0.01	0.013	1.7	19.5/1.5	60↓	60↓	None	Very Good
15	"	8376	22.5/0.8	348	42	0.03	0.012	9.2	20.0/1.5	50↓	35↓	Becomes Strong	Poor
16	Brown o. Liquef.	5058) 7846)		332	48	0.02	0.011	1.7	19.5/1.5	50	50	None	Good
17	"	7846	22.5/0.8	319	48	0.02	0.007	2.5	19.5/1.5	65	65	? None	Very Good
18	"	8376	22.5/0.8	320	51	0.02	0.009	3.1	20.0/1.5	46	38	Moderate	Moderate
19	"	5058) 7846)		318	47	0.90	0.008	3.1	19.5/1.5	63	63	None	Very Good
20	"	5058) 7846)	22.5/0.8	320	51	0.02	0.007	4.6	19.8/1.5	60	53	Slight	Good
21	"	5058) 6719)		322	38 ?	0.14	0.004	5.5	20.0/1.5	50	42	Moderate	Moderate
22	"	8376	21.0/1.0	325	46	0.12	0.007	8.5	19.5/1.5	35	35	Distinct	Poor
23	"	5058		311	48	1.20	0.009	9.0	20.0/1.5	50	42	Slight	Moderate
24	Brown o. Tar	6434		318	50	1.43	0.009	48.0	20.5/1.5	46	32	? None	Poor
25	Petrol.	8376	22.5/0.8	350	63	0.02	0.008	0.7	19.0/1.5	62	74	None	Poor
26	"	8376	22.5/0.8	350	66	0.03	0.010	0.9	19.5/1.5	65	65	None	Very Good
27	"	7846	24/0.8	325	60	0.02	0.006	10.0	21.5/1.5	50	24	?	Poor

II

The vapor phase was operated as a single stage process
up to 1935, towards the last using catalyst 5058. All kinds of
liquid products from coal, tar, petroleum or synthesis with not
too high an end point could be split to gasoline. The thruput
and the temperature were set depending on the nature of the feed
in a way to produce a maximum amount of gasoline in the catchpot,
while keeping the gasification at a minimum. This method is shown
schematically in Figure I.

The catalyst 6434 was discovered in 1935. It does not
hydrogenate as strongly as 5058 and gives a gasoline with a higher
octane number. It has been found, however, that this catalyst
could not be used like the catalyst 5058 because it rapidly loses
its splitting activity when splitting O, N and S-containing liquid
phase middle oils. It can be used, according to the scheme in Fig-
ure I, only for the splitting of clean petroleum A middle oils. All
other middle oils had to be worked up in a two-stage process (Fig-
ure II). The feed in this process is first operated under minimum
splitting conditions over a prehydrogenation catalyst (5058 or one
of the new dilute catalysts 7846 or 8376). Gasoline is separated
from the product, and the practically O and N-free prehydrogenated
middle oil is split in accordance with the methods shown in Figure
I over catalyst 6434. The products from the prehydrogenation con-
verters and from the 6434 converters are jointly distilled indus-
trially.

A closer study of the relationships existing when working with 6434 showed among other: that splitability of an oil over 6434 is essentially determined by

1). The boiling point curve of the oil, in particular its end point.

2). The hydrogen content of the oil characterized by the aniline point.

3). Oxygen content, characterized by the content of acid oils.

4). By its N content.

The effect of the end boiling point is taken into consideration by limiting it to 325°C, or with especially good properties of the oil to a temperature of 350°C. The boiling tailings above 360°C have extraordinarily great splitting-inhibiting effect in all cases so far investigated.

The effect of the aniline point on oils having good properties is slight in the principally interesting field of over about 40°C. Feed with an aniline point of -10°C could still be well split if the oils were largely free from N and O, e.g. 8376 B middle oil from the DHD residue. According to our experience the acid oil content should be below 0.1% to produce good splitting of the oil over 6434. This is regularly produced by the dilute pre-hydrogenation catalysts of the 7846 type.

The rule has, up to now, been used for the N content of oil that it should be less than 0.010% by the Kjeldahl method. In general, the N content is the principal splitting-inhibiting factor in common industrial practice.

The experimental material of the last four years was reviewed and a few systematic tests were carried out in order to permit numerical expression of the splitability of oils. The results were, e.g. expressed in the concentration of gasoline of a definite end boiling point in the catchpot, indicating the experimental conditions (type of converter, catalyst, pressure, temperature, thruput, gas:oil proportion and the sulfurizing of the feed). A comparison of two tests is often very difficult because of the large number of experimental requirements. It was therefore important to standardize conditions for a comparative test, and make the gasoline concentration _alone_ the principal item in the judging of the splitability of an oil. Dr. Peters' group has standardized the tests as follows:

Type of converter	50 mls with upward flow
Catalyst	6434 T pills, standard sample
Pressure	250 atm
Thruput	1.5 (= 75 g/h)
Gas:oil proportion	2.7 (= 200 l1/h)
Sulfur addition	0.75% CS_2:oil

The temperature is regulated from time to time to have slightly over 50% gasoline below 150°C end point in the catchpot, but should not be over 22.5 mv = 434°C, because the splitting hydrogenation is of no practical interest above that temperature. The temperature is set in this way because the tests give information on the yield and quality of the gasoline under industrial conditions, i.e. when operating for about 50% gasoline -150°C in the catchpot, in addition to determining the splitability of an oil.

The splitability of an oil is therefore characterized by gasoline concentration and the temperature required for it.

The splitability of an oil could be expressed by a single number if the relationship between the gasoline concentration and temperature were found, which would permit recalculating the gasoline concentrations obtained at different temperatures to some standard temperature.

The voluminous experimental material of the last four years shows that when the temperature is raised 1/2 mv, the gasoline concentration in the catchpot (in particular the concentration of the unstabilized fraction boiling below 150°C) rises by 1.2 times. This relationship is varied in the interval from 20-75% gasoline in the catchpot (Figure III).

This relationship permits recalculating the gasoline concentrations obtained at any temperatures, but especially between 18 and 22.5 mv, to a fixed temperature. 19.5 mv has been selected for our tests (Dr. Peters' group). This gasoline concentration calculated to 19.5 mv gives in a single number, without any sub script, a measure for the splitability of an oil over the 6434 catalyst. It has been called by us the "splitability". We can characterize this magnitude as follows:

0-20	Unuseable
21-35	Poor
36-50	Moderate
51-55	Good (Normal)
56-65	Very Good
66 and over	Exceptional

A certain connection between the splitability of an oil over 6434 and its N content has been known for some time.

Tests on the splitting hydrogenation of oils alone or
with the addition of N compounds show the great effect of small
amounts of added N compounds on the splitability (Figure IV).

One could therefore have expected a clear connection
between the analytically obtained N values of different oils
(Kjeldahl) and their splitability. The results are shown in the
Diagram I, precoeding article. One might have expected a general
distribution of the points from the upper left corner to the lower
right corner. Such is not the case however. Systematic experi-
ments performed later show that the Kjeldahl determination was too
inaccurate for the range in question (0.000-0.010%). The N values
obtained by this method with synthetic middle oils would have made
one expect a much poorer splitability of these oils, than was act-
ually the case, and which couldn't be correct from the method of
preparation of these feeds.

A new method of N determination became known in the spring
of 1941, which was used in Leuna for the control of the N refining
during the prehydrogenation. Dr. Wittmann will make a report on
this method. It will be merely mentioned here that in general two
liters, but at least one liter of oil, are used for a double deter-
mination. The results are expressed in mg $NH_3/11$ oil. This number
has been called the "basicity".

We have immediately applied this method for the investi-
gation of our oils. The relationship between the splitability of
many oils found from splitting hydrogenation tests was studied in
the light of the basicity of these oils. The results are shown in
Figure V. One might have expected in this case a distribution of

the points from the upper left corner to the lower right corner,
as in the relationship between the splitability from the Kjeldahl
nitrogen. The diagram in the main justifies these expectations.
The width of the band is caused by the use of B middle oils from
different sources (DHD residues, bituminous coal tar, bituminous
coal liquefaction products, brown coal liquefaction and petroleum).
Also by the differences in the aniline points, phenol contents and
boiling points of the B middle oils used. We believe, however,
that a more quiet operation of the prehydrogenation converters than
is obtained in our 200 ml converters would result in an improvement,
i.e. that presumably the basicity will be even more to be recommen-
ded in industrial evaluation of splitability than we have found. It
is, moreover, not excluded that the analytical method itself can be
further improved.

We must add to our discussion of Figure V: tests in which
the catalyst efficiency dropped more rapidly cannot be considered
in this connection. This was obtained also with oils having very
good basicity, e.g. with the B middle oil from 5059/7846 stall in
Leuna. High N content of oils causes, according to our experience,
a low, but constant space/time yield over 6434. The drop in acti-
vity may be caused by other factors, possibly by a certain propor-
tion of di-olefines present in the oil.

The figure shows that poor splitability has not yet been
observed by us with correctly cut products with low basicity values,
as long as tests in which the catalyst activity dropped were not
considered. Far more frequently has been observed an unexpectedly

good splitability with higher basicity. We have no reason whatsoever to assume wrong results from the laboratory. It rather seems to us that the oil was contaminated by NH_3 or something like it, the source of which is as yet unknown to us. The sensitivity of the method may be judged from the following:

If a properly prehydrogenated bituminous coal B middle oil with a basicity of 3.0 is contaminated with 1/10% of crude product, it will immediately be expressed by an increase in the basicity to 3.8. If the contamination is with 1% of the crude product, the basicity will rise to 11.0 which will make the B middle oil practically unuseable for working up over 6434.

Brown coal tar and bituminous coal l.t.c. tar have not been included in the feed in Figure V. They occupy a special position with respect to many hydrogenation properties. In all cases investigated, the splitability of the B middle oils from these materials was better in order of magnitude than could have been expected from the basicity values. A basicity value of over 10 represents moderate splitability in Figure V, but the middle oils of the above mentioned materials were well splitable even with basicity numbers of over 70, i.e. they could be used industrially as 6434 feed if properly cut (end point not over 340°C). A parallel case is found in the a- or s-middle oils from brown coal tar as the only feed which could be prehydrogenated over 6434, and the 6434 reduces its activity relatively very little in this operation.

The petroleum A middle oils also behave differently from the B products of bituminous or brown coal. Among the large number

of oils investigated there were some with a basicity between 20
and 40 and while not good they still could be split with satis-
factory industrial efficiency, i.e. about like the B feed from
bituminous coal with basicity values between 5-10. On the other
hand, a Japanese oil which differed in its hydrogenating proper-
ties from all our known oils was difficult to split with a basi-
city number of 1.9.

In general, the critical basicity of the petroleum A
middle oils may be about three times as high as of the brown and
bituminous coal B middle oils.

Four petroleum S middle oils were split since the intro-
duction of the basicity method. The aniline point of all the four
oils varied between 1 and 52, their iodine numbers were similar
and the acid constituents were the same as in the corresponding
A middle oils, but their basicity numbers were about 50 times
higher (450-750). All of them were unsuited for-splitting hydro-
genation.

All of this points to the effect of nitrogen not being, in
all cases, proportional to its concentration. We suspected that
the form of combination of this nitrogen in the molecule affected
its splitting inhibiting action. This suspicion led to testing of
nitrogen added in different forms upon the splitability of a largely
N-free oil (refined Bruchsal gasoil P-1203). 0.015% N was always
added to the oil, using in individual instances compounds like di
butyl amine, aniline, di methyl aniline, methyl naphthyl amine,
pyrrol, pyridin and quinolin. Nitrogen was therefore added in the
form of aliphatic amines, aromatic amines and unsaturated hetero-

cyclic compounds. Piperidin is yet to be tested as a representative of saturated heterocyclic compounds.

The gasoline concentration obtained with the untreated oil was invaribly determined first. The figures 64, 62, 63, 66, 67, 69 and 65 prove the good reproducibility of the tests. The gasoline concentration fell in the course of five days through the addition of nitrogen to 30, 34, 41, 30, 54, 41 and 37% of the initial values. Omitting nitrogen increased the concentration in every case again to 102, 87, 89, 86, 78, 93 and 96% of the original values. According to these tests nitrogen in the form of methyl naphtnyl amine acted most harmfully. It was followed by aniline, quinoline, pyridin, di methyl aniline, di butyl amine and pyrrol, which appears to damage the activity of 6434 the least. Attempts to introduce any kind of systematic arrangement of these results were fruitless. Further tests in this field are in progress.

. . . .

We may summarize by saying that we consider the basicity as eminently suitable for evaluation of the splitability of B middle oils or for the control analysis of the effectiveness of prehydrogenation. We could make no such claims for the Kjeldahl determinations. The determination of basicity of B middle oils has been included in all the prehydrogenation tests made for over a year by Dr. Peters' group.

/s/ Günther
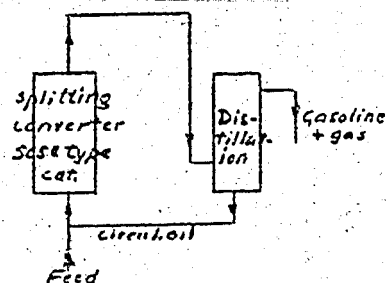
C223   T- 4 78 - II

Fig. 1. Single stage Vapor Phase

splitting
converter
S4se type
cat.

Dis-
tilla-
tion

Gasoline
+ gas

circul. oil

Feed

Fig. 2. Two stage Vapor Phase

Prehyd-
rogen.
5+5e

gasoline
+ gas

Distil/n

Splitt.
convert.
E636

gasoline
+ gas

Distil/n

B-m.o.

8636 circul. oil
+ C m.o.

A feed

%
90
80
70
60
50
40
30
20
10

16 17 18 19 20 21 22 mv
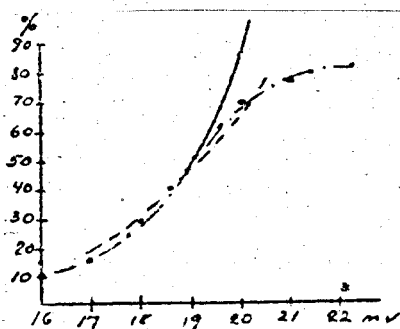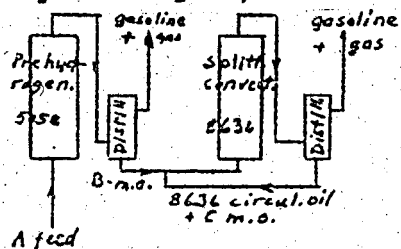
Fig 3. Gasol. conc. from petrol. gasoil

no
aniline

a.1% aniline
To oil

no
aniline

% gasoline
conten in catalyst

70
60
50
40
30
20
10

1 2 3 4 5 6 7 8
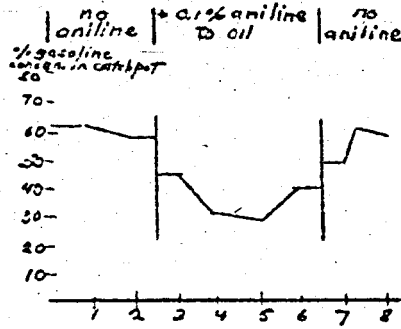
Fig. 4. Effect of aniline on splitting
petrol. gasoil over 6434

90
80
70
60
50
40
30
20
10

splitability

1 2 3 4 5 6 7 8 9 10 11 12 13 14
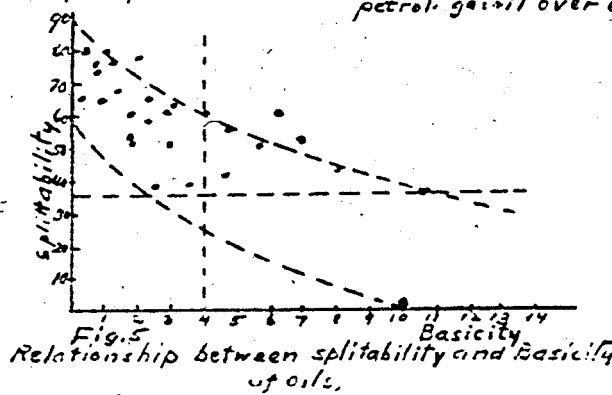
Basicity

Fig. 5
Relationship between splitability and Basicity
of oils.

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III

Summary

    A clear relationship of splitability of oils composed of mixtures of practically nitrogen-free gasoil and bituminous coal liquefaction middle oil from Scholven, with calculated basicity numbers of 0.0, 1.3, 2.5, 5.0, 10.0, 20.0 and 50.0 showed differences which could be attributed only to the nitrogen content of the oils.

                              /s/ Günther

The Bruchsal gasoil P-1203, 180-330°C, washed with 50% sulfuric acid (basicity by the methyl orange method 0.0, and in every case below 1.0) and the bituminous coal liquefaction middle oil of Scholven P-1271, 180-325°C (basicity about 5,000) were used to prepare mixtures containing 0.025, 0.05, 0.10, 0.20, 0.40 and 1.00% of P-1271. The analyses of these mixtures may be seen from the table below:

Oil	% P 1203	% P-1271	Sp.Gr.	A.P.	Init. B.P.	% -22.	E.P.	Calcul. % Phenols	Calcul. m.o. Basicity
A	100.000	0.000	0.818	65	155	35	330	0.000	0.0
D	99.975	0.025	0.818	66	150	35	323	0.003	1.3
E	99.950	0.050	0.818	66	150	34	323	0.007	2.5
F	99.900	0.100	0.819	65	154	35	325	0.013	5.0
G	99.800	0.200	0.818	65	150	35	325	0.026	10.0
H	99.600	0.400	0.818	66	155	34	325	0.052	20.0
C	99.000	1.000	0.819	65	155	34	327	0.130	50.0
B	0.000	100.000	0.977	-23	185	26	335	13.000	5000.0

The analyses show that oils A, D, E, F, G, H and C had practically the same aniline points and boiling point curves. Experience has moreover shown that the phenol content of 0.1% and up to 0.5 in hydrogen-rich feed, (and such are the mixtures used) was but of slight influence on the splitability of oils.

No effect of hydrogen content, boiling point curve or phenol content of these oils upon splitability was to be expected, and the difference in splitability must be attributed to differences in the nitrogen contents of the oil. The mixtures were so compounded that a noticeable difference in splitability was to be expected between the oils A and D.

All oils were split under strictly comparable conditions, as follows: different converters of the same type were used, and in each converter a blank test with oil A was carried through. The conditions were:

Type of converter	50 mls with upward flow
Catalyst	6434 P pills, 30 li charge for Dr. Peters
Pressure	250 atm gas (= 245 atm H_2)
Temperature	19 mv = 373°C
Thruput	1.5 kg oil/li catalyst/h = 75g/h
Oil:gas	2.7 cbm/kg = 200 li/h
Sulfur addition	0.75% CS_2 to oil

The blank runs with oil A give the following results:

Converter	Gasoline Concentration	Splitability
2	66	79
3	67	80
7	67	80
8	65	78

These results indicate their excellent comparability.

The splitting hydrogenation of oils A, D, E, F, G, H and C give the following results:

| Oil	Theoretical Basicity, mo method	Sp.Gr.	Catchpot % -150°C	Splitability
A	0.0	0.727	66	79
D	1.3	0.734	62	74
E	2.5	0.742	57	68
F	5.0	0.742	53	64
G	10.0	0.751	48	58
H	20.0	0.764	43	52
C	50.0	0.774	35	42

As was to be expected, a clear relationship between split-ability and the basicity of the oils can be seen. The curves in the appendix show it graphically.

/s/ Günther

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Relation between splitability and basicity.
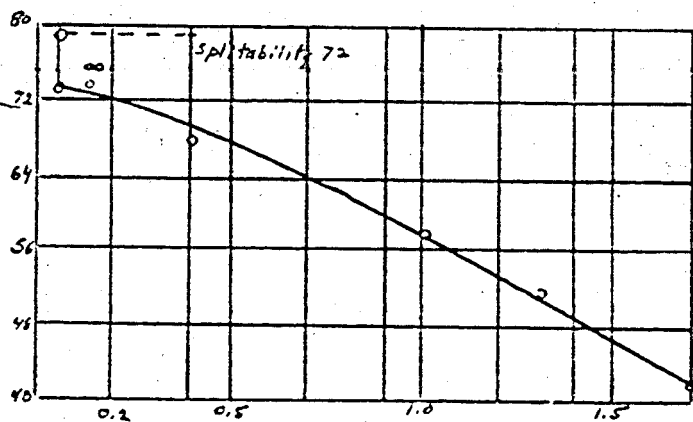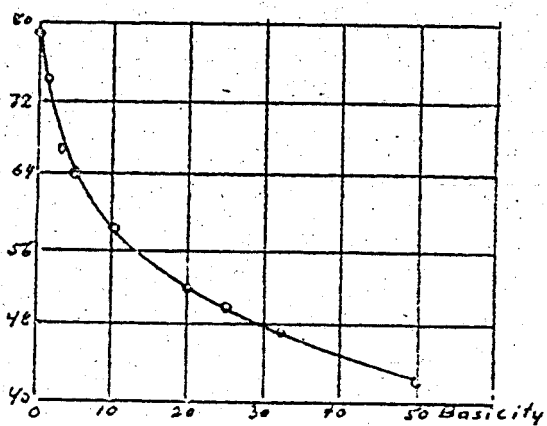
REPLACING OF TERRANA IN 6434 BY SYNTHETIC SILICATES

Summary

        Catalysts were prepared of precipitated aluminum sili-
cate and WS_2, similar to 6434. These catalysts were compared
with 6434 by working with Elwersther gasoil. They were inferior
in space/time yield and purification by about 20%, but are super-
ior in the quality of gasoline (aniline point and octane number)
to 6434. Bituminous coal B middle oil (obtained from 5058 as well
as over iron tungsten catalysts) could be worked up perfectly with
these catalysts.

        The motor gasolines obtained with the 5058 B middle oil
had an octane number 5 to 6 units higher than when prepared with
6434, while the space/time yield and gasification were by about
25% poorer than with 6434.

                        . . . . . .

        Different catalysts were prepared to correspond with 6434
in which precipitated silicates were used as carriers instead of
the natural bleaching earth. The precipitation was done by acidi-
fying with hydrochloric acid an alkaline solution of sodium sili-
cate, an aluminum salt (and occasionally small amounts of iron and
magnesium salts), and the acid neutralized with ammonia to a defi-
nite pH value. The silicate precipitated gradually from the sol
and was finally filtered and washed.

        The following carriers were prepared:

For Catalysts	Composition	
7344	Aluminum silicate precipitated at pH	4.5-5.0
7401 Ch I	" " with some Fe + Ng	
	precipitated at pH	6.5

7401 Ch II	Aluminum silicate with some Fe + Ng precipitated at pH	6.5
7369	Aluminum silicate with some Fe + Ng precipitated at pH	9.0
7378	Aluminum silicate with some Fe + Ng precipitated at pH	11.5

10% WS_2 in the form of yellow salt was added to these catalysts in the usual way. The catalysts so obtained were tested with the Elwersther gasoil (P 189 gasoil redistilled). The table gives the results together with the usual results with 6434.

The following is to be noted in the results:

The individual tests were as nearly as possible conducted to the same boiling point behavior of the gasolines (% below 100°C). A comparison with 6434 showed that: the space/time yield is throughout smaller than with 6434; it is better with the acid precipitated catalysts than with the base precipitated. The same applies to the percentage of gasoline in the product.

Gasification also is throughout higher than with 6434, and highest with the acid precipitated catalysts.

The quality of the gasoline produced is better with the catalysts upon synthetic carriers, than with 6434. Here again the acid prepipitated catalysts are better than the alkaline. The octane numbers in the acid catalysts, compared with 6434, are about ac follows:

R.M.	6 points better
M.M.	6 points better
M.M.+ 0.09 Pb	0 points better
Lead sensitivity	6 points poorer

The difference in the octane number is at least partially to be attributed to the lower aniline point of the gasolines (49

against 53 with the 6434 gasoline). For this reason no conclu-
sions can be reached on isomerization.

The nitrogen sensitivity of some of the catalysts is also
included in the table. A comparative test with 6434 is not avail-
able.

Some of the catalysts were tested with 5058 B middle oil
from Scholven (a.p. 39.5°C, boiling range 195-302°C), or even with
an Fe-W B middle oil from Scholven liquefaction middle oil (a.p.
30°C, boiling range 205-313°C). With the 5058 B middle oil, 6434
had a thruput of 1.5, space/time yield 1.1 and 8% gasification.
R.M.75.0, M.M.73.5, M.M.+ 0.09 pB 87.0 without loss of efficiency,
7378 thruput of 1.5, space/time yield 0.8 and 12% gasification, R.M.
81.0, M.M.75.5, M.M.+ 0.09 pB 87.0 without loss of activity.

The Fe-W B middle oil was used with the catalyst 7401 Ch I.
With a thruput of 2 and 21 mv the space/time yield was 1.05 with
14% gasification and without loss of activity. The gasoline with
the end point 185°C had a R.M 87, M.M.78 and M.M + 0.09 pB 88.5.

This appears as if all these catalysts can be perfectly sat-
isfactorily used at least with the 5058 B middle oil from bitumi-
nous coal.

                              /s/ Günther, Hartmann and Simon

TERRANA-ZINC SULFIDE-TUNGSTEN AND TERRANA-ZINC SULFIDE-MOLYBDENUM CATALYSTS FOR SPLITTING HYDROGENATION

Summary

1). The catalyst combination terrana HF + zinc sulfide had a very high maximum activity with 15-20% ZnS.

2). The addition of 1% Mo or W sulfides appreciably increased this maximum.

3). Catalysts 7420:85 terrana HF + 15 ZnS + 1% WS_2 and 7421:85 terrana HF + 15 ZnS + 1% MoS_3 gave about the same space/time yield and gasification during the splitting hydrogenation of petroleum as 6434. The knocking values of the gasolines were on the average 1-2 units higher than with 6434.

4). These catalysts were reversibly harmed by nitrogen compounds, similar to the catalyst 6434.

5). The bituminous coal midle oil prehydrogenated with 5058 can be split over 7421 without difficulties.

6). In the combination of terrana W-zinc oxide (+ 1% WS_2) the mixture 85:15 is much more active than the components. The activity of the catalysts with zinc sulfide additions have, however, not been reached by far.

7). Addition of cadmium, iron and lantnanum to terrana-ZnS-1 W catalyst lowered the activity.

TESTING THE CATALYST WITH PETROLEUM MIDDLE OIL

Operating Conditions

The tests were run in a 50 ml vapor phase converter at 200 atm using redistilled Elwersther gasoil, boiling range 200-325°C,

with the addition of 0.75% carbon di-sulfide with a thruput of
2 (in a few cases also 1.5) and 2.5 cbm H_2/kg of the feed.

The catalysts were made with the addition of zinc in
amounts corresponding to the chloride additions in the catalyst
7426 (composed of 80% HF-treated terrana and 20 parts zinc chlo-
ride and prepared by sulfurizing at 400°C); they contained there-
fore instead of 20 parts zinc chloride about 15 parts zinc sulfide
or 13 parts ZnO.

Results

The results are presented numerically in Table I (arranged
in order of the catalyst numbers). (Not reproduced)

Table II contains catalysts prepared from terrana and zinc
acetate by precipitation and saturation with Mo or W in the form of
sulfates and arranged according to their zinc content and alwayc
characterized by the splitting hydrogenation temperatures used and
the motor gasoline yields obtained. (Not reproduced)

The HF-treated terrana as well as the precipitated zinc
sulfide are but little active by themselves, even after the addi-
tion of 1% Mo or W and at 200 atm pressure. All mixtures of these
components are more active and the activity of the mixture 85 parts
terrana with 15 parts zinc sulfide has an extraordinarily strongly
expressed maximum, which is still appreciably increased by the addi-
tion of 1% Mo or W. Even as little as 0.1% Mo causes a remarkable
increase in the activity of the terrana-zinc sulfide catalysts.
Fig. 1 shows the gasoline production graphically against the terrana:
zinc sulfide ratio. The temperatures of splitting hydrogenation

show that a very strong maximum of the splitting is obtained with
terrana:ZnS = 85:15, although catalysts with other mixing propor-
tions were operated at higher temperatures. The tendency of the
catalysts to lose their activity, which is very great with catalysts
containing high Zn content, is reduced with increasing activity.

Tests with catalysts 7426 and 7445 show that the catalysts
prepared from $ZnCl_2$ by sulfurizing with H_2S at 400°C are almost as
active as those produced by the precipitation from the acetate. A
catalyst produced by precipitation from $ZnCl_2$ was; however, appre-
ciably less active (7444).

Substituting zinc hydroxide for the ZnS (catalyst 7444)
results in the formation of a very little active catalyst. On the
other hand the ZnO-terrana containing 1% WS_2 (7458) still had a re-
markably high activity. With 0.98 space/time yield it was, however,
considerably lower than the corresponding sulfide catalysts (7420
with 1.35 space/time yield). The addition of chromium oxide to ZnO
reduced the catalytic activity of this catalyst (7451).

A partial replacement of ZnS by cadmium sulfide (catalyst
7466) appreciably reduced the catalyst activity. The addition of
iron sulfide was also unfavorable (catalyst 7461). It causes simul-
taneously reduction in the octane number of the gasoline (R.M. 65
instead of about 69). A partial replacement of the zinc sulfide by
lanthanum oxide (catalyst 7453) in 85 terrana-15 ZnS-1 WS_2 reduced
the space/time yield still further than the corresponding cadmium
addition.

85 terrana-15 ZnS-1 Mo and 1 tungsten catalyst produced gas-
olines with somewhat lower aniline points (3-5°) and correspondingly

somewhat higher octane numbers (1-2 points). The space/time yield
was in general the same as that of 6434. The latter does not, how-
ever, lose its activity with a thruput of 3 kg/li/h, while the terr-
ana-zinc sulfide catalysts with one-tenth of the amount of tungsten
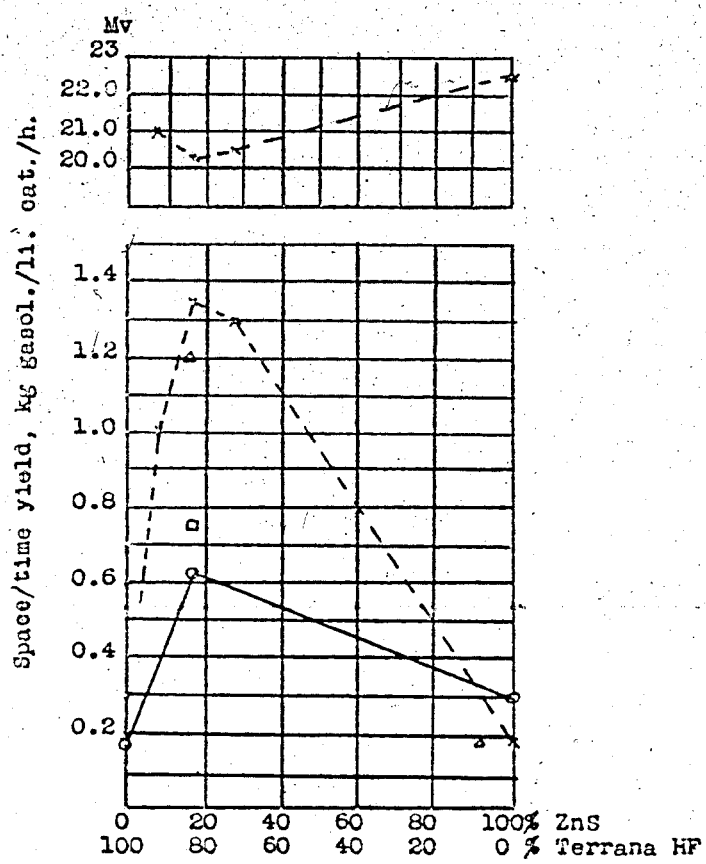reach their maximum load with a thruput of 2.0.

The nitrogen sensitivity is equally prominent in the zinc
catalyst as with 6434, and the damage is also reversible. The addi-
tion of 0.1% of aniline to the injection feed caused the space/time
yield to drop to one-half in the course of a few hours, and omitting
the aniline addition caused the space/time yield to rise again to
the original value in a short time (converter 10, 9/14/39). In
agreement with the nitrogen sensitivity a middle oil apparently in-
sufficiently prehydrogenated over 6719 could not be split with good
space/time yield and without a loss in activity over the 85 terrana-
15 ZnS-1 Mo catalysts. No good results could be obtained with this
feed over 6434, and no final judgement therefore is possible on the
inferiority of the terrana-zinc sulfide catalysts with 1% Mo or W
in comparison with the terrana 10% WS_2 catalysts.

The 5058 prehydrogenated bituminous coal liquefaction middle
oil could be perfectly operated with the 85 terrana-15 ZnS-1 Mo cata-
lyst. A special report is made on that point.

/s/ Peters and Günther

Mv

Space/time yield, kg gasol./li. cat./h.

23
22.0
21.0
20.0

1.4
1.2
1.0
0.8
0.6
0.4
0.2

| 0 | 20 | 40 | 60 | 80 | 100% ZnS |
| 100 | 80 | 60 | 40 | 20 | 0 % Terrana HF |

Terrana HF
+ x% ZnS

o   no addition
x   1% WS₂
△   1% MoS₂
□   0.1% MoS₂

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W. M. Sternberg

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COMPOSITION AND PREPARATION OF 6434 CATALYST

The composition of the catalyst 6434 with 10% WS_2 does not correspond to the optimum activity of dilute catalysts. Catalysts with much smaller amounts of WS_2 have already been prepared, which had equal activity. Thus, the catalyst 112931 with 3% WS_2 was compared with catalyst 6434 containing 10% WS_2 and it was found that the space/time yield was almost the same with 3% WS_2 at higher temperatures and with somewhat greater amounts of gasification. A conclusion was at that time drawn that with hydrogen-rich products the catalyst with 3% WS_2 was satisfactory, while with hydrogen-poor or oxygen-containing feed (poorly refined feed) the hydrogenation activity of this catalyst is no longer sufficient and the catalyst with 10% WS_2 must be used. With MoS_2 as a hydrogenation component the necessary MoS_2 content may reach 20% (Dr. Simon's report on No. 1231 31).

There is in addition the possibility of attaining erroneous results with the lower WS_2 content because of the variations in the fuller's earth quality, insufficient care during the HF treatment or WS_3 saturation, and these variations were much higher than with the 6434 catalyst with the higher WS_2 content. The industrial refining of middle oils during prehydrogenation was not

always perfect and could be more readily done with the 6434 catalyst than with the catalyst containing only 3% WS₃. There was an additional reason in the longer life of the 6434. This latter assumption may not have been justified, but I will point out that in my opinion the loss of activity of 6434 is not to be attributed to the inactivation of WS₂, but to the changes in the surface of the HF-treated fuller's earth.

Acoording to the present status of prehydrogenation in the works using 8376, and followed by a washing, the question of the lowering of WS₂ content to 5 or to 3% would be important when we do not consider the recovery of WO₃ from the used up 6434, which can be done with good yields. In the recovery of WO₃ from the catalyst with over 7.5% WO₃ the yield of FeW is 93%, and only 65% with 5% WO₃ in the catalyst. We lose, therefore, during recovery 7 kg of WO₃ when recovering one ton of catalysts with 10% WO₃, and 17 kg WO₃ from the 5% WO₃ catalyst. The present 6434 catalyst uses double the amount of WO₃ as the 5% WS₂ catalyst, but the relative and the absolute losses of WO₃ are smaller and the operation of the splitting hydrogenation stall, and the quality of the 6434 products is more certain. The preparation of 6434 has been changed somewhat for the production of perfect catalysts. Changing the process on an industrial scale has so far been avoided for safety reasons. One may, e.g., eliminate the production of the yellow salt and dissolve WO₃ directly in (NH₄)₂S by saturating, or simply saturating the fuller's earth with WO₃ dissolved in HF. Both catalysts are as good as 6434.

REFINING CATALYSTS 7525, 7675, 7360, 7846

The refining catalysts 7525 and 7675 produced middle oils with a lower aniline point than 5058. They could be worked up with 6434 with the same space/time yield as the middle oils prehydrogenated with 5058, but at a temperature 0.5-1 ov higher.

In the meantime, refining catalyst 6719 had been developed with the same 5058 contents as the 7525, but which is a much better prehydrogenation catalyst, and has to date been tested industrially with bituminous coal feed. The aniline point of the b-middle oils and the splitting hydrogenation efficiency of the 5058 prehydrogenation have not, however, been completely reached with this catalyst.

The subsequent development of 7360 has led us to refining catalyst 7846, which has a very good refining action with bituminous coal as well as with brown coal feeds (elimination of O and N compounds). The aniline point of the prehydrogenation middle oil was not as high as reached with 5058, but the middle oils could be worked up with the same space/time yield of 6434, which is to be attributed to the even better phenol and nitrogen reduction than with the 5058. One advantage of this refining catalyst is the higher octane number of the 6434 gasoline produced. The splitting is less with 7846 than with 5058, and less prehydrogenation gasoline is obtained.

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A combination of 20% by volume of 5058, followed by 80% of 7846, the splitting and the aniline point can closely approach the values for the 5058 prehydrogenation.

We recommend therefore the use of 7846 alone or in combination with 5058, the described above.

PREHYDROGENATION CATALYSTS

The Use of 8376 Prehydrogenation Catalyst (Alumina-W-Ni) For Various Feeds

Summary

1.) The space/time yield of the liquid phase was reduced in Magdeburg because of the changing over from Mo to iron. It has been proposed to equalize that by cutting the a + s distillation higher (up to 325°C). A feed cut -434°C in the first stage cannot be worked up and the prehydrogenation in Magdeburg was done by introducing a special catalyst, e.g. 8376.

2.) The present Magdeburg vapor phase feed with the boiling point -310°C, as well as the feed obtained by a higher cut of the a + s distillation, boiling point -360°C, were worked up over the catalyst 8376. Products were prepared with a s-middle oil, aniline point of over 60°C (maximum hydrogenation), and with 3-middle oil, aniline point 45-50°C (corresponding to hydrogenation over the catalyst 6434). The four 3-middle oils were split over the catalyst 6434.

3.) The catalyst 8376 hydrogenated appreciably stronger than 6434 at its optimum temperature.

4.) When hydrogenating the same 3-middle oil with an aniline point about 45-50°C as with the catalyst 6434, the gasoline is more

strongly hydrogenated over the catalyst 8376 and its octane number is not as good as of the 6434 prehydrogenation gasoline. The 8376 B-middle oil cannot be split as readily as the 6434 B-middle oil in spite of the better basicity of the former.

5.) When 6434 gasoline is compared prepared from 6434 and 8376 B-middle oils with the same aniline point, we find that from the 8376 B-middle oil a gasoline is obtained with much less aromatics than from the 6434 B-middle oil. The octane number M.M. of the 6434 gasoline from the 8376 B-middle oil is about three points lower with the same out (68.5 against 71.5) than the 6434 gasoline from the 6434 B-middle oil.

6.) The finished gasoline obtained by the methods 6434/6434 and 8376/6434 differ materially in their composition and octane number. The 8376/6434 gasoline contains the same proportion of paraffins, less aromatics (9 against 17) and correspondingly more naphthenes (34 against 27). In spite of the low content on prehydrogenation gasoline the octane number is 3-4 points lower (65-66) than the 6434/6434 gasoline (octane number 69).

7.) The principal experimental results have been collected in tables. They show that the space/time yield of the liquid phase could be increased by a higher cut if the first 6434 stage of the vapor phase is replaced by 8376 stage. This increase in the space/time yield would, however, be accompanied by a reduction of the octane number of the finished gasoline from 69 to 65-66.

/s/ Günther

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0242

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HYDROGENATION GASOLINES. EFFECT OF RAW MATERIALS, CATALYSTS AND
OPERATING PROCEDURES

By: M. Pier

General Information on High Pressure Hydrogenation

The world reserves in petroleum oils are much smaller than
the coal reserves. Moreover the proportion of gasoline to the
higher boiling constituents in natural petroleum is not in the
quantitative relationship in which they are used industrially.
For this reason gasoline yields from the crude oils are increased
by suitable operations, and increasing amounts of solid fossil
fuels are used for the production of liquid motor fuels. In
addition to the purely thermal processes for the production of
the low boiling hydrocarbons formerly exclusively used, such as
the cracking of petroleum, coking, or low temperature carbonization
of solid fuels, some other processes have in the course of time
become important, e.g. the polymerization of gaseous hydrocarbons
from natural gas and cracking gases, catalytic cracking, catalytic
hydrocarbon synthesis from carbon monoxide-hydrogen mixtures, and
in particular the catalytic pressure hydrogenation. Liquid fuels
are produced by purely thermal processes from coal and other raw
materials of high molecular weight, but the yield from distillation

and refining is relatively small, because of the low original
hydrogen content. However, a conversion of such hydrocarbons
into liquid products, accompanied by only slight losses may be
produced by splitting at high pressure in the presence of catalysts,
and with a simultaneous addition of hydrogen.

The hydrogenation of coal and oil under pressure has already
been done by Bergius in 1913, but the process has acquired practical
importance only after the introduction of poison-resisting catalysts
by the I. G. Farbenindustrie A. G. Bituminous coal, brown coal,
peat, coal extracts, pitch, high and low temperature tars, oil
shale, petroleum and its distillation, extraction, and cracking
products, etc. can be used as raw materials. High yields of fuel
oils or high grade diesel oils, illuminating oils, lubricants,
paraffins and gasolines in great variety of properties are the
products obtained. It must be in particular emphasized that
catalytic hydrogenation enables one to meet the continuously
rising requirements in the quality of the products, in particular
for gasolines.

The adaptation of the process to the different raw materials
and to the required properties of the final products is facilitated
by dividing the high pressure hydrogenation into two different
stages of operation: the high molecular weight, asphalt rich,
and also ash-containing raw materials, such as coal and heavy
oil residues, are first worked in the liquid phase with a finely
divided catalyst, using only small amounts of catalysts for the
usually considerable amount of splitting. The hydrogenation is

next carried on with fixed bed catalyst, over which hydrogen is conducted together with the middle and heavy oils obtained in the liquid phase either in the form of vapors or occasionally in part liquid, depending on the boiling point and the operating temperature used.

The first effect of the catalyst upon the high molecular weight asphalts in the liquid phase consists in the characteristic acceleration of their greatly increased regulated break-down. This permits an increase in the thruput, while the thermal side reaction and the gas formation are repressed. The character of the raw materials is still distinctly recognizable in the products of the liquid phase reaction, because of the small amounts of catalysts mostly used.

In the vapor phase the course of the reaction over solid bed catalyst is almost completely determined by the catalyst which is used in this case in the highest concentration. The effect of the catalyst action is therefore here very much stronger than in the liquid phase. Efforts are therefore made to enlarge the field of application of the fixed bed catalysts as much as possible. A life of many months or even of several years is expected from them today. They may be used anywhere where their long life will not be effected by deposition of high molecular weight substances, in particular of asphaltic nature. This is true for all the oils of a middle boiling range; however, certain high molecular weight asphalt-poor raw materials can also be worked with fixed bed

catalysts. Thus, industrial brown coal low temperature tar can
be converted in one stage directly into paraffin, lubricating oil
and diesel oil, or in a middle oil which could be next treated by
vapor phase hydrogenation.

A large number of specifically acting poison-proof catalysts
are available today, and in them the relative hydrogenation and
splitting effects are such that the operations can be directed
in any desired way. One may for instance take advantage of the
different reaction possibilities for the production of gasolines
of definite properties, entirely independently from the raw
material. The products obtained over fixed bed catalysts are
well refined and stabilized. A further advantage of the operations
with high concentrations of catalysts is the lower production of
gaseous hydrocarbons, in particular less methane and ethane, than
in the liquid phase hydrogenation. This is particularly important
because of the large amount of hydrogen used up in the formation
of gaseous hydrocarbons, while the hydrocarbons themselves are of
a lower value than gasoline, even if they can reach the fuel market
in the form of liquefied gases.

The effect of temperature is of predominating importance
for the course of the reaction: the velocity of the hydrogenation
reaction, especially the splitting, rises with rising temperature;
moreover the equilibrium in reactions involving the combination
with breaking-off of hydrogen is always displaced in the direction
of dehydrogenation as the temperature rises. Olefinic double
bonds are hydrogenated in the presence of catalysts at temperatures

as low as 200°C. Refining is the principal process at temperatures
of around 300°C; reactions therefore take place with no splitting
of the C-C bonds. At higher temperatures of around 400°C there
is much splitting to gasoline by the catalyst, or else there is a
large amount of hydrogenation of the feed by the hydrogenating
catalysts. In this way gasoline is produced with a small amount
of gas, and in addition good illuminating oils and lubricants are
produced, or asphalt-containing low temperature tars hydrogenated
and refined. If the temperature be further raised to 450°C,
middle oils are obtained from high boiling oils or from coal, with
increasing amount of splitting. Above 500°C splitting can be
produced with proper catalyst without hydrogenation, or even with
dehydrogenation, producing gasolines with high content in aromatics.
Temperatures at which these types of reaction proceed may of
course be greatly affected by the catalysts and pressure.

In general, higher hydrogen pressure results in greater
hydrogenation. It prevents therefore the separation of low hydrogen
products, permitting operations at higher temperatures than can
be done at lower pressures. The oils and gasolines obtained
under such conditions may be even lower in hydrogen than with
lower hydrogen pressures. Higher pressures produce higher
reaction velocities, permitting a greater thruput of raw material
through the same reaction space. We may illustrate the effect
of pressure on the liquid phase operations by telling that older
bituminous coals or high molecular weight asphalts are changed
very little at 200-300 atm, while at much higher pressures, such

as are already used industrially, i.e. at 700 atm and over,
the reactions proceeds without difficulties and at a rate satisfactory
for large industrial operations. The use of fixed bed catalysts
at higher hydrogen concentrations still further widens the range
of applicability of the different catalysts. It permits e.g. to
produce hydrogenation action with greatly reduced splitting, or
to produce anti-knock gasolines when using only weakly hydrogenating
splitting catalysts.

In addition to the total pressure, the proportion of oil
vapor pressure to the partial pressure of hydrogen is also important.
In general the amount of hydrogenation is reduced by increasing
the partial pressure of oil. In addition, the time of residence
of the feed in the reaction space must be adjusted to the nature
of the reaction.

The reactions during the catalytic pressure hydrogenation
are not conducted to a complete conversion in one pass, but as in
most hydrocarbon conversions, the non-converted portions are
either returned, or else reacted in a special reaction stage. The
liquid phase hydrogenation of coal produces heavy oil which is
returned when a middle oil with but little liquid phase gasoline
is desired. When the middle oil is returned and the heavy oil
formed is removed from the process, only heavy oils are formed
from coal as the final reaction product, in addition to the
liquid phase gasoline. The raw material could be completely
converted into gasoline by a complete recirculation of the
middle oil, but this method is not used because it would result
in a much greater amount of gasification than is obtained by

leading the middle oil over fixed bed catalyst to convert it to gasoline.

The conversion of middle oil to gasoline in one pass in the vapor phase is not usually permitted to go beyond 50 to 80%, and the middle oil is separated by distillation from the gasoline, and recirculated. This increases the gasoline yield with a better utilization of the reaction space; and it permits in addition to obtain gasolines with the desired boiling point curve.
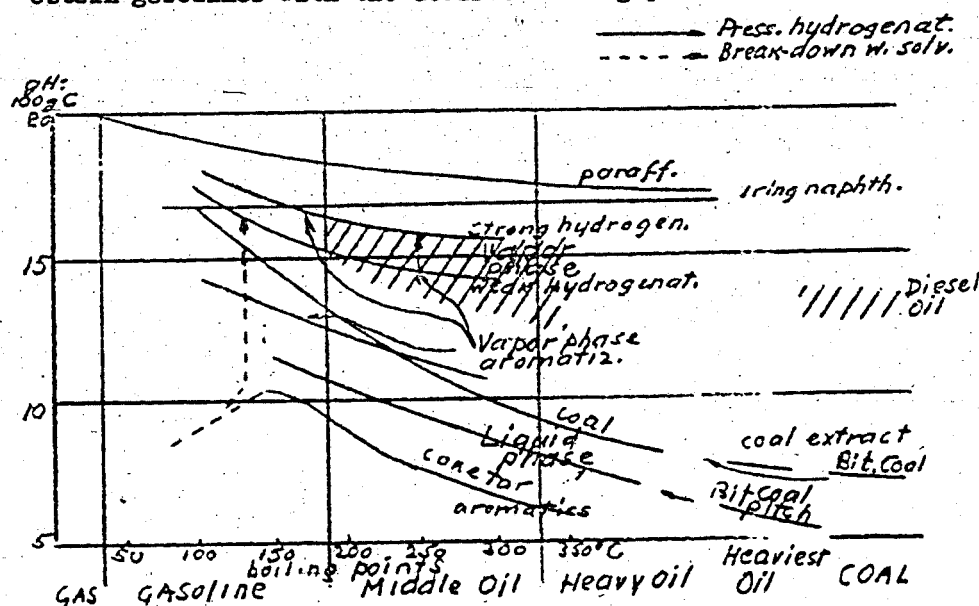

Fig. 1

Figure 1 represents schematically an example of the course of pressure hydrogenation reactions of a bituminous coal, in accordance with the description given above of the characteristic features of these reactions. It shows how much the character

of the liquid phase products depends on the raw materials, and
how readily it can be changed in the vapor phase using fixed bed
catalysts.

Liquid Phase Hydrogenation

The purpose of the liquid phase hydrogenation is to produce
intermediate products from high molecular weight raw materials,
with gasoline as the end product. These intermediates fill more
or less uniformly the whole boiling point range from the gaseous
hydrocarbons to the heaviest oils. It has already been mentioned
that the properties of these products are similar to the properties of
products obtained in the distillation or low-temperature carbonization
of the corresponding raw materials.

When petroleum distillation residues with an asphalt base or
a mixed base boiling above $325^{\circ}C$ are used as the   liquid phase
feed, middle oils are obtained which will form good diesel oils,
and are very similar in properties with the distillation middle
oils of the original petroleum, as can be seen from table 1.

Table 1

DISTILLATION AND LIQUID PHASE MIDDLE OILS FROM DIFFERENT OIL FEEDS

Middle Oil 180-325°	Sp. Gr. $15^{\circ}C$	A.P. $^{\circ}C$	A.P. of the Fractions 210-230	240-270	280-310°C
From mixed base oil feed:					
Distillation middle oil	0.840	61	56	59	66
Liquid phase middle oil	0.838	57	52	56	61
From asphalt base oil feed:					
Distillation middle oil	0.856	50	47	50	54
Liquid phase middle oil	0.851	51	49	52	54

The aniline points show the similarity in the hydrogen
content of the corresponding fractions of the liquid phase and
the distillation products. The regularity illustrated here in
the two examples is so general, that the properties of hydrogenation
middle oils can be very accurately predicted from the petroleum
residues, when the properties of the middle oil contained in the
original crude are known.

A similar although not as close relationship exists also
with coals when the hydrogenation middle oils of coals are compared
with the corresponding middle oils from l.t.c. tars, after the
phenols have been removed from both.

Table 2.

TAR MIDDLE OIL AND LIQUID PHASE MIDDLE OILS FROM COALS

| | % phenols in the total middle oil 180-325° | Phenol-free middle oil 180-325° | | | |
| | | d₁₅ of the fractions | | A.P. of the fractions, °C | |
		240-270	280-310	240-270	280-310
From brown coal:					
l.t.c middle oil	24	0.899	0.912	15	31
liquid phase middle oil	14	0.878	0.906	24	33
From bituminous coal:					
Original middle oil	27	0.940	0.980	-6	-10
Liquid phase middle oil	9	0.938	0.972	-15	-14

The agreement in the hydrogen values can be seen here to be
not as perfect as in the petroleum products, which may be explained
e.g. that by the fact that the l.t.c. oils contain only a relatively
small fraction of the original coal substance, while practically

the whole of the coal substance is converted into oil by hydro-
genation. The phenol content of the raw middle oils is greater
in the l.t.c. of coals than in the products of the liquid phase
hydrogenation; the total phenol yield, however, referred to coal,
is greater in hydrogenation.

The paraffin yield is also appreciably greater during the
direct hydrogenation of brown coal, than the amount of paraffin
obtained in l.t.c. of the same amount of brown coal.

Middle oil is the main product of liquid phase hydrogenation
in the production of gasoline from heavy oils or from coal.
In addition about 20% gasoline is also obtained. This gasoline
still shows the character of the raw materials as can be seen in
table 3 on samples of several liquid phase gasolines.

Table 3.

LIQUID PHASE GASOLINES FROM DIFFERENT RAW MATERIALS

Liquid phase gasoline from:	Residue from mixed base petroleum	Residue from asphalt base petroleum	Cracking residues from asphalt base gas oil
Sp. gr.	0.719	0.731	0.788
% to 100°	36.5	26.1	13.0
% to 170°	90.5	88.7	82.0
Aniline point of fractions:			
80-100	53	56	37
110-140	52	53	25
150-180	53	52	11
190-210	-	-	7
Octane number (research method)	53	57	73

The octane number of the liquid phase gasoline rises from the
mixed base gasoline to the asphalt base gasoline and to the

aromatic cracking residue. A liquid phase gasoline of an octane
number of 73 is obtained from the cracking residues. The aniline
point of the fractions permit one to see that the drop of the
aniline point is greater with increasing boiling point of the
high-aromatic products than from the hydrogen-rich. The gasoline
from the readily splitting mixed base crude is high in constituents
boiling below 100°C, while the hydrogen-poorer oils produce
gasoline with a lower content of lower boiling constituents.

Table 4 shows an example of properties of the chemically
refined liquid phase gasoline from coal.

The octane numbers of the liquid phase gasoline from coal
are higher than of the gasoline from petroleum and when derived
from bituminous coals nearly reach the values obtained on working
up gasol residues. The fatty coals give, as one might expect
hydrogen-poorer gasoline than the hydrogen-richer long flame
coals from the same deposit. As a general rule, the liquid phase
gasolines from coal contain much low boiling constituents, because
they are produced with strong splitting.

Table 4.

LIQUID PHASE GASOLINES FROM DIFFERENT COALS

Liquid phase gasoline from:	Brown coal			Bituminous coal	
	Young		Old	Long flame coal	Fatty coals
	Bitumen -rich	Bitumen -poor			
% phenols in the crude gasoline	6.0	5.0	5.5	6.3	2.8
Refined gasoline:					
Sp. gr.	0.738	0.758	0.739	0.734	0.737
% -100°C	36	38	49	47	43
Composition:					
% paraffin	50	37	40	38	28
% naphthenes	28	39	44	45	54
% aromatics	18	13	12	14	16
% unsaturated	4	11	5	3	2
Octane number (research method)	62	67	69	69	70

The knock values of the liquid phase gasoline in the higher fractions of the relatively hydrogen-richer raw materials drop in the higher fractions of the products, but not as much as with natural gasolines or even with pure paraffinic gasolines. With hydrogen-poorer gasol residue the knock values of the fractions above 130° rise again; the rise is still greater with bituminous coal gasoline, which is related to the higher proportion of aromatics in the higher fractions. It is therefore profitable to cut the liquid phase gasoline from aromatic raw materials very high, and from the hydrogen-rich coals lower. Liquid phase gasolines from aromatic hydrocarbons are further improved when refining is done not chemically, but with catalysts under dehydrogenating conditions, when any phenols present are simultaneously reduced with hydrogen under pressure to aromatic hydrocarbons.

Hydrogenation With Fixed Bed Catalysts

The hydrogenation with fixed bed catalysts has found so many applications, as mentioned above, because the reactions can be effected by proper selection of the catalyst, temperature and pressure. It is possible either to work with much splitting, or else without splitting the carbon structure, and with a more or less strong hydrogenation.

The pressure hydrogenation without splitting has an important application in the refining of gasolines and benzol obtained in cracking, low temperature carbonization, coking or in the liquid phase hydrogenation.

The crude benzol obtained in the coking of bituminous coal is already converted catalytically under pressure of 40 atm into a stable product hardly enriched in hydrogen. More motor benzol can be obtained by hydrogenation, not merely by eliminating the usual losses in the benzol refining but also by permitting the use of the middle and heavy benzol-fractions boiling above the motor benzol. These fractions from which hardly any motor fuels is produced with sulfuric acid, are saturated by careful pressure hydrogenation at 50-200 atm without any appreciable reduction of octane number. Table 5 shows the saturation by showing the iodine number changes of 140-180°C middle benzol fraction. It follows from the specific weight as well as from the octane number that the hydrogenation of aromatics is very slight. Moreover the color becomes water clear and the product is free from sulfur to within 0.006%.

Table 5

HYDROGENATION OF MIDDLE BENZOL FRACTION

Middle benzol	Crude	Hydrogenated
Sp. gr.	0.883	0.865
Initial boiling point °C	136	134
50% boiling point °C	155	154
95% boiling point °C	178	179
Color	Straw yellow	Water clear
Iodine number	61	4.5
% sulfur	0.18	0.006
Octane number (M.M.)	abt. 100	abt. 100

LTC gasolines from bituminous and brown coal are refined
in the same way and produce at 200 atm water clear, stable, almost
sulfur-free gasolines.

Table 6 shows another example of refining of liquid phase
product by showing a liquid phase gasoline with a boiling point
215°C obtained from a younger bituminous coal.

Table 6.

HYDROGENATION OF LIQUID PHASE GASOLINE FROM BITUMINOUS COAL

Liquid phase bituminous coal gasoline	Chemically refined	Refined by pressure hydrogenation	
		A	B
Sp. gr.	0.794	0.790	0.785
% -100°C	33	35	43
% -170°C	75	78	80
End point °C	215	212	220
% paraffins	28	29	28
% naphthenes	36	38	18
% aromatic	32.5	31.5	52.5
% unsaturated	3.5	1.5	1.5
Octane number:			
Research method	72	71	85
Motor method	66	67	77

The losses during the refining of this gasoline with sodium hydroxide and sulfuric acid are greater because of the high olefin and phenol contents, and the fuel produced has an octane number of 72 by the research method and an aromatics content of 32%. When pressure refining is done with a well hydrogenating catalyst at 200 atm and 300°C, the gasoline is obtained without the loss and with an octane number and aromatics content roughly equal to that of the chemically refined gasoline. When such catalysts are used under dehydrogenating conditions and in presence of hydrogen, refining as well as a considerable improvement of the motor qualities of the gasoline are obtained in one step. The research octane number is then equal to 85 and the aromatics content is over 50%.

The phenols in the crude gasoline from coal must be eliminated during the chemical refining, which strongly reduces the gasoline yield. In the pressure refining they are converted into hydrocarbons and remain as such in the gasoline. Either aromatics or naphthenes are formed depending on the hydrogenation conditions used, without any loss through splitting of hydrocarbons.

The pressure refined gasolines are colorless, odorless, light-stable and equal in their tests and the boiling point behavior to the best commercial gasolines. The percentage of unsaturated is 1-1.5, the gum always under 10 mg/100 ml, the sulfur content below 0.01%.

The splitting hydrogenation of middle oils to gasoline is the principal purpose of the vapor phase. The properties of the feed are reflected here in the properties of the gasolines, just

as in the liquid phase products. However, the catalyst and the operating conditions are the principal influences.

One may see best the influence of the chemical composition of the feed in the motor behavior of gasolines. Table 7 shows the specific gravities and the octane numbers of a few gasolines produced under comparable conditions, from different raw materials. The octane numbers of the gasolines increase with reducing hydrogen content of the middle oils. With the hydrogen-poorer feed, such as brown coal, asphaltic petroleum oils, cracking residues and bituminous coal, the octane number is around 67-75. A higher octane number, is obtained with lower cuts of gasoline. Very hydrogen-poor aromatic middle oils can also be obtained from hydrogen-rich middle oils by solvent extraction. One method of obtaining larger yields of good gasolines from very hydrogen-rich middle oils, such as are produced e.g. in the carbon monoxide-hydrogen synthesis consists in their joint hydrogenation with hydrogen-poor middle oils.

Table 8 shows to what extent the quality of the gasoline from the same feed is affected by catalysts and operation conditions. Different groups of catalysts are today available. The first group, and so far technically the most important one, includes the catalysts (A) which are strongly hydrogenating, strongly splitting and are applicable to any vapor phase feed. Gasolines obtained with them have about the same octane numbers as obtained by the distillation or low temperature carbonization gasolines from the same raw materials. Table 8 shows under (A) a gasoline so obtained from bituminous coal middle oil.

Table 7.

MOTOR GASOLINES FROM DIFFERENT FEED

Raw material:	Motor gasoline	
	Specific gravity	Octane number (M.M.)
Paraffin	0.68	45
Petroleum, mixed base	0.722	64
Petroleum, asphalt base	0.728	67
Shale oil, paraffinic	0.712	65
Shale oil, asphaltic	0.732	66
L.t.c. brown coal tars	0.734	65
Brown coal liquefaction products	0.735	66
Petroleum cracking residue	0.745	74
Bituminous coal liquefaction and extracts	0.745	74
Bituminous coal coking tars	0.748	75

Table 8.

MOTOR GASOLINES FROM BITUMINOUS COAL MIDDLE OILS PREPARED WITH DIFFERENT CATALYSTS

Catalysts	A	B	C	D
Specific gravity	0.735	0.745	0.770	0.830
Octane number:				
Research method	67	75	78	95
Motor method	66.5	74	75	83

The octane numbers are much better with equally high gasoline yields when catalysts of the second group are used which are weakly hydrogenating and strongly splitting. Gasolines obtained in that way are illustrated in the table under B and C. These catalysts show their complete splitting action with almost all petroleum middle oils. With oxygen and nitrogen-containing oils, such as obtained from coal and tars, a pretreatment is advantageous, and consists in chemical refining or in hydrogenation with hydrogenating catalysts in a so called prehydrogenation stage.

This is frequently advantageous when working at higher pressures,
e.g. at 600 atm. and higher. Under such conditions impure products
may be worked up, and there is in addition the advantage of
operation with very weakly hydrogenating catalysts.

All hydrogenation gasolines obtained with these two groups
of catalysts are relatively high in naphthenes and iso-paraffins
and show a good sensitivity of their octane numbers to lead.

A third group of catalysts (D) permits the production of
particularly aromatics-rich, low hydrogen gasolines. They are
used at higher temperatures of around 500°C. The motor gasoline
yields amounts to about 90% by weight in the first mentioned
methods of operation, and is below 90% when the last method is used.
It becomes smaller when operating for the production of higher
aromatics content of the gasoline and when the middle oil used
is paraffinic. Table 8 shows that (D) obtained from such
bituminous coal middle oil has an octane number of 95 (R.M.)
with 50% of aromatics.

Table 9.

MOTOR GASOLINE FROM MIXED BASE PETROLEUM MIDDLE OIL OBTAINED WITH
DIFFERENT CATALYSTS

Catalysts	A	B	C	D
Specific gravity	0.716	0.722	0.730	0.787
Octane number:				
Research method	57	64	72	80
Motor method	58	64	70	74

Gasolines obtained in splitting of mixed base petroleum middle oils are shown in table 9 to differ depending on the catalysts used, and in a similar way. Gasolines with octane number 80 (R.M.) are obtained using catalysts of group D, and these gasolines contain over 30% aromatics. Lower hydrogen middle oils from petroleum, e.g. cracked or asphalt base middle oils, give still better octane numbers and the difference in gasolines obtained with different catalysts can be seen in the aniline point curves of the gasoline or middle oil fractions shown in figure 2. The hydrogen content lowering from catalysts A to C can be clearly seen.
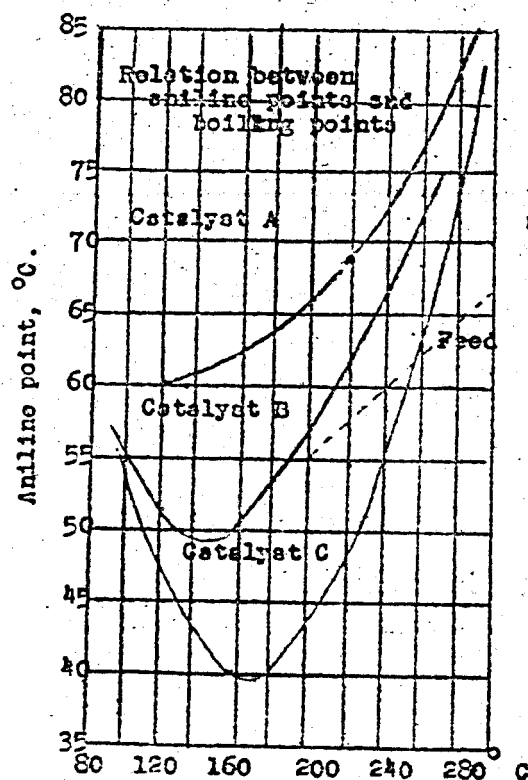
Fig. 2
Splitting of mixed base petroleum middle oils.

Table 10.

MOTOR GASOLINES FROM BROWN COAL MIDDLE OIL OF DIFFERENT ORIGIN

Middle oil produced with:	Finely dispersed catalyst	Fixed bed catalyst
Motor gasoline: Specific gravity Octane number	0.734 .65	0.730 . 69

The gasoline quality is also affected by the method of preparation or the pretreatment of a middle oil. Table 10 shows two gasolines from brown coal tars. The middle oil feed of the first column was obtained by splitting liquid phase hydrogenation product of brown coal l.t.c. tar, in the second column by careful hydrogenation with little splitting of tar over fixed bed catalyst. The paraffin of the tar was not split in this case to middle oil, but previously separated and recovered as such. The boiling point curves are nearly the same, also the specific gravities and aromatics content, but the second gasoline has an appreciably better octane number.

Hydrogenation gasolines are exceptionally well suited for use in aviation motors because of their high stability, good octane number rating and lead sensitivity.[1] Properties of gasolines obtained in this way from middle oils are shown in table 11.

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[1] Brown and Tilton, Oil Gas Journal, Vol. 36 (1938) No. 46 Page 74.

Table 11

HYDROGENATION AVIATION GASOLINES FROM PETROLEUM MIDDLE OILS

Hydrogenation gasoline from:	Mixed base petroleum middle oil	Asphalt base petroleum middle oil
Specific gravity % -100°C	0.718	0.725
End point °C	57	72
Reid vapor pressure 38°C	145	135
Octane number (M.M.)	0.48	0.49
Motor method + 0.9% by vol. of TEL.	72	77
Motor method + 0.27% by vol. of TEL.	90	91.5
	98	100

Table 11 shows the high octane number of the aviation gasolines obtained by hydrogenation, and in particular their high lead sensitivity. The motor method octane number of the asphalt base oil-gasoline is 77, it becomes 91.5 with 0.09% by volume of TEL. and 100 with 0.27% by volume. Figure 3 shows that the lead sensitivity of hydrogenation gasolines is very good in spite of the high octane number of lead-free gasoline, and is better for the same initial octane number with hydrogenation gasolines then with the distillation gasolines from petroleum.

o.n.(M.M.)
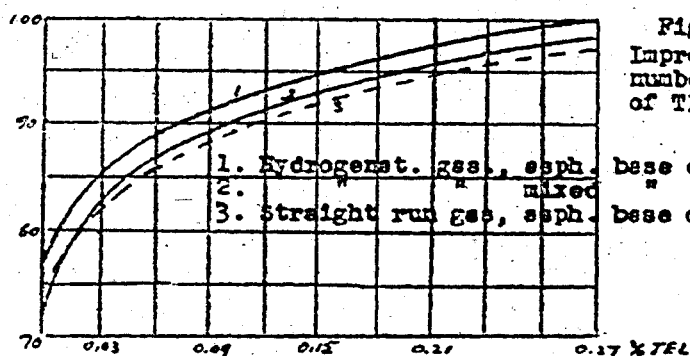
Fig. 3
Improv. in octane number by addition of TEL.

1. Hydrogenat. gas., asph. base oil
2.   "   "   "   mixed "   "
3. Straight run gas, asph. base oil

Industrial Application of Hydrogenation

Some of the progress made with catalytic hydrogenation in the chemical and physico chemical fields has been illustrated with a few characteristic examples. The industrial applications of the results to high pressure processes had to keep step with this development. The magnitude of the task which had to be solved in cooperation with the steel makers may be judged from the fact that sulfur-containing materials can be treated today with hydrogen in converters of over 10 cbm content at 500°C and a pressure of 700 atm.[2]

"Leuna-Benzin" has been produced in the Ammoniakwerk Merseburg since 1927. By far most of it is produced from Mid-German brown coal. Occasionally other available raw materials are used: brown coal l.t.c. tar, bituminous coal tar, German petroleum oil. Other hydrogenation plants in Mid-Germany use the local brown coal; this is not, however, hydrogenated directly, but is first carbonized at a low temperature and the tar hydrogenated to gasoline, because the large power plants can use to advantage the coke obtained as the principal product of the low temperature carbonization. Bituminous coal has also been successfully hydrogenated in Germany since 1936 on an industrial scale. In addition to the direct hydrogenation of bituminous coal, bituminous coal extract and bituminous coal pitch has been successfully hydrogenated.[3]

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[2] Editors remarks: We refer to Naumann's article on steels for the fuel production plants, Chem. Fabrik, Vol. 11, (1938) P. 365

[3] Pier "Zur Frage der Kohlehydrierung", Chem. Fabrik, Vol. 8 (1935), P. 45.

The process has been used industrially in other countries
as well, in the U.S.A. for the working up of oil, in England
for hydrogenation of bituminous coal, and in different countries
for the production of iso-octane. Two plants are being constructed
in Italy, where high grade gasoline and lubricating oils will be
produced from asphalt base or mineral oil. Other raw materials
can also be used as feeds.

The process has been found industrially profitable. The
newer factories have reached the expected production in a relatively
short time.

It is here of particular importance that all raw materials
that might be used, coals, peat, tar, shale oil, petroleum and
their fractions can be equally well worked-up in hydrogenation
plants. Production can be changed from one raw material to another
one using either imported or domestic materials as a feed. One
part of the installation, namely the high pressure part, remains
essentially unchanged; the parts of the installation used for
working up of the raw materials and of the products must be ad-
justed to the feed.

One may equally freely select the end products of the catalytic
hydrogenation as the raw materials. Diesel oil and fuel oil,
instead of or together with high test gasoline, can be produced
and lubricating oils and paraffin/different proportions from
suitable raw materials.

The efficiency and flexibility of catalytic pressure
hydrogenation, and the success reached until now have resulted
in making the process by far the most important source of the
future German supply of fuels and mineral oils. The significance
already reached by the process is shown by the fact that in
1937 almost double of the benzol production, i.e. 800,000 to
900,000 te gasoline, has been obtained from domestic raw materials
by catalytic pressure hydrogenation.

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W. M. Sternberg
December 7, 1948

K-4

DEVELOPMENT OF THE TECHNIQUE OF HYDROGENATION OF SOLID FUELS AND OF THEIR BY-PRODUCTS *

By Louis Thibaut
Director of the Compagnie Francaise des
Essence Synthetiques

Summary

After the factory at Liévin was built in compliance
with, and following instructions of the National Research
Society, using the processes of that Society, The French
Company of Synthetic Gasoline has tried to make an original
contribution to the hydrogenation technique. Their efforts
have culminated in 1938 in a method to cause, in the same
equipment units, a progressive hydrogenation of the fuel and
a simultaneous fractionation of the products obtained, and to
remove in that way from the circuit the light products, while
retaining the more difficult-to-hydrogenate heavier products,
until completely hydrogenated. The feed was completely hydro-
genated in a single operation, all manipulations and all the
intermediate processes on heavy oils are avoided, as well as
the treatment of middle oils. This resulted in a simplifi-
cation of the equipment used, and in an appreciable reduction
in the operating costs. The C.F.E.S. has also introduced a

* Paper presented at the XX Congress of Industrial Chemistry,
Paris, September 22-28, 1946.

new hydrogenation catalyst with a base of iron activated with
cyanides of the metals of the 5th group. It has finally succeeded
in the industrial hydrogenation of the heavy fractions of the
coal tar and in the introduction of a large number of new pro-
ducts into the lubrication field.

INTRODUCTION

The Inspector General of Mines, Crusard, has been
charged by the Government with a comparison of the different
classical German and French processes of hydrogenation and tests
performed under his direction have shown that the conversion of
pure organic substances differed but little in principle in the
different processes, and the French Company for Synthetic Fuels
has directed its efforts toward the search of a technique capable
of effecting a saving in the amounts of raw materials used dur-
ing the course of the reactions, as well as a reduction in fixed
charges.

It started, accordingly in 1938 on the development of
a new procedure of hydrogenation of solid combustibles, which
was to a certain extent different from foreign practices and
for which a patent has been applied in 1939, after the equipment
for the process was constructed on an industrial scale and has
confirmed the expectations (1).

(1) French Patent 450,376, of August 17, 1939, recorded in the
    U.S. on February 3, 1945.

The full development of this process demanded a more active catalyst than the French Company for Liquid Gasoline possessed, and they introduced a new catalyst which met these requirements (1).

Later, the heavy tar derivatives have been hydrogenated, such as have not until then been subjected to such treatment. The hydrogenation of the heavy oils of tar, such as the anthracene fraction of the oil, distilling above 300°C and the red oils--true tar oils--obtained in the vacuum distillation of tar was particularly successful, thus finding a number of new products (particularly as lubricants) (2).

The article below contains a review of this work.

THE PROCESS FOR HYDROGENATION OF SOLID FUELS

This process consists in a progressive hydrogenation of the fuel with a simultaneous fractionation in the same unit of the products obtained, in such a way that the light fractions are removed from the circuit, while the more refractory heavy fractions are additionally hydrogenated to a complete conversion.

The hydrogenation reactions are conducted at variable increasing temperatures from 300 to 500°C in a way to act upon the reacting substances under conditions of maximum efficiency

(1) French Patent 478,267, of April 16, 1943.
(2) French Patent 472,220, October 5, 1942.

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of hydrogenation, instead of within a very narrow temperature range in which the action of hydrogen is practically constant.

A decomposition of the hydrogenation products formed at certain temperature by subjecting them to higher temperatures is avoided by leading them into a zone of lower temperatures than those at which they were formed.

The process thus becomes a progressive process, in the course of which the fuels become gradually hydrogenated at the lowest possible temperatures, and the products formed are separated as soon as formed.

The different reaction temperatures are produced in a single vertical autoclave (Fig. 1). In order to do so, it is subdivided into a certain number of sections, separated by means of plates equipped with a riser for a gas and a drain for the liquid, like in a distillation column. Among other
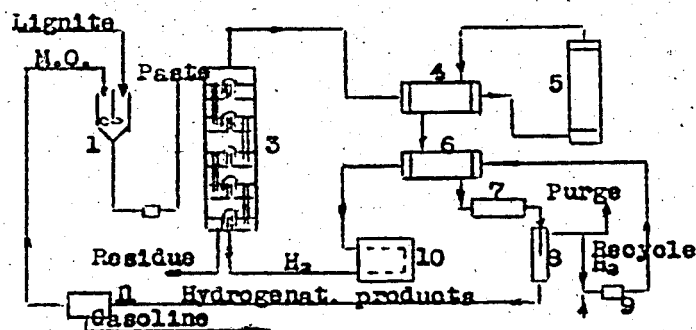
1. Mixer   2. Paste Pump   3. L.P. Autoclave   4. H. Exchanger
5. V.P. Autoclave   6. H. Exch.   7. Cooler-Condens.   8. Catchpot
9. H₂ Circul. Pump   10. H₂ Preheater   11. Distillation

FIG. 1.   FLOW SHEET OF HYDROGENATION OF COAL

advantages, such an arrangement permits the use of catalysts
best suited for their particular purpose and in directing
their action and localizing the hydrogenation effects.

The finely pulverized fuel to be hydrogenated is
mixed with a middle oil from a previous operation, is intro-
duced in the form of a paste into the top of the autoclave
at the selected pressure (250-500 kg/cm^3, depending on the
material used) and at a temperature of below 100°C.

Hydrogen is compressed to the selected pressure,
preheated to 450-500°C, introduced into the bottom part of
the autoclave, and made to circulate counter-currently to the
feed. It thus bubbles through the autoclave from plate to
plate and carries over the sufficiently light products to
the upper reaches. The heavy products remain in the unit
until completely converted.

Temperature gradations are formed inside the auto-
clave with the highest temperatures on the bottom to the low-
est on top because of: the introduction of the feed at low
temperatures (below 100°C) into the upper part of the unit;
the introduction of highly heated hydrogen to the bottom of
the autoclave; the heat of the reaction.

The recovered condensible products consist, exclud-
ing the heavy oil or complex products which require fractiona-
tion, on one hand of middle oil, on the other hand of a diffi-
cult-to-hydrogenate fraction of the feed, forming what is com-
monly called the hydrogenation residue.

The residue withdrawn at the hottest part of the
autoclave will contain, in this case, up to 50% of mineral sub-
stances and 10% benzol-insolubles, and their regulated removal
creates a particularly delicate mechanical problem. A satis-
factory solution has been found after a number of trials in a
combination action of loss of pressure in definite size ori-
fices and of the temperature of the products to be removed.

The production of middle oils is regulated by the vari-
ation either of the amount of hydrogen introduced into the auto-
clave, or of the temperatures in the upper sections. The total
amount of middle oil recovered equals to the amount of oil used
in pasting, plus the amount produced.

The mixture of middle oil and hydrogen leaving the
autoclave under pressure is next used in the production of gaso-
line after reheating, but without releasing the pressure or
recompression, in an auxiliary autoclave with a fixed bed cata-
lyst intended to convert the middle oil produced into gasoline.
The catalyst (described below) is very active and has the pecu-
liarity of being little sensitive to the proportion of middle
oil to hydrogen. It is therefore perfectly suited to this case,
where it leads to a conversion of all of the middle oil into
gasoline in a single stage with an amount of middle oil left in
the hydrogenated product sufficient for the pasting of fresh
amounts of hydrogenation feed.

Cut at 160 or 180°C, this hydrogenation product delivers
an amount of gasoline depending on the fuel hydrogenated and on

the amount of middle oil required for pasting. The cycle is
therefore a closed cycle with a single circuit.

The consequences of conducting hydrogenation by this
process are many:

1. The solid fuel feed is completely hydrogenated in
the course of its passage through the autoclave, and at
no time are heavy oils removed from the unit. This eli-
minates the extraction operations, filtration and return-
ing the products to outside cycles for the purpose of
making them lighter. Unlike the operation practices of
the classical methods, the solid fuel is pasted with a
middle oil as an intermediate vehicle, instead of the
heavy oils obtained in a preceding cycle of operations.

In the autoclave, the middle oils are gradually
replaced by the heavy oils formed, and the fuel is put
under conditions, especially of solubilization, which
are the preferred conditions for hydrogenation.

2. The middle oils are obtained at as low tempera-
tures as possible and contain products which would be
partially or completely decomposed at higher tempera-
tures. They are, in particular, richer in the lower phe-
nols than the light oils produced by the usual methods.

3. The upper part of the autoclave requires cool-
ing to produce a gradation of temperatures and the paste,
as mentioned above, is introduced at about 80°C, which

makes its preheating unnecessary, and eliminates a difficult and costly operation, such as the installation of the special equipment necessary for such preheating.

4. The middle oil entrained into the upper part of the autoclave by the stream of hydrogen can be converted into lighter constituents and converted into gasoline without breaking into the cycle. The required operations of cooling, pressure release, distillation and recompression necessary for a later vapor phase treatment are thus eliminated, together with the equipment required to carry out these steps.

5. The hydrogenation is very far advanced in the bottom part of the autoclave, where the temperature of 500°C may be reached and the residues withdrawn contain only materials unsuited for any subsequent treatment, so that the recovery of oils usually admixed with these residues becomes unnecessary, which eliminates all the equipment used for that purpose.

The above remarks show the economic advantages of the process. One may state as a fact that the energy of hydrogenation of solid fuel: the energies of compression, of heating, of handling the products at the different stages of manufacture, is greatly superior to the energy of the hydrogenated solid fuel. All processes, therefore, which will simplify or eliminate the auxiliary or intermediate operations of the con-

version will result in substantial savings in the raw material
and a notable reduction in the installation costs.

The savings in the application of this process in
comparison with the classical processes were studied in exten-
ded studies on a scale of 20 te/day, using coals from the Bouche-
du-Rhône and the Landin basins. For the hydrogenation proper
they are in the neighborhood of 40% of the total energy used,
and 40% in fixed charges.

CATALYST FOR THE CONVERSION OF MIDDLE OIL TO GASOLINE

Hydrogenation catalysts are essentially molybdenum or
tungsten deposited upon some porous carrier, and the C.F.E.S.
has first of all attempted to replace these rare and costly
metals with other metals, in particular with iron. They pre-
pared a catalyst based on iron sulfide, which produces results
comparable with those produced by the molybdenum sulfide cata-
lyst previously used. Efforts were subsequently made on the
production of catalysts little sensitive to the proportion of
hydrogen/oil, and capable of causing a conversion of as high a
proportion of oil as possible, and systematic studies have shown
that cyanides, and in particular sulfocyanates of the metals of
the 5th group, notably iron, chromium and aluminum, had marked
activation powers. This addition does not exceed 3% of the
iron sulfide in the catalyst. It is prepared in the wet way
by precipitation with ammonia, and care must be taken to elimi-
nate completely any traces of ammonium salts which will form
in this reaction.

The use of this catalyst in hydrogenation under 300 kg/sq.cm pressure with the production of motor gasoline, starting with the coal middle oil, has produced a 95% conversion of the oil into gasoline in a single pass while the best results previously obtained in conversions in a single pass were of the order of 50%.

On the other hand, the temperature in this procedure is 480°C, or 15° lower than in processes employing molybdenum catalysts, and the formation of gaseous hydrocarbons is accordingly much lower, and the proportion by weight of yield of gasoline:middle oil is 90%, as against 82% with the molybdenum catalyst.

Equally to be noted is an increase in the octane number by two units, from 75 to 77, which is not the result of an increase in the concentration of aromatics, but results from isomerization reaction more pronounced for paraffinic and naphtenic hydrocarbons.

HYDROGENATION OF THE HEAVY
FRACTIONS OF COAL TAR

Middle oils of the most diversified origin have been hydrogenated at Liévin (middle oil from coal hydrogenation, middle oils from primary tars and of high temperature tars), and because of their conversion into high-grade gasoline, the C.F.E.S. has undertaken the hydrogenation of higher boiling

particular the catalyst described above). The gravity of the hydrogenation product was 1.040, as against 1.160 of the anthracene oil. It was clear and fluorescent, stable at high temperatures and held no traces of asphalts or heavy constituents insoluble in petroleum gasoline or in benzene. The odor of the anthracene oil had completely disappeared. On the other hand, anthracene crystals which were present in the original feed to the extent of 20-30% were not entirely eliminated and still were present in the hydrogenation product to the extent 5-7%, chiefly in the form of carbazole.

The hydrogenation of the heavy oil at 300 kg and a temperature of 380-400°C was about 90% complete, with a hydrogen consumption of 1,000 cbm/te of heavy oil. Fractionation and refining of this product gave:

  45% of middle oil, which could be converted into gasoline.

  25% of an oil, viscosity 1.7°E/50°C, which could be used for transformer oil or for the greasing of refrigerators.

  30% of oil from the tailings of the distillation, viscosity 4°E/50°C, which could be used for the greasing of engines.

This last fraction, with the addition of 2.5% polystyrolene, acquired a viscosity of 10°E/50°C, which made it suitable for the greasing of motors.

b) <u>Red Oils by Vacuum Distillation of Tars</u>.

The production of lubricating oils starting with the anthracene oil was used industrially for several months, when the problem of hydrogenating the red oils was suggested to the C.F.E.S.

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These oils are heavier than the anthracene oils, and
are obtained in a vacuum distillation of tar. They are solids
at room temperatures:

    m.p.   40-50°C

    Engler viscosity 5-6°/100°C

    Distillation range 350-450°C

    Gravity, at 15°C 1.200

   They are homogeneous and do not deposit any crystals,
and congeal as a whole upon cooling, without separation. They
are essentially composed of aromatic hydrocarbons with several
benzene rings.

   The very first tests in the laboratory convinced us
that they could be treated by exactly the same methods and under
the same conditions, as the heavy anthracene oils. The results
obtained were comparable, but while the products remained fluo-
rescent, they were composed of heavier molecules of a higher
viscosity. On the other hand, since the red oils contained
no crystals, the refining was simplified.

   When treated industrially under the same condition as
the heavy anthracene oils, the hydrogenation yield was 92%, with
a hydrogen consumption of 1,000 cbm/te of oil. Fractionation
and refining of the products gave:

    20% middle oil, which could be converted into
     gasoline.

    20% of insulating or refrigerant oil.

    60% of a very viscous oil (25°E/50°C) which
     could be used as the base oil for a number
     of blends.

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CONCLUSIONS

The above article furnishes information on the methods developed by the Compagnie Francaise des Essence Synthetiques in the field of hydrogenation of solid fuels, as well as the results they have succeeded in obtaining by these methods.

They offer economic advantages in industrial applications, and apparently furnish a nucleus of scientific staff for later studies of the very complex reactions of hydrogenation.

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THE EFFECT OF HIGHLY COMPRESSED HYDROGEN UPON UNALLOYED STEEL

By Friedrich Karl Naumann, Essen

Samples of steel from ammonia and hydro-
genation plants attacked by hydrogen.
Arrangement of tests for high pressure
experiments with hydrogen. Effect of the
hydrogen pressure, temperature and time
upon the beginning and progress of decar-
burization of unalloyed steel. Structural
forms of decarburization. Effects of ori-
ginal structure and cold working. Effects
of the hydrogen attack upon the mechanical
properties. Limits of stability of unalloyed
steels. Remarks on the decarburization process.

The construction material of containers in the hydro-
genation processes, in particular in the ammonia synthesis and
the hydrogenation processes, comes in contact with hot hydrogen
under pressure. The ammonia synthesis is done under pressures
of 100 to 1000 atm/sq.cm. and at temperatures of 400 to 600°C in
the different processes [1], and in the modern coal liquefaction
processes, disregarding the normal pressure operations of the

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[1] F. Muller, Arch. Eisenhuttenw., Vol. 1, 1927/1928, pp. 517-528;
B. Waeser, Die Luftstickstoffindustrie (Leipsic, O. Spanner,
1932); C. Bosch, Chem. Fabrik, Vol. 6, 1933, pp. 127-142;
cf. Stahl und Eisen, Vol. 52, 1933, pp. 1187-1189.

Fischer-Tropsch processes, 2/ under pressures of 700 atm and
temperatures of 450-550°C 3/.

MANIFESTATIONS OF ATTACKS BY HYDROGEN

The attack of hydrogen upon unalloyed steels was already
observed in the first industrial attempts of ammonia synthesis
by the Haber method, and described by C. Bosch 4/, who found
that the high pressure vessels were attacked and destroyed.
Manifestations and results of hydrogen attack have been described
by Bosch in detail. They consist essentially in a decarburization
connected with a loosening of the grain contact and with a great
loss in strength and ductility. The pictures below illustrate
the hydrogen attacks.

Fig. 1 shows the cross section of a high pressure bomb
which burst under the effect of hydrogen. The decarburized inner
zone is made visible by etching with copper ammonium chloride.
In addition to the crack which caused the bursting, there are
several other cracks, in the vicinity of which the attack pro-
gressed deeper than in the crack-free parts. Fig. 2 shows the
attack of hydrogen upon a separator from a hydrogenation plant,
after four weeks of operation at 500°C and 200 atm pressure.

2/ Brennstoff-Chem., Vol. 7, 1926, pp. 97-104; cf. Stahl und Eisen,
   Vol. 46, 1926, pp. 752-753.
3/ E. Galle, Hydrierung der Kohlen, Teere und Mineraloele, Vol. 27
   of the Technische Fortschrittsberichte (Dresden and Leipzig,
   Theodore Steinkopf, 1932). C. Zerbe, Chem.-Ztg. Vol. 55, 1931,
   pp. 4-5; 18-19, 38-40, 94-96, 114-117, 136-137 and 152-153; M.
   Pier, Chem. Fabrik, Vol. 8, 1935, pp. 45-54; C. Bosch, Chem.
   Fabrik, Vol. 7, 1934, pp. 1-10; F. Mueller, Stahl und Eisen,
   Vol. 48, 1928, pp. 405-406.
4/ Chem. Fabrik, Vol. 6, 1933, pp. 127-142; Z.VDI, Vol. 77, 1933,
   pp. 305-317; cf. Stahl und Eisen, Vol. 53, 1933, pp. 1187-1189.

Figs. 3 and 4 (Plate 1) are longitudinal sections of a
bottom sheet which was in operation for two years at 100 atm
and 450°C in a heat exchanger inside a nitrogen reactor, with
the hydrogen acting upon both sides of the piece. Numerous
cracks may be seen even in the unetched section (Fig. 3). The
structure is criss-crossed with decarburized branches and the
cracks wormed their way amongst them. It is remarkable that
the attack follows the cells of the structure. Appreciable
amounts of gas were evolved during the etching of this section.
We succeeded in collecting some of this gas by drilling under
water; it consisted of 90% by volume of methane, a product of
the decarburization reaction, and 10% by volume of nitrogen.
Hot extraction of the drilling filings gave only methane and
nitrogen, which leads to the conclusion, that methane can only
exist occluded mechanically in the cracks and cleavages of the
structure. The strength was greatly reduced in comparison with
the usual values for material of that kind. Hardly any elongation,
reduction in volume and impact resistance was left.

It frequently occurred in ammonia synthesis plant opera-
ting under a pressure of 1000 atm, that a round rod of 80mm dia-
meter inside the apparatus, maintained at 450°C was cracked longi-
tudinally. The study of the structure of one such rod showed it
to be almost completely decarburized. No outside forces acted
upon the rod, and the cracking must have resulted from inside
strains. Such strains are unquestionably caused by the diffusion-
incapable methane formed during the decarburization. They may

also result in considerable changes in length, as has been learned in other cases, and cause trouble in operation.

Another manifestation of hydrogen attack, the formation of blisters, is also to be attributed to strains resulting from decarburization. An example of such is shown in Fig. 5 (Plate 1). These blisters which are very similar to the pickling blisters (and have resulted from similar causes) appear particularly often upon the surface of not killed steel. Fig. 6 shows that the separation results mostly in the particularly impure layer between the edge and the liquation zones; the presence of large amount of contamination is not, however, a prerequisite. Gas found in one such blister consisted of 60% by volume of methane and 40% of carbon dioxide.

A high pressure tube in an ammonia synthesis plant broke suddenly after eight months of operation. It was made of unalloyed steel and served to conduct synthesis gas under 850 atm pressure and at 280 to 290°C. Figs. 7 to 11 show the appearance of the crack and the structure at the break. The affected zone, about 10mm deep, can be told by its mat appearance. Decarburization can be distinctly seen in the structure; beyond that, the hydrogen attack is manifested by a strong accentuation of the grain boundaries (Fig. 10). The carbon content dropped at the inner edge from 0.30 to 0.13%.

This case proves the importance of supervision of the condition of the material of construction of the containers, and in particular to know and observe the condition of the reaction vessels. This may be done by a metallographic study of a surface

section or by removing a radial drill core. Fig. 12 shows the
instrument for the microscopic surface examination which was
found satisfactory for vertical pressure containers. The
microscope is mounted on a bridge, and the latter is kept in
place on the inside of the container under examination. Should
it be found, that the material was attacked, a drill core might
be removed to determine the depth of the attack.

Fig. 13 shows the results of examination of such a
drill core. One half of the wall thickness of a 60mm piece has
here been attacked. The reaction vessel was then discommissioned
and studied in detail. Samples for longitudinal tensile strength
and impact strength were taken from four different zones. Accord-
ing to Fig. 14, tensile strength and ductility dropped greatly
from the outside towards the inside, with the ductility dropping
faster than the tensile strength, and the impact resistance ear-
lier and more than the elongation and the reduction in area. A
tensile strength test sample was taken to include the whole wall
thickness to learn the effect of such zones of different strength
of the composite wall. The tensile strength has been found below
the average value of the intact and the damaged pieces; the elonga-
tion and reduction in area were even below those of the innermost
zones. The superior deformation properties of the unaffected
zones is made unavailable by the lower impact strength of the
adjoining zones. Hot drawing experiments have shown (Fig. 15)
that at higher temperature as well (a temperature of 450°C was
selected because of the operating temperature of the vessel) the
behavior of the attacked parts is no better.

EFFECTS OF PRESSURE, TEMPERATURE AND TIME DURING ATTACK BY HYDROGEN

The damage due to hydrogen multiplied with the rapid expansion of high pressure installations and the constantly rising demands upon construction materials, and we decided in 1928 to study experimentally the effect upon steel of hydrogen under high pressure, and a short account of these experiments is given below, as related to unalloyed steel.

The experimental arrangements are shown schematically in Fig. 16. The usual unpurified and undried cylinder hydrogen was used in the experiments, because it corresponds the closest to practical conditions. Hydrogen was taken from a steel cylinder (F), compressed to the desired pressure in a 5 stage compressor (K), and first led into a collector (H). Tubes were made from the material investigated and hydrogen (2000 ll/h) was led through them (a,b,c,d); or else round rods made, i.e. test rods for tensile strength or notched bar tests, which were placed inside a larger high pressure tube through which hydrogen was passed (A,B). In the first case the sample was under mechanical strain resulting from the pressure, but not in the second.

The tubes were made by drilling rods 500mm long, 30mm o.d. and 12mm i.d., and had therefore a wall thickness of 9mm. According to C. Bach, the tangential tensile stress is equal to about 5 kg/mm^2 under a pressure of 300 atm. The tubes were placed for 300mm of their lengths into small furnaces and heated from the outside. The thermocouple for the measurement and regulation of the temperature was inserted into the middle of the furnace and

sunk somewhat into the tube walls; in addition, temperature drops
to the outside were observed by three additional thermocouples.

The high pressure tubes used in the tests with the inserted
samples were 1500mm long, 80mm o.d., 35mm i.d. The tubes were
heated from the outside to a length of 1000mm, which produced a
length of about 200mm which was at a uniform temperature. The
temperature was read in the middle of the furnace on a thermo-
couple set somewhat into the wall and maintained automatically
within $\pm$ 5°C. The samples inside the tube were so placed on a
support, that hydrogen had free access from all sides. The gas
filling was renewed every two hours. The effect here was the
same as with a current of hydrogen.

The tubes were also heated to a high temperature under
some pressure before the beginning of every test, and when the
experimental temperature was reached they were put under the full
hydrogen pressure. The gas from the tubes passed through a deli-
cate regulating valve into an intermediate vessel (Z), and from
that through another throttling valve was returned to the com-
pressor. Tests were occasionally conducted to the bursting of the
tubes, and some of the hydrogen was lost, and had to be replaced
by make-up gas. The hydrogen was in this way continuously slowly
renewed, and the circulating gas did not become enriched in methane.

A comparison of the two series of tests showed that the
attack took place exactly alike, regardless of whether the steel
was under strain (tubes) or not (inset samples). I.e., Fig. 17
shows the longitudinal cross section through 3 tubes 30mm o.d.

and 12mm i.d., and of inserted rods 10mm in diameter, which were subjected for 10 hours at 500, 550 and 600°C to hydrogen under a pressure of 300 atm. The rods under no strain were evidently as strongly attacked as the tubes, even possibly somewhat deeper, because the hydrogen concentration is more rapidly reduced inside the tube due to the diffusion into the walls, than to the inside of the samples 4/. Because of the greater ease of preparation and manipulation, most of the samples were therefore used as inset pieces.

Two open hearth steels were used in the first series of tests. Their composition was:

%C	%Si	%Mn	%P	%S	%Ni	%Cr
0.22	0.31	0.84	0.021	0.020	0.15	0.14
0.76	0.16	0.25	0.01	0.016	0.10	0.07

Samples of 20mm diameter and 50mm long were made from normalized rods 22mm diameter, and polished all over with emery paper size 1 F. The samples were de-fatted with benzene before the experiments, weighed and measured. After the tests, the rods were cooled in the furnace under a slight hydrogen pressure.

A strong attack by hydrogen was frequently manifested by the formation of small methane blisters, which occasionally were ranged along the fibers of the metal. (Fig. 25, Plate 2).

The samples were next weighed, measured, cut longitudinally and polished. The depth of decarburization was then measured on the etched section, and namely the total depth and the width of the ferritic edge layer. Decarburization was also determined from the loss in weight. The value so obtained represented a state which could never be entirely reached in practice,

but was approached under certain experimental conditions at
high temperature; in such case the agreement with the measured
decarburization values was rather good (Fig. 18). The process
of determination of the decarbonization from the loss in weight
offers the advantage of objectivity in the presentation of the
results, and is unaffected by the chance structure of the decar-
burized material. The depth of the decarburization was accord-
ingly always based on the following reasoning.

Experimental conditions were changed within the follow-
ing limits: pressure from 25 to 1000 atm., temperature from
400 to 600°C, and time from 1 to 100 hours.

Fig. 19 shows the effect of the hydrogen pressure. Decar-
burization starts at a certain pressure, and the depth of decar-
burization increases rapidly at first with increasing pressure,
then slower. The decarburization starts at lower pressures as
the temperature rises and the time increases. Presumably as a
result of the high manganese and chromium content, the start of
decarburization in the 0.2% C steel is at a higher pressure than
in the other sample.

The effects of the length of experiment is shown in Fig.
20. The depth of decarburization at first increases rapidly with
time, and then seems to increase in a straight line. C. R. Aus-
tin 5/ has obtained similar results in his decarburization experi-
ments. It is worthy of notice that decarburization of the carbon-
richer steel does not start immediately, but that the process

5/ J. Iron Steel Inst., Vol. 105, 1922, pp. 93-142.

requires a certain "incubation period", which is the longer, the
lower the temperature and pressure. Thus, decarburization of
the carbon-richer steel begins only after 10-20 hours at 500°C
and 100 atm pressure, and after 50-100 hours at 400°C and 300 atm.

      The effect of temperature is shown in Fig. 21. The
decarburization starts at a definite temperature, and its extent
depends on the pressure and the time, and then extends to uni-
form depth into the steel. We may well conclude from the shape
of the curves, that the start and the progress of decarburization
does not depend primarily on the diffusion rate of hydrogen;
since in that case the course of the curves would be entirely
different, because the amount of hydrogen diffusion is an expo-
nential function of the temperature 6/. It must therefore be
assumed that the progress of the process is determined primarily
by the rate of the actual decarburization reaction.

      After the attack has started, it progresses rapidly as
the temperature rises, and the knowledge of the temperature at
which the action begins is therefore particularly important.
Fig. 22 shows the relationship between the temperature and the
pressure of hydrogen for the sample of steel containing 0.76% C.
It becomes at first rapidly lower as the pressure rises, up to
about 150 atm, and then drops much more slowly. The effect of
time is to be seen in this case, too. The true connection can
only be found in experiments over long periods of time.

6/ G. Borelius and S. Lindblom, Ann. Phys., Vol. 82, 1927, pp. 201-226.

The attacked samples show an increase in both the length
and diameter when measured before and after the exposure.— The
increase depends on the amount of carbon removed (Fig. 23). At
times the volume increase is quite considerable; one sample of
the 0.76 steel increased 0.70mm in diameter and 1.05mm in length.
This increase in dimensions must be the result of decarburization
and the loosening up of the arrangement of the grain which resulted.

CONNECTION BETWEEN THE ATTACK BY HYDROGEN AND STRUCTURE

Fig. 24, Plate 2 shows a series of etched longitudinal
sections of samples of steel with 0.76% C, where the upper row
was decarburized at 500 and the bottom row at 600°C. Not merely
is the decarburization deeper at the higher temperature, but also
more complete, and the ferritic edge zone changes rather sharply
into the unattacked grain structure, while the carbon content of
samples treated at lower temperatures changes gradually from the
edge towards the center. (see also Fig. 18). The aligned orien-
tation of decarburization evidently results from the original
structure of the samples, and deserves consideration. Samples
decarburized at 400 and 450°C show it still more clearly. E.g.
Fig. 26 (Plate 2) reproduces an etched sample of steel treated
for 10 hours at 1000 atm at 450°C. The effect of hydrogen has
accentuated the primary structure by a stronger decarburization
along the dendritic axes. The decarburization has, in addition,
proceeded into the grain of the sample in side branches. Figs.
27 to 30 show the structure of this sample on the surface and at

different levels underneath. The strong markings of the grain
boundaries are striking, as well as the strong decarburization
of the inside of the grain. Fig. 31 (Plate 3) shows the corres-
ponding series of structure of samples treated at 400°C. One may
see even better in this case, that the attack proceeds only from
the grain boundaries, and not from the surfaces in immediate con-
tact with hydrogen. In contradiction to it, Fig. 32 (Plate 3)
shows the structure of a sample decarburized at 600°C, which con-
sists of a completely decarburized edge zone, which merges with
the unattacked grain of the material.

Steel with 0.22% C behaves similarly; in this case, the
attacks at lower temperatures are however, less clearly distin-
guished, and are perhaps manifested chiefly in a greater accentu-
ation of the grain boundaries.

We will mention here briefly an experiment which shows
clearly the connection between decarburization and the primary
structure. A number of samples of the 0.76% steel, 20mm in dia-
meter and 20mm long were forged to a different extent, and then
subjected to the action of hydrogen at 300 atm and 450°C. The
reduction in weight was the same in all cases, but the nature of
decarburization was very different, as may be seen in Fig. 33
(Plate 3). The differences must be explained by the difference
in the original structure, as proven by a comparison of the sec-
tions etched by P. Oberhoffer's method. The dendritic axes are
attacked first. Fig. 34 shows the structure in the decarburized
zone of the unforged test pieces in a larger magnification. Decar-
burization is found only in the dendritic axes, and inside of these
it starts from the grain boundaries of the secondary structure.

It is definitely known, that a number of elements diffuse
into metals more readily along the grain boundaries than inside
of the crystals 7/. A grain boundary diffusion of hydrogen must
also be assumed from the looks of the structure. J. E. Stead 8/
is of the opinion that gases enter metals easiest between the
crystallites, and W. Rosenhain 9/ assumes a gaseous diffusion
along the grain boundaries. The majority of the investigators
have reached the conclusion that hydrogen diffuses through the
metal lattice, and not only through the grain boundaries 10/.

Whenever decarburization starts at the grain boundaries,
the fine grained test pieces may be expected to be stronger decar-
burized than the coarse grain. Such however, is not actually the
case. Test pieces from the two steels made coarse-grained by heat-
ing to 1150°C lost as much weight as the normalized pieces. The
coarse-grained test pieces had a much finer network of hydrogen
attack along their edges, than corresponded to their grain size.
(Figs. 35 and 36, Plate 4). In this case carburization started
at a grain boundary and then evidently worked its way into the
grain itself, apparently along certain preferred planes (Fig. 36).
The grain boundaries appeared, however, to be preferred, at least
at the start. In agreement with this, the diffusion experiments
at 300 atm pressure and 300°C have shown that the hydrogen perme-
ability became smaller within increasing grain size. The intrusion

7/ R. F. Mehl, Amer. Inst. Min. Met. Eng., Techn. Public No. 726,
    46 pp. Met. Techn. Vol. 3, 1936, No. 5.
8/ J. Iron Steel Inst., Vol. 103, 1921, pp. 271-275.
9/ J. Iron Steel. Inst., Vol 92, 1915, p. 119.
10/ G. Borelius, Ann. Phys., Vol. 83, 1927, pp. 121-136; W. Baukloh
    and H. Guthmann, Z. Metallk., Vol. 28, 1936, pp. 34-40; C. J.
    Smitnels and C. E. Ransley, Proc. Roy. Soc., London, A 150 (1935),
    pp. 172-197; Met. Progr., Vol. 29, 1936, pp. 92-94; W. R. Ham,
    Trans. Am. Soc. Metal. Vol. 25, 1937, pp. 563-570.

of hydrogen into certain preferred octhedral surfaces have been proven metallographically on palladium by D. P. Smith and G. J. Derge 11/.

It has further been found metallographically, that individual stamped test pieces, in general unattacked, were completely locally decarburized underneath the stamp (Fig. 24) L. Jacqué 12/ has made a similar observation. Hydrogen attack is therefore favored by cold working. The magnitude of the effect of cold working was tested by cold hammering two series of test pieces from 10 to 50%, on a 20mm diameter and 20mm length, and then acting on each series with hydrogen at 550°C and 300 atm and at 600°C and 100 atm. Fig. 39 shows the losses in weight in relation to the amount of working. They increase with increasing amount of cold working up to 40%. Fig. 39 (Plate 4) shows the longitudinal section of the test pieces. Cold working causes a deeper penetration of decarburization at high temperatures, while at low temperature the effects are a complete decarburization of the worked zones. One of the test pieces worked to 50% was cracked by the methane pressure at the points of greatest deformation. Diffusion processes accelerated cold working 13/ and the greater decarburization tendency must be attributed to the increased hydrogen diffusion in the cold worked parts. The hydrogen enters the body along the glide planes which are in many respects similar to the grain boundaries, according to P. Langmuir 14/ and H. J. van Liempt 15/, and can in that way cause a complete decarburization.

11/ J. Am. Chem. Soc., Vol. 56, 1934, pp. 2513-2524.
12/ C. R. Acad. Sc., Paris, Vol. 195, 1932, pp. 878-880.
13/ R. F. Mehl. Am. Inst. Min. Met. Eng., Techn. Publ., 726, 40 pp. Met. Techn., Vol. 3, 1936, No. 5.
14/ J. Frankl. Inst., Vol. 217, 1934, pp. 543-570.
15/ Rec. Trav. Chim. Pays-Bas, Vol. 51, 1932, pp. 113-142.

Table 2. Changes in Mechanical Properties Resulting from Attack by Hydrogen

% C in Steel	Length of Test Hrs.	Pressure Atm.	Temperature °C	Yield Point kg/mm²	Tensile Strength kg/mm²	Elongation (l = 5d) %	Reduct. in Area %	Impact Strength mkg/cm²	% C	Appearance of Surface	Fracture	Structure
0.013	-	-	-	28/25	35.7	34.0	94	27.2	0.013	-	Fibrous	-
	100	300	350	22/21	29.5	54.7	89	0.9	0.010		Coarse grain, brill.	(1)
	100	300	400	18	27.9	50.0	76	0.6	0.007	Blisters	Coarse grain, brill.	(1)
	10	300	600	16/13	24.8	32.0	31	2.6	-	-	Mat grey	(1)
0.11	-	-	-	33	43.6	40.5	79	>26.7	0.11	-	Fibrous	-
	100	1	600	30/27	39.8	42.0	77	>30.5	0.11	-	Fibrous	(2)
	100	1	650	31/27	38.1	38.0	80	>30.5	0.10	-	Fibrous	-
	100	1	700	25	35.6	45.0	84	>30.9	0.06	-	Fibrous	(4)
	100	50	400	33/29	42.7	37.3	79	>27.8	0.11	-	Fibrous	(2)
	100	50	450	31/30	42.5	39.7	79	>27.6	0.11	-	Fibrous	(2)
	100	50	500	~22	28.4	16.3	12	0.5	0.09	-	Mat grey	(5)
	100	100	400	34/32	43.1	40.0	72	9.9	0.11	-	Mat grey	(1)
	100	100	450	~26	32.4	~12	11	1.4	0.05	Blisters	Mat grey	(6)
	100	200	400	~28	40.2	12.0	22	1.3	0.05	-	Mat grey	(1)
	100	300	350	30/29	42.6	41.3	79	26.7	0.11	-	Fibrous	(2)
	100	300	400	26	29.4	5.0	6	0.6	0.013	Blisters	Mat grey	(7)
	100	300	500	22	25.3	0	0	0.4	0.01	Blisters	Mat grey	(7)
	10	300	600	18	[illegible]	0	0	1.1	-	Blisters	Mat grey	(7)
	100	600	350	32	35.6	9.7	27	0.2	0.11	-	Mat grey	(1)
	100	1000	300	29.2	40.3	42.0	79	26.4	0.11	-	Fibrous	(2)
0.24	-	-	-	31	56.8	29.7	66	17.6	0.24	-	Grain, fibrous edge	-
	100	1	600	[illegible]	43.7	24.7	70	10.9	[illegible]	-	Grain, fibrous edge	(2)
	100	1	650	33/31	45.8	33.7	79	22.4	[illegible]	-	Grain, fibrous edge	(8)
	100	1	700	30/29	45.0	[illegible]	[illegible]	>[illegible]	[illegible]	-	Fibrous	[illegible]
	100	50	450	35	54.4	[illegible]	[illegible]	[illegible]	[illegible]	-	Grain, fibrous edge	[illegible]
	100	50	500	~25	[illegible]	10.0	[illegible]	1.5	[illegible]	-	Mat grey	(10)
	100	100	400	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible] fibrous edge	(2)
	100	100	450	35/34	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Mat grey	(11)
	100	200	400	38	58.9	17.0	[illegible]	[illegible]	0.21	-	Outer edge, mat grey	(12)
	100	200	450	~[illegible]	33.6	~10	[illegible]	[illegible]	[illegible]	[illegible]	Mat grey	[illegible]
	100	300	350	34	56.9	30.7	[illegible]	[illegible]	[illegible]	-	Fibrous	[illegible]
	100	300	400	~32	34.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Mat grey	[illegible]
	10	300	600	21	26.1	0	[illegible]	1.6	0.01	[illegible]	Mat grey	[illegible]
	100	600	350	32	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	Grain, gray edge	(2)
	100	1000	300	35	57.0	[illegible]	[illegible]	14.9	[illegible]	-	Grain, fibrous edge	(2)
0.45	-	-	-	60	61.4	[illegible]	[illegible]	7.2	0.45	-	Grain	-
	100	300	350	62	[illegible]	[illegible]	[illegible]	6.2	0.45	-	Grain	[illegible]
	100	300	400	53	56.0	~3	[illegible]	0.8	[illegible]	Blisters	Mat grey	[illegible]
	10	300	600	25	[illegible]	[illegible]	[illegible]	2.7	-	Blisters	Mat grey	[illegible]

(1) Grain boundary attack. (2) No attack. (3) 0.5mm edge decarburization. (4) 2 mm edge decarburization. (5) Grain boundary attacks throughout, [illegible] decarburization. (6) Grain boundary attacks throughout, branched decarburization. (7) Grain boundary attacks throughout, complete decarburization. (8) 0.2mm edge decarburization. (9) 0.9mm edge decarburization. (10) Grain boundary attack, 1.4mm depth complete decarburization, 2.5mm branched decarburization. (11) Grain boundary attack, with branched decarburization along edges. (12) Grain boundary attack along edges. (13) Grain boundary attack throughout, decarburization along boundaries. (14) 3.5mm boundary attack with strong decarburization.

EFFECT OF HYDROGEN ATTACK ON THE
MECHANICAL PROPERTIES

Some statements have already been said in the beginning
upon the effects of the hydrogen attack on the tensile strength
and ductility of the material. The effects of compressed hydro-
gen and temperature upon the mechanical properties of steel were
studied in a series of tests with unalloyed basic hearth steels
with a C content of 0.013-0.45%, and summarized on Table 1. The
samples were forged either to round bars 12mm diameter, or to
square rods with 13mm edge, normalized, then cold worked to test
pieces 6mm diameter and 30mm length, or to notched bar test pie-
ces 10 x 10 x 55mm with a 2mm round notch. The duration of the
test was generally 100 hours. A shorter time was only used at
600°C, because the attack at that temperature was very rapid.
The limits of stability were found varying with the temperature
and pressure for steels with 0.11 and 0.24% C: with the other the
pressure of 300 atm was maintained throughout, and only the tem-
perature changed. The samples were tested after heating in hydro-
gen. One-half of the notched bar test pieces were always tested
metallographically by preparing a section, and the carbon deter-
mined in the edge zone in the corresponding other half, for which
purpose a 1mm layer was filed off.

Table 1. Composition of Steels Tested
for Mechanical Strength

% C	% Si	% Mn	% P	% S	% Ni	% Cr
0.013*	0.01	0.02	0.01	0.01	-	-
0.11	0.14	0.41	0.014	0.020	0.10	0.06
0.24	0.29	0.60	0.036	0.022	0.15	0.13
0.45	0.26	0.81	0.020	0.020	0.14	0.24

* Armco iron

The hydrogen attack manifests itself in the strong
reduction in tensile strength and in an almost complete des-
truction of ductility. Figures 40 and 41 show the changes in
mechanical properties of steels with 0.11% C with increasing
temperature and hydrogen pressure. The passing of the limits
of stability are seen in Figure 40 between 350-400°C by a sudden
drop of all mechanical strength values and in the carbon content.
Notched bar tests are the most sensitive indication of hydrogen
attack. In the limiting cases, the drop in the impact value
may be the only indication of a hydrogen attack (of the steel
with 0.11% C, 100 atm, 400°C). The hydrogen attack, in such
cases, cannot be proven analytically and with great difficulty
metallographically. The mat gray appearance of the fracture is
a sure indication of attack by hydrogen (Fig. 38, Plate 4) and
the fracture is the darker the stronger the attack and the higher
the original carbon content. The structure of the attacked sam-
ples shows the well-known phenomena described previously (Figs.
42-53, Plate 5). An attack, if present, may extend to the cen-
ter of the samples. The noticeable attack upon the grain bound-
aries on the very low carbon Armco iron is remarkable.

The influence of carbon content is relatively small.
The Armco iron is already attacked at 350°C under 300 atm hydro-
gen pressure, but still retains a good share of mechanical
strength properties in spite of the attack. The attack upon
steels begins between 350 and 400°C. Fig. 54 shows the changes
in the mechanical properties after treatment with hydrogen at

300 atm and 400°C in relation to the original carbon content of
the material; the values of the attacked samples are given in
percent of the original values.

Fig. 55 shows the limits of stability for the two steels
with 0.11 and 0.25% C. There is no true hydrogen attack at the
pressure of 1 atm. On the other hand at 650°C both steels show
a simple decarburization without loosening up of structure and
accordingly also without harmful effects upon the ductility of
the material.

We will discuss later the reasons for the appearance of
such entirely different kinds of decarburization. The limits of
stability under 50 atm pressure are between 450 and 600°C; when
exceeded, a regular hydrogen attack starts (marked with an x).
The limiting temperature is displaced with increasing pressures
towards the corresponding lower values and drops at 100 atm
pressure to about 300°C. Steel with 0.24% C is more stable by
several degrees than steels with 0.11% C. These data apply natu-
rally only for tests lasting for 100 hours. In agreement with
operational experience, tests extended to 2,000 hours have shown
that the limits of stability are but 50-70° lower still. H. P.
Inglis and W. Andrews 16/ have come to the conclusion of very
long experiments at 250 atm pressure that the limits of stability
of unalloyed steels are around 150°C for coarse grained structure

16/ J. Iron Steel Inst., Vol. 128, 1933, pp. 383-397.

common for large containers; the operational experience avail-
able to them led him to believe this data to be too low.

Tubes strained by inside pressure were also treated
in this series of tests. A soft iron of Krupp containing 0.04% C
was used in the place of the Armco iron. The attack began at 300
hours under 300 atm pressure at 350-400°C, in agreement with the
tests performed with rods. The attack was already extended to a
great depth at 400°C. The attack was so strong at 600°C that
the tubes burst in 7-35 hours; and steels with higher carbon con-
tent had the longer life.

We must mention tests on steels with 0.1% C, with addi-
tions of 0.2% P, 0.2% S, 0.08% O and 0.15% N (by nitriding).
The pressure was 300 atm, the temperature 350-400°C. It was
found that none of the elements added, except nitrogen, were
removed by the action of hydrogen upon steel. The steel, pre-
sumably as a result of the breaking down of the unstable iron
nitrides, began to soften already at 350°C, without reduction of
the ductility of the steel. All the steels were unattacked at
350°C, and were decarburized and attacked at 400°C. No decar-
burization was found either analytically or metallographically
only in the phosphorous steel and the ductility remained also
somewhat higher than in the other materials.

PROCESSES DURING ATTACK ON
STEEL BY HYDROGEN

The processes of the attack of hydrogen upon steel can
be described on the strength of the phenomena observed: hydrogen

first penetrates through the grain boundary, and starting from
there attacks the preferred grain surfaces in the steel, and
begins to decarburize the material, if conditions are favorable
to it. The decarburization proceeds very slowly at low tempera-
tures and pressures, and will first attack the carbon dissolved
in the α iron. The carbon is displaced there by diffusion in
the α iron, a process which also will proceed very slowly at low
temperatures. The attack first becomes visible in the dendritic
axes, because the carbon present in the pure metal can diffuse
over them the easiest. J. H. Whitely [17] has found that the
solubility of carbon in α iron is reduced by impurities. The
effect of phosphorus is probably the result of its known reduc-
tion of the solubility of carbon in the γ iron [18]. This is also
indicated by the lower decarburization of the phosphorus steel
tested. The more complete decarburization at higher temperatures
may be explained by the stronger carbon diffusion. It is pro-
bable, that at higher temperature decarburization by oxygen or
by steam is added to that by hydrogen, and this also produces a
more complete removal of carbon, because oxygen diffuses pre-
ferentially inside the grain [19].

The methane formed during decarburization cannot diffuse
and as a result it collects in situ where the process takes place,

[17] J. Iron Steel Inst., Vol. 116, 1927, pp. 293-303.
[18] F. Wuste, Metallurgie, Vol. 5, 1908, pp. 73-87; P. Goerens
and W. Dobbelstein, Ibid. Vol. 5, 1908, pp. 561-566; Ibid.
Vol. 6, 1909, pp. 537-550.
[19] D. H. Rowland and C. Upthegrove, Trans. Amer. Soc. Met.,
Vol. 24, 1936, pp. 96-132.

i.e. on the grain boundaries and on the preferred grain surfaces,
and produces strong tensions which ultimately may result in rup-
tures. The removal of a very small proportion of carbon content
may be sufficient to cause this action as shown by experiments
with Armco iron. The first separations appear already before
the decarburization becomes visible microscopically, as can be
proven by other means. This must be attributed to the widening
of the grain boundaries which is visible during decarburization
under a microscope. The whole process undergoes a change the
moment the first cracks are formed. Methane now can leave the
steel, and hydrogen acquires an easier entry into the inside.
Wherever these cracks have formed the reaction becomes more lively.
This explains the appearance of the deeply intruding decarbur-
ized branches as well as the sudden appearance and rapid visible
progress of the decarburization after a certain time, while the
rest of the steel appears to be unattacked.

The process is fundamentally different than in the usual
edge decarburization of steels, and differs from the latter in
the manifestations and in its action. The usual edge decarburi-
zation is manifested only in samples heated at atmospheric press-
ure (Table 1); the beginning of the decarburization is between
600 and 650°C. The hydrogen-resistant chromium steels showed a
different type of decarburization also at high pressures and
correspondingly lower temperatures down to 550°C. Unlike the
hydrogen attack, the edge decarburization proceeds relatively
slowly and quite regularly, and leaves a structure unaltered

except for the disappearance of perlite; accordingly the samples attacked retain their complete ductility even when the decarburization has extended to the center of the samples.

To what are to be attributed these fundamental differences in the two decarburization processes? Diffusion experiments show that the appearance of the one or the other form of decarburization is not related to the diffusion velocity of hydrogen. The edge decarburization may appear in the same steel at the same diffusion velocity of hydrogen at which steel is attacked at the grain boundaries under other conditions. The absence of grain boundary attack can therefore not be explained by the possibility of diffusion for the methane produced at higher temperatures.

As mentioned above, the edge decarburization takes place in alloyed steels at relatively low temperatures, and there remains therefore only the conclusion that in this type of decarburization no methane at all is formed inside the steel structure. An indication of the nature of the process is given by the investigation of structure of the edge decarburized chromium steels. This shows finely distributed oxides near the edge. Decarburization is therefore most likely caused not by hydrogen but by oxygen, because in the unpurified hydrogen there always exists oxygen, both as the free element and in the form of water vapors.

It has been shown by many investigators that moist hydrogen acts much more strongly decarburizingly than dry hydrogen [20].

---

[20] E. D. Campbell, J. Iron Steel Inst., Vol. 100, 1919, pp. 407-415; E. D. Campbell, J. F. Ross and W. L. Fink, J. Iron Steel Inst., Vol. 108, 1923, pp. 173-187; A. Bramley and K. F. Allen, Engineering, 1932, pp. 92-94, 123-126 and 229-231.

F. Wüst and C. Geiger [21], F. Wüst and E. Sudhoff [22] and J. V.
Emmons [23] have found no decarburization whatever when using pure
dry hydrogen. The experiments of F. Schmitz [24] et al prove that
even pure hydrogen may decarburize under atmospheric pressure and
high temperatures. According to E. H. Schulz and W. Hülspruch [25],
decarburization begins in dry chemically pure hydrogen, but only
at 950°C, while technically pure hydrogen acts strongly decarburi-
zingly already at 750°C. C. R. Austin [26] has found that very pure
dry hydrogen produces a decarburization at 800°, but it is then
highly limited in extent and unprovable metallographically. D. H.
Rowland and C. Upthegrove [19] have also established the fact that
oxygen is the principal decarburizing agent when moist hydrogen
is used, and that the oxygen forms a solid solution in iron and
diffuses through it. The hydrogen decarburization proceeds, how-
ever, at atmospheric pressure much slower and only begins at appre-
ciably higher temperatures than the beginning of decarburization
by water vapors. Our own experiments have also shown that very
pure hydrogen does not act noticeably decarburizingly at 750 and
800°C, while moist hydrogen decarburizes very strongly. It must
therefore be considered proven that the edge decarburization on
samples heated at atmospheric pressure is not caused by hydrogen
but by oxygen.

/

21/ Stahl u. Eisen, Vol. 25, 1905, pp. 1134-1139.
22/ Metallurgie, Vol. 7, 1910, pp. 261-264.
23/ Trans. Amer. Inst. Min. Met. Eng., Vol. 50, 1915, pp. 405-423.
24/ Stahl u. Eisen, Vol. 39, 1919, pp. 373-381 and 406-413.
25/ Arch. Eisenhuttenwes., Vol. 1, 1927/28, pp. 225-240.
26/ Trans. Amer. Soc. Met., Vol. 22, 1934, pp. 31-67.

Carbon monoxide is a product of the reaction of decir-
burization by oxygen. This can readily diffuse through steel 19/
without causing any tensions and separation. This was proven by
a test made at another opportunity. A small plate was welded
longitudinally into a tube of 12mm i.d. made of 5mm thick unalloyed
steel with 0.34% C. An unpurified moist hydrogen was introduced
into one-half of the tube, while the other was evacuated. The
test temperatures were 650, 700, 750, 800, 850 and 900°C, the
length of the experiment was always 12 hours. Table 3 shows that
the evacuated gases consisted only of carbon monoxide produced
in the decarburization of the plates, and of hydrogen. All the
tests were made successively on the same plate, and the latter
was finally almost completely decarburized, which naturally
resulted in the reduction of the carbon monoxide contents of the
evacuated gas.

Table 3

TESTS ON DIFFUSION OF HYDROGEN AT A
PRESSURE OF 1 ATM

Temperature °C	Evacuated	
	mls H₂	mls CO
650	1.60	1.34
700	1.76	2.91
750	1.65	3.83
800	2.67	4.27
850	3.72	2.48
900	4.52	0.35

Even assuming that hydrogen participates in decarburi-
zation at higher temperatures, as may be accepted on the strength

of the work of Austin 26/ and Rowland and Upthegrove 19/, this
process differs, however, from the decarburization under high
pressure probably in that it takes place on the surface of the
steel, where the methane formed can freely escape.

SUMMARY

After a brief discussion of the manifestations and
results of hydrogen attack illustrated by samples of attacked
structural parts of high pressure hydrogenation vessels, a report
is made on experiments for determining the effects of pressure,
temperature and time on the beginning and the progress of decar-
burization of unalloyed steels. The length of the experiment is
of deciding influence for the attack, as well as the pressure
and the temperature. After the attack has already exceeded the
limits of stability (depending on length of test) the process
proceeds relatively rapidly inside the steel. At low tempera-
tures (400-500°C) decarburization proceeds in an incomplete and
branched form. It starts at the grain boundary and on certain
preferred surfaces inside the grain. The dendritic axes are
more rapidly decarburized than the rest of the material. A cold
working favors the starting and the progress of the hydrogen
attack.

The mechanical properties, and in particular the ductility
of the steel, are strongly lowered by the hydrogen attack. Armco
iron is also attacked by hydrogen, in spite of its low carbon

content. Phosphorus, sulfur and oxygen are not removed by
hydrogen under conditions at which decarburization already starts.
Part of the nitrogen escapes before decarburization, without
affecting ductility.

Hydrogen attack differs fundamentally in form and action
from the low pressure edge decarburization. The difference is in
the formation of methane through decarburization with hydrogen,
while in the surface decarburization oxygen (water vapors) acts
with formation of carbon monoxide.

DISCUSSIONS

F. Korber, Dusseldorf

I wish to ask a question on some groups of pictures pre-
sented among the information offered by Mr. Naumann and which
gives a deep insight into the mechanism of the attack of hydro-
gen upon carbon. It deals with Fig. 37 which shows that the
attack is greatly intensified after cold working. You might first
be inclined to interpret this by the fact of the cold working,
namely to the disturbances in the lattice, tensions in the struc-
ture, formation of glide planes, the more so that the strongest
attacked samples at 600°C show tearing of the edges. We must,
however, bear in mind that the cold worked samples remained for
hours above the recrystallization temperature; the cold working
structure must have disappeared shortly after the beginning of
the tests. I would like to ask Mr. Naumann whether the mechan-
ism of the introduction of hydrogen has been investigated more

in detail on these cold worked samples; it may be that the mechanism of the intrusion into the grain of the recrystallization structure is different after cooling to a temperature above the transformation point. We might consider the distribution of the occlusions which are entirely different in the two cases.

H. Guthmann, Dusseldorf

Mr. Naumann has stated in his important communication that in his opinion the carbon content had a small influence upon the hydrogen decarburization. I can briefly report my own investigations carried out last year with Mr. W. Baukloh in the Blast Furnace Institute of the Technische Hochschule in Berlin, which brought us to entirely different conclusions 10/. According to our plans we studied the hydrogen permeability and decarburization in steel tubes with hydrogen under high pressures and at high temperatures, using steels of different carbon content. We have conclusively proven that carbon had quite a considerable influence upon decarburization, and namely in that the increasing carbon content reduced the permeability to hydrogen, and also to a very great extent the decarburization directly connected with it.

We have studied unalloyed steels as well as a series of chrome alloy steels with a chromium content between 0.5 and 6%, with a arbon content of 0.15 and 0.35%. We could confirm the same effect of carbon upon the permeability to hydrogen and to decarburization. The chromium content affects decarburization

favorably, aside from the well-known effect of the higher chromium contents, in that chrom-iron mixed carbides are formed with higher carbon concentrations, and these carbides are hydrogen resistant. It may be mentioned that a steel containing 0.30 to 0.35% C and about 1% Cr had precisely the same hydrogen permeability and is decarburize like steel with 0.15% C and about 6% Cr.

I would be grateful to Mr. Naumann for informing me whether he has carried out similar investigations with chrom alloys with a higher carbon content and what results he has obtained.

F. Rapatz, Dusseldorf-Oberkassel

Mr. Naumann shows in Fig. 33 the decarburization inside the primary crystallites is stronger along the dendritic axes than in the rest of primary crystallites. Is the assumption justified that the effect of phosphorus mentioned at the end is to be attributed to the effect of phosphorus liquation upon the primary crystallites?

W. v. Kronenfels, Berlin

Our own work has shown that the carbon content of pure steels up to 700°C had an important influence upon the decarburization rate in a stream of hydrogen at 1 atm pressure, and the decarburization decreased in that temperature range with increasing carbon content 27/. This result has already been proven

27/ Arch. Eisenhuttenwes., to appear shortly.

conclusively by W. Baukloh and H. Guthmann 10/ at pressures of
20 atms. These relationships change above 700°. It is unnecessary
to discuss these results here because they will shortly be published.

F. K. Naumann, Essen

I would like to reply to Mr. Korber that similar phe-
nomena have been observed in cold worked samples at 400-450° at
which no noticeable recrystallization could yet have taken place.
For instance, cold bending tests of steel with 0.11 and 0.24% C
were completely decarburized in the cold worked parts after 10
hours action of hydrogen under 600 atm pressure and 450°C, while
in the not worked legs only a grain boundary attack with slight
decarburization of grain boundaries could be observed. If these
samples were heated, however, prior to the hydrogen treatment at
730-780° to recrystallize them, the attack was visible in the
finely grained as well as in the coarse grained recrystallized
zones and was no stronger than in the deformed parts. We might
conclude from that that the deformation is in itself a cause for
stronger decarburization rather than the recrystallization. I wish
to remark to Mr. Guthmann's question that I have made tests with
chrome alloy steels with different carbon concentrations, but unlike
him I have found that with equal chrome content the carbon-richer
alloys were less hydrogen resistant than the carbon-poorer.

W. Baukloh, Berlin
(A later contribution in writing)

I do not consider it correct to make a fundamental assump-
tion such that the decarburization does not depend on the diffusion

of hydrogen through the iron, from experimental results found
in such a narrow temperature range. The diffusion property of
hydrogen is not an exponential function of hydrogen as claimed
by Mr. Naumann. The effect of transformation of metal on the
diffusion properties of hydrogen has been recognized 28/, the
character of the temperature relationship of hydrogen permeabi-
lity is identical with the decarburization 10/, with the reduc-
tion of iron ores 29/ or the desulfurization of iron 30/ with
hydrogen, as we have proven it here in our Institute, and the
relationship between diffusion of gaseous agents and the actual
reaction can no longer be contradicted by results of experiments,
which in my opinion are on too narrow a basis to answer this
question (too small a temperature interval!).

F. K. Naumann
(In writing)

Mr. Baukloh has covered a larger temperature range in
his test than have I, but a much narrower pressure range. The
same objection to conclusions over the connection between hydro-
gen diffusion and decarburization which Mr. Baukloh has made
against my conclusions, namely that the tests covered too narrow
a range, could therefore be also made to his work. Most of the

28/ W. Baukloh and H. Kayser, Z. Metalkeva, Vol. 27, 1935, pp. 285.
29/ W. Baukloh and K. Froeschmann, Stahl u. Eisen, Vol. 54, 1934,
    pp. 415-416.
30/ W. Baukloh, Metallwirtsch., Vol. 15, 1936, pp. 1193-1196.

tests of Mr. Baukloh and his co-workers were made at high tempera-
tures and relatively low pressures while I preferred working in
the field of higher pressures and lower temperatures because of
the particular industrial importance of that field. This field
appears to me, however, particularly suited to study the action
of hydrogen, because at high temperatures the carbon diffusion
becomes very high, and even when purified hydrogen is used,
non-provable traces of steam impurity may affect the results.

×½

Fig. 1. Pressure vessel burst under H_2 attack
Abbildung 1.
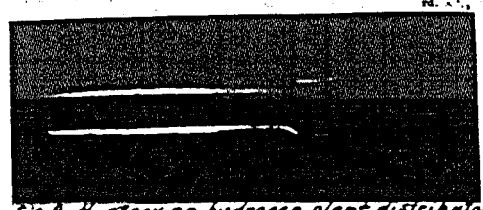Durch Wasserstoffangriff aufgeplatztes Reaktion-gefäß.

rd. ×½

Fig. 2. H_2 attack on hydrogen plant distributors
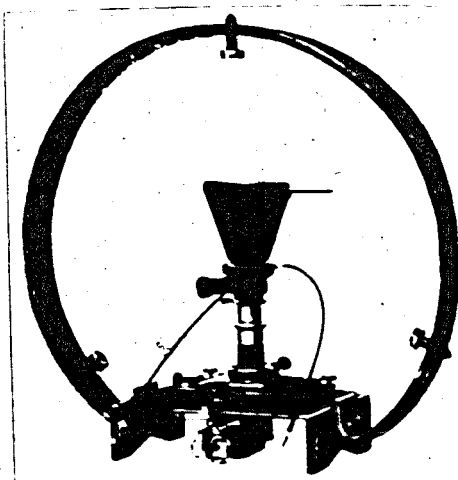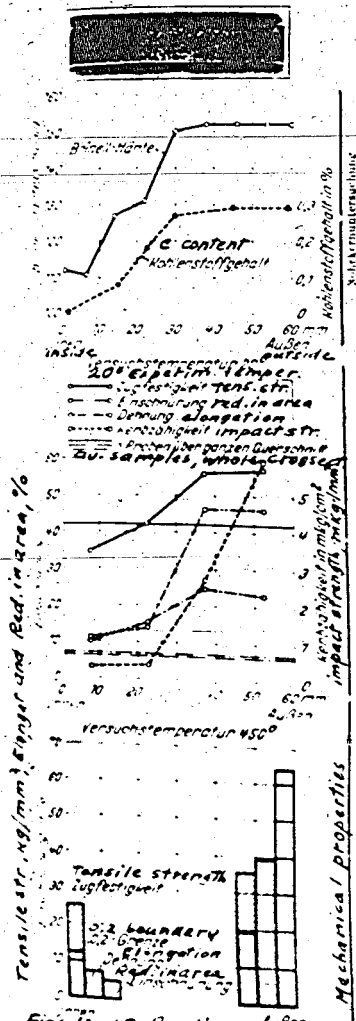Abbildung 2. Durch Wasserstoffgas aufgegründer Verteilklotz
aus einer Hydrieranlage.

Abbildung 12. Gerät für metallographische Untersuchung
in stehenden Hochdruckgefäßen.
Fig. 12. Apparatus for metallogr. study of press. vess.

Brinellhärte

c content
Kohlenstoffgehalt

Kohlenstoffgehalt in %

inside   Außen   outside

20° Zimmertemperatur 20° temper.
— Zugfestigkeit tens. str.
— Einschnürung red. in area
— Dehnung elongation
— zertchligkeit impact str.
— Proben über ganzen Querschnitt
Zu. samples, whole crosses.

Versuchstemperatur 450°

Tensile str. kg/mm², elong. and red in area, %
Impact strength, kgm/mm²

Tensile strength
Zugfestigkeit

0.2 boundary
0.2 Grenze
Elongation
Red. in area

Mechanical properties
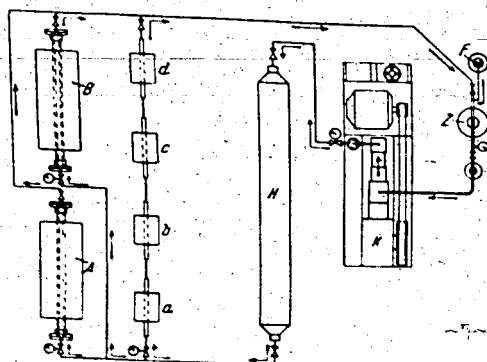
Figs. 13-15: Reaction vessel
affected by hydrogen attack

Abbildung 16.
Versuchsanordnung für Wasserstoff-Hochdruckversuche.
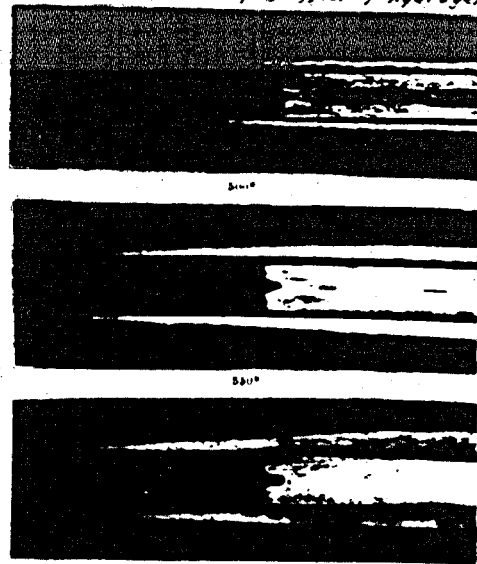Fig. 16 Appar. for study of effect of hydrogen

Fig. 17 samples decarburized with hydrogen.
Abbildung 17. Durch Wasserstoff entkohlte Proben
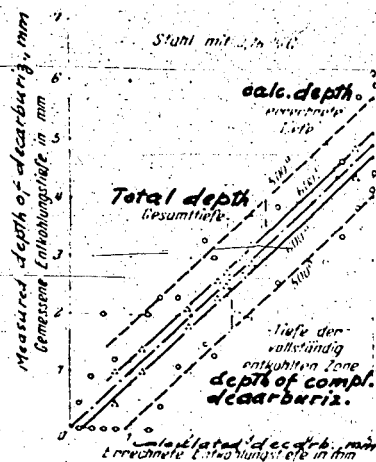(Stahl mit 0,76 % C. 10 h Versuchsdauer. Wasserstoffdruck
300 kg/cm²)

Abbildung 18
Vergleich zwischen gemessener und
errechneter Entkohlungstiefe.
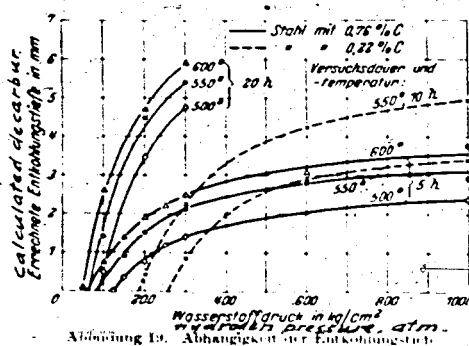Fig. 18 Comparison of measured
and calculated decarburiz.

Abbildung 19. Abhängigkeit der Entkohlungstiefe
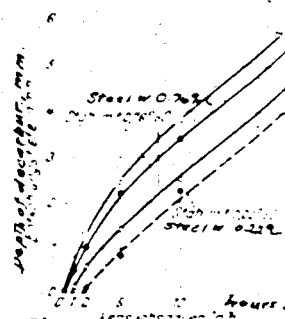vom Wasserstoffdruck.
Fig. 19 Relation between decarb. and H₂ press.

Fig. 20. effect of time on
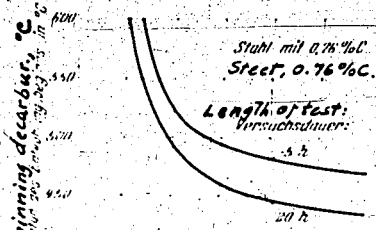decarburization with H₂
Entkohlung (Druck 300 kg/cm²)

Beginning decarbur., °C

Stahl mit 0.76 %C
Steel, 0.76 %C.

Length of test:
Versuchsdauer:

5 h
20 h

Hydrogen press., atm

Fig. 22. Decarb. temp. and H-press.
Abbildung 22. Temperatur des Ent-
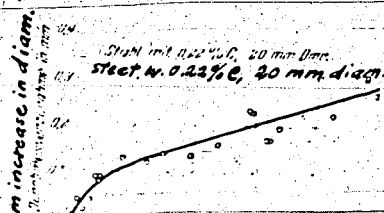kohlungsbeginns in Abhängigkeit vom
Wasserstoffdruck.

mm increase in diam.

Stahl mit 0.22 %C, 20 mm Dmr.
Steel, w. 0.22 %C, 20 mm diam.

Depth of decarburisation
Fig. 23. Increase in diameter during
Abbildung 23. Durchmesserzunahme in
Abhängigkeit von der Entkohlungstiefe.
decarburisation

Loss in weight, g
Gewichtsverlust, g

0,30
0,25
0,20
0,15
0,10
0,05

5 h, 550°, 300 kg/cm²
5 h, 600°, 700 kg/cm²

Stauchgrad in %
% of swaging

0 10 20 30 40 50

Fig. 39. Effect of cold swaging
Abbildung 39. Einfluß der
Kaltverformung auf Ent-
kohlung durch Wasserstoff.
(Stahl mit 0,76 %, C)

Wasserstoffdruck, 300 kg/cm²
Hydrogen pressure, 300 atm.

yield point, tensile str., elongation and
reduction in area (%), impact strength

yield point
tensile strength
Elongation
Reduct. in area
impact strength
C content

Versuchstemperatur in °C
300 400 500 600
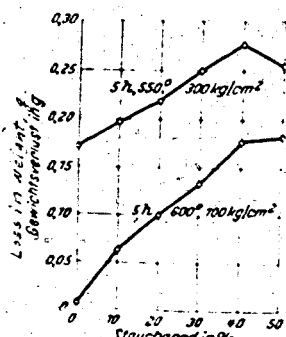
H₂-pressure,
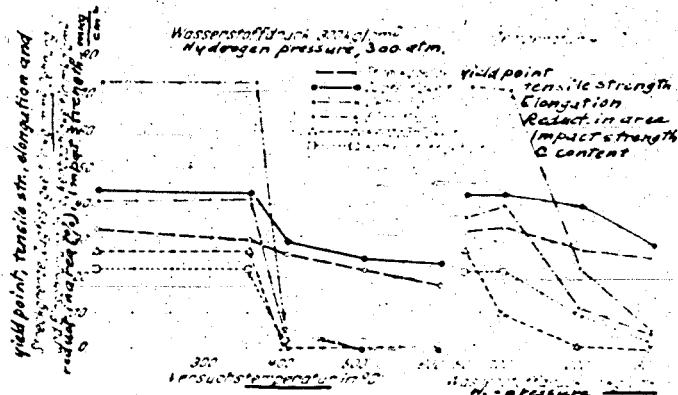
Figs. 40-41. Changes in mech. properties by H₂ attack
Abbildung 40 und 41. Änderung der Eigenschaften durch H₂ Wasserstoff.
(Stahl mit 0,11 % C)

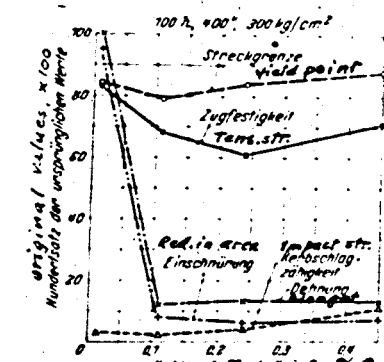original values, × 100
Hundertfache der ursprünglichen Werte

100 h, 400°, 300 kg/cm²

100
80
60
40
20

Streckgrenze
yield point

Zugfestigkeit
Tens. str.

Red. in area
Einschnürung

impact str.
Kerbschlag-
zähigkeit

Dehnung
Elong.

Kohlenstoffgehalt in % % C
0 0,1 0,2 0,3 0,4

Fig. 54. Hydrogen attack on steel with varying C content
Abbildung 54. Wasserstoffangriff in Abhängigkeit vom
Kohlenstoffgehalt des Stahles.

H₂ pressure, atm

dauer.

Steel, 0.11 %C   Steel, 0.24 %C

no effect
edge decarburis.
grain boundary
attack
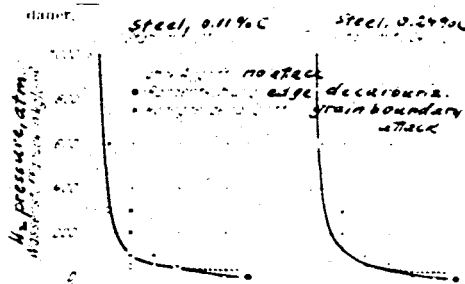
Fig. 55. Limits of stability of 2 steel samples
Abbildung 55. Beständigkeitsgrenzen zweier
Stähle. (Versuchsdauer je (100 h. test)

... IN EISEN ... K-5. PLATE 1

... ich Karl Naumann: Einwirkung von Wasserstoff unter hohem Druck auf unlegierten Stahl.

Outside view
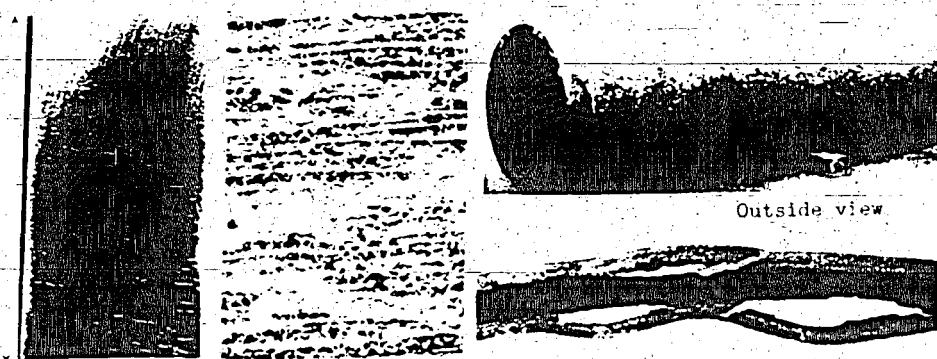
Figs. 3-4. Longitudinal section of
sheet attacked by hydrogen

Figs. 5-6. Blisters caused by
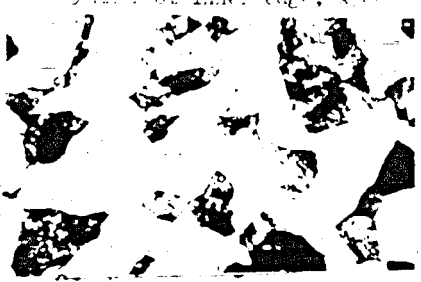hydrogen. Inner Jacket, 24 mm
thick
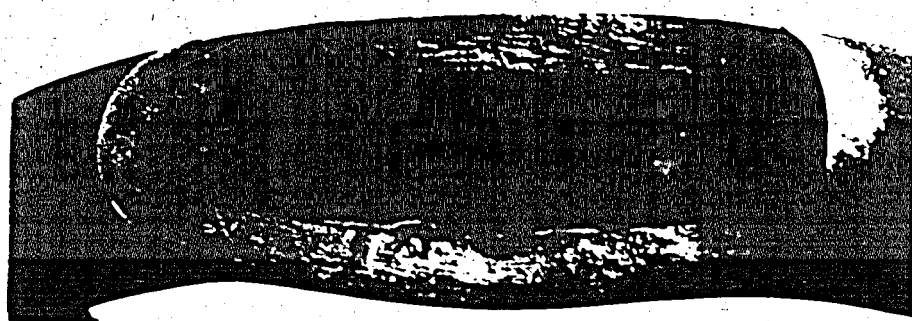
Appearance of break

... inner edge, ...

5 mm from inner edge, ...

10 mm from inner edge, x500

outer edge, x500

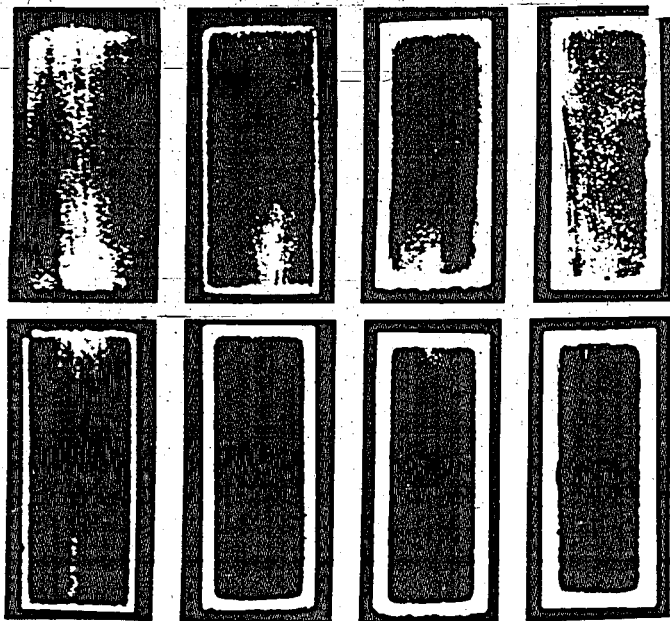Figs 7 - 11. High pressure pipeline, attacked by H_2

Fig. 24. Pieces of steel, 0.76% C, decarburized with hydrogen
(5 hour tests).
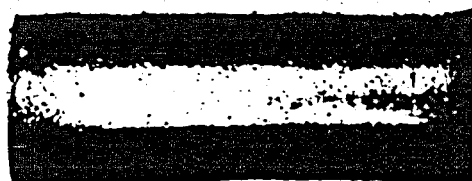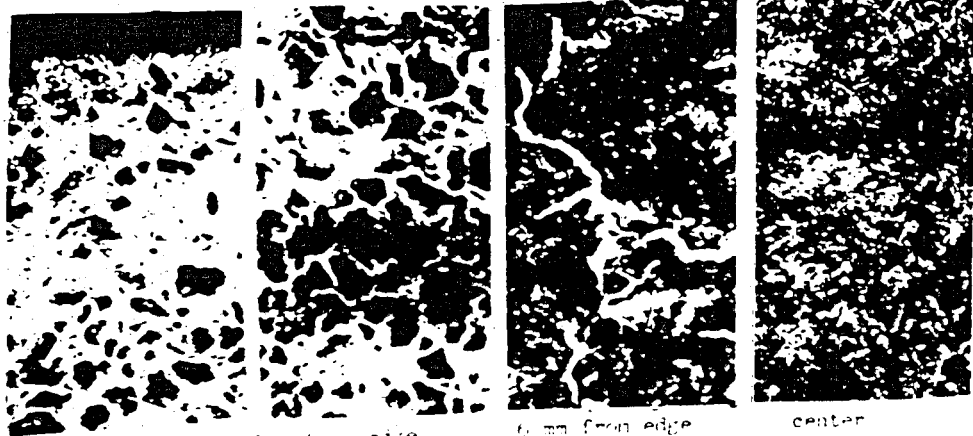
Fig. 27-30. Microstructures of a steel sample, 0.76% C, heated 10 h. to
2500° C under 1000 atm hydrogen pressure.

Edge   mm from edge   5 mm from edge
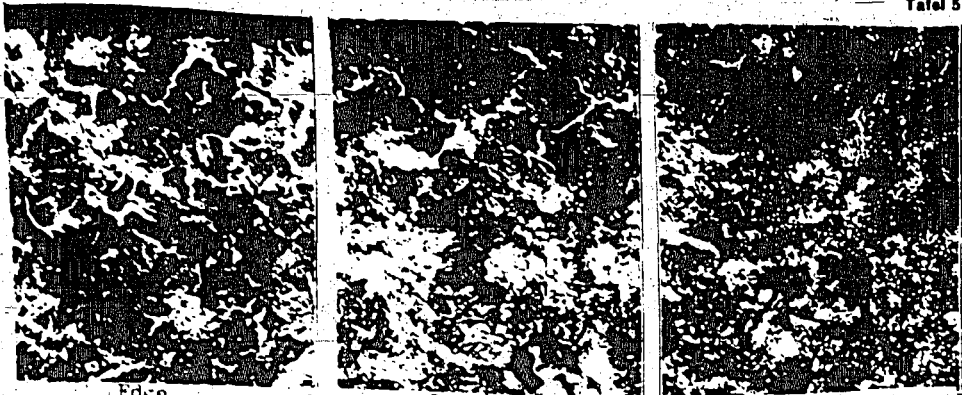
Fig. 31. Structure of steel with 0.76% C, decarburized in 50 h at 400° C under hydrogen pressure of 600 atm. (x200)

Edge   Transition zone   Center
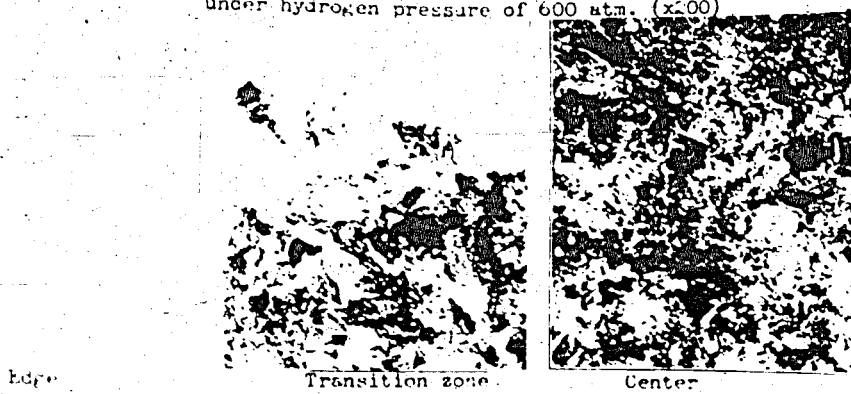
Fig. 32. Structure of steel, 0.76% C decarburized in 5 h at under hydrogen pressure of 300 atm.

Unforged   forged 4 times   forged 16 times

Etched, Oberhoffer's method
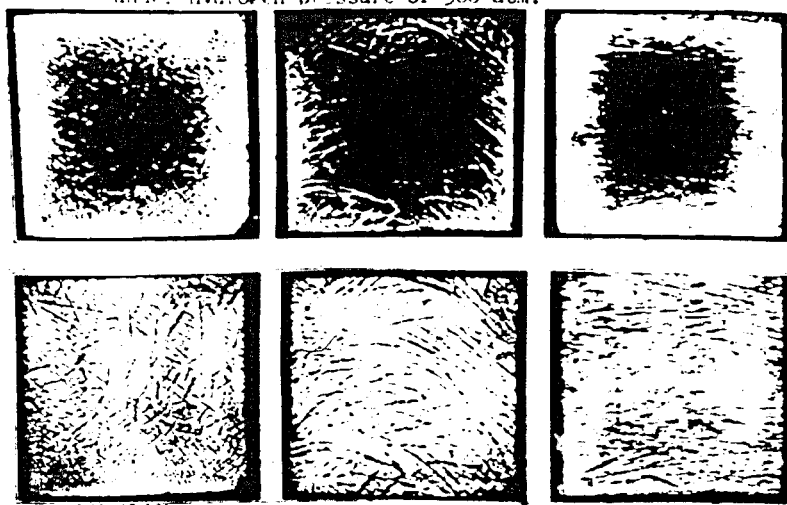
Fig. 33. Decarburized samples, varying amount of forging. (0.76% C, 20 h, 540° C, in hydrogen at 300 atm. x)

edge   3 mm from edge

Fig. 34. Hydrogen attack
on an unforged sample, 0.70%
c, 20 h., 450° C. 300 ata.

Figs. 35 and 36. Hydrogen attack on a coarse
grained sample, 0.70% C, 19 h., 450° C,

actual size

Compression
Fig. 37. Effect of cold working upon attack by hydrogen

Initial state
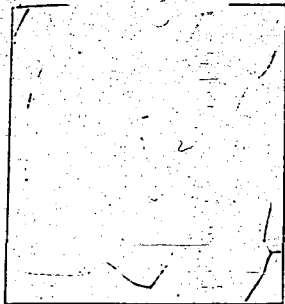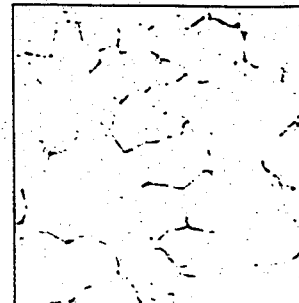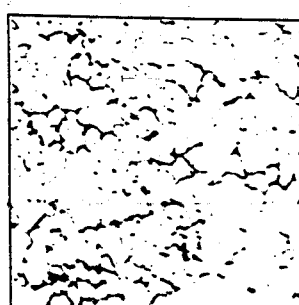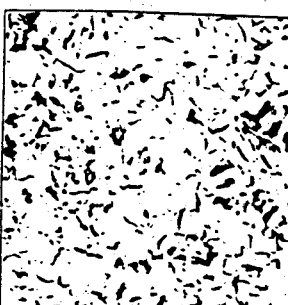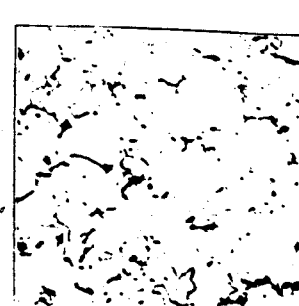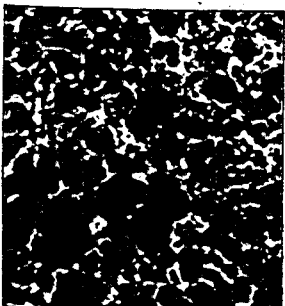
Figs. 42 - 53. Changes in the structure of unalloyed steel by hydrogen attack (x100)

THE EFFECT OF ALLOYING ADDITIONS ON THE RESISTANCE OF STEEL TO HYDROGEN UNDER HIGH PRESSURE

By F. K. Naumann, Essen

Addition of Carbide-Forming Metals: Silicon,
Nickel, Copper.
Effect of Carbide-Formers with Considerable
Solubility in Iron Carbide: Manganese,
Chromium, Tungsten, Molybdenum.
Hydrogen Resistant Chromium-Molybdenum Steels.
Hydrogen Attack and Edge Decarburization.
Comparison Between Permeability to Hydrogen
and Hydrogen Resistance of Carbon, Chro-
mium and Titanium Steels.
Effect of Other Carbide-Formers: Vanadium,
Columbium, Tantalum, Titanium, Zirconium
and Thorium.
Connection Between the Hydrogen Resistance and
the Phase Diagram of the Alloys Studied.

Highly compressed hydrogen, such as is used in the ammo-
nia synthesis and coal hydrogenation plants, attacks unalloyed
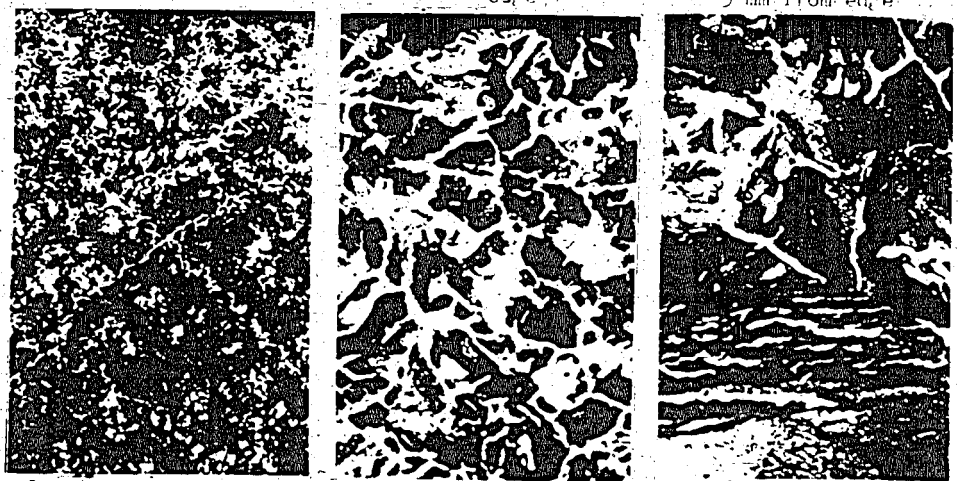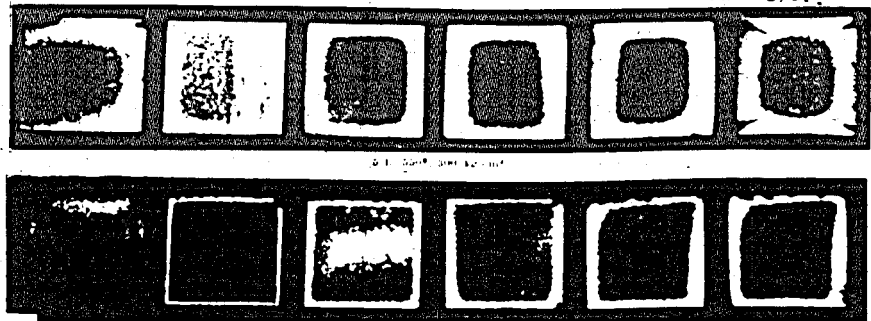steels already at low temperatures. The attack by hydrogen is a
decarburization process characterized by the formation of a gas,
methane, which is incapable of diffusion. The formation of methane
results in tensions and cracks in the steel structure, which will
cause a loss in mechanical strength and particularly in ductility.
The manifestations of the hydrogen attack as well as the effect of
pressure, temperature and time have already been discussed 1/.

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1/ Stahl und Eisen, Vol. 57, 1937, pp. 889-899.

The present report deals with tests which were intended
to develop steels by the addition of suitable alloying elements,
which will resist better the attack by hydrogen, than the unalloyed
steels. The effect of the individual alloying elements was studied
for that purpose systematically. The attack by hydrogen consists
in a decarburization, i.e. in decomposition of the carbides, and
it seemed that the addition of such materials would be most success-
ful which form more stable carbides than iron. For that reason the
tests with carbide-forming elements were particularly stressed.

Experimental

The study was started at the suggestion of B. Strauss in
1927 and carried out in the laboratories of the firm Freiderich
Krupp A.-G. in Essen. The apparatus was the same as described in
the previous article 1/. Tensile strength pieces, 6mm in diameter,
were prepared from the steels studied and 10 x 55mm test pieces for
notched bar testing with 2mm deep round notch, 2mm diameter, were
made, and exposed to the action of hydrogen in high pressure tube
of austenitic chrome-nickel steel heated from the outside. The
hydrogen was not purified. The tests extended always over 100
hours, the pressure used was usually 300 atm.

The test pieces were broken after the test. The attacked
test pieces showed a big drop in ductility; however, evaluation
by the results of impact strength determinations did not appear
as dependable as with the unalloyed steels, because in many steels
brittleness phenomena appeared without attack by hydrogen, simply

as a result of the long heating time. We have used therefore
always the reduction in area as a measure of the behavior of
steels. In doubtful cases a definite indication of difference
was furnished by the appearance of the fracture of the notched
bar samples; pieces which were attacked had a mat gray fracture,
the unattacked pieces had a clear granular or fibrous structure
of the fracture. With a strong hydrogen attack methane blisters
appeared on the surface. Furthermore the carbon content was
determined in the edge layer 1mm thick and also cross section
was prepared for the study of the structure. Whenever hydrogen
would attack the sample, it would usually extend to the center
of the test pieces, and no measurements were made of the depth
of decarburization, except for the special case of edge decar-
burization. It was instead determined qualitatively whether any
effect was observed and under what conditions of pressure and
temperature it would start.

The effect of individual alloying elements was studied by
using only simple alloyed steels in the first experiments. The
results are discussed below arranged by the alloying elements or
groups of alloying metals.

Effects of Silicon, Nickel and Copper

The first alloys studied were with additions of elements
not forming carbides, namely silicon, nickel and copper. The com-
position of the alloys used is shown in Table 1. A transformer
steel was used as a representative silicon steel, a perlitic and
austenitic nickel steel and a copper steel of the usual composition.

0322

... ... NICKEL AND COPPER SHEETS
... ... AT 300 ATM PRESSURE
(... ... ... CO ... H₂) 2/

Steel	Ni %	Cu %	Treatment	Beginning of Attack °C
... ...	...	–	Normalized	350-400
Silicon steel	...	–	Not heated	350-400
Ferritic steel	4.05	–	Annealed	350-400
Austenitic steel	0.80	–	Heated	360-400
Copper sheet	–	0.43	Normalized	350-400

... ... Individual tests will be shortly published
... ... Abt. A.

All steels were attacked at 400°, like the unalloyed
steel. The drop in ductility may be plainly seen between 350
and 400° in Fig. 1. The structure of the attacked pieces appears
like that of the unalloyed steels. The changes in structure of
the purely ferritic silicon steel and the austenitic nickel steel
are worthy of notice (Figs. 27-29 and 30-32, Plate 1). Grain
boundary cracks can be seen in both. The decarburization of sili-
con steel at high temperature manifests itself in the disappear-
ance of the carbide particles scattered among the ferritic grain,
and in the austenitic nickel steel in formation of martensite at
the grain boundaries. The resistance to hydrogen has therefore
not been increased by the addition of silicon, nickel and copper.

Effect of Manganese

The effect of manganese was determined on three steels
with 1.57, 2.26 and 4.50% Mn and with a low carbon content (Table
2 and Fig. 2). The steel with 1.57 manganese was already attacked
at 400°, and was therefore not superior, or at least not markedly
superior than the unalloyed steel. On the other hand the two
higher alloy steels showed improved resistance.

Unlike the first studied elements, manganese forms a stable
carbide Mn_3C with carbon. It is, however, not to be assumed that
this carbide exists by itself in the manganese steels; we must
assume that as a result of identity of structures, the carbides
Mn_3C and Fe_3C are to a considerable extent mutually soluble [3].

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[3] E. Houdremont, "Einfuehrung in die Sonderstahlkunde", Berlin, 1935.

The reason for the somewhat improved hydrogen resistance of the manganese steels must be found in the higher resistance of these mixed carbides.

Effect of Chromium

A series of steels with 0.1% C and increasing chromium content from 1 - 5%, as well as a series of steels with 3% Cr and increasing carbon content from 0.1 - 0.7% were melted in induction furnaces of 50 kg capacity. (Table 2). All steels were annealed.

Table 2

STABILITY OF MANGANESE, CHROMIUM, TUNGSTEN AND MOLYBDENUM
STEEL AGAINST HYDROGEN AT 300 ATM PRESSURE
(100 HOUR TEST)

C %	Si %	Mn %	Cr %	W %	Mo %	Treatment	Beginning of Attack °C
0.14	0.33	1.57	-	-	-	Annealed	350-400
0.19	0.42	2.25	-	-	-	Annealed	400-450
0.09	0.18	4.50	-	-	-	Annealed	400-500
0.10	0.36	0.54	1.02	-	-	Annealed	400-450
0.10	0.38	0.51	1.97	-	-	Annealed	450-500
0.10	0.18	0.46	3.11	-	-	Annealed	600 1/
0.32	0.22	0.41	3.00	-	-	Annealed	500-600
0.50	0.27	0.48	2.90	-	-	Annealed	450-500
0.07	0.29	0.66	2.90	-	-	Annealed	450-500
0.10	0.22	0.51	3.90	-	-	Annealed	600 2/
0.11	0.29	0.55	4.95	-	-	Annealed	600 3/
0.11	0.38	0.5	-	0.99	-	Normalized / Annealed	450-500 / 450-500
0.10	0.38	0.55	-	2.08	-	Normalized / Annealed	500-600 / 500-600
0.11	0.26	0.52	-	-	0.63	Normalized / Annealed	450-500 / 500-600
0.13	0.23	0.52	-	-	1.22	Normalized / Annealed	500-600 / 500-600
0.12	0.17	0.40	-	-	1.82	Normalized / Annealed	500-600 / 500-600

1/ Edge decarburization 0.1 mm at 600°.
2/ Edge decarburization of 0.05 mm at 600°.
3/ Edge decarburization of 0.03 mm at 600°.

Among the steels with 0.1% C, the steel with 1% Cr was stable up to 400° (Fig. 3), and therefore already behaved better than an unalloyed steel. The stability increased to 450° with a steel containing 2% Cr. The steels with 3, 4 and 5% Cr were not attacked by hydrogen even at 600° and showed only a slight edge decarburization without any loss in ductility, which should not be considered the result of a hydrogen attack, as will be discussed later. In the series of alloys with 3% Cr and increasing carbon content, the steel with 0.1% C was stable up to 600°C. The steel with 0.32% C was already strongly attacked at 600°C, but was as yet undamaged at 500°C. The stability was lowered to 450°C in the steels containing 0.50 and 0.67% C.

The hydrogen resistance is therefore considerably improved by the addition of chromium and reduced by increasing carbon content with the same amount of the alloying metal. These results are in complete agreement with the results by J. B. Vanick, W. W. de Sveshnikoff and J. G. Thompson [4] in their investigation of steels for ammonia synthesis. M. P. Inglis and W. Andrews [5] and others [6] have found a strong increase in resistance to hydrogen with increasing chromium content. Contradicting this are the results by W. Baukloh and collaborators [7]. They stated that chromium increased decarburization resistance only up to a certain most

4/ Techn. Pap. Bur. Stand., Vol. 22, 1927, pp. 199-233.
5/ J. Iron Steel Inst., Vol. 128, 1933, pp. 383-418.
6/ L. Jacqué: C. R. Paris, Vol. 203, 1936, pp. 936-938, ... J.
     Serjant and T. H. Middleham, Trans. Chem. Eng. World Power
     Conf., London, 1936, Vol. 1, pp. 66-110.
7/ W. Baukloh, W. v Kronenfels and H. Guthmann, Stahl und Eisen,
     Vol. 54, 1934, pp. 1334-1336; W. B. Giesserei, Vol. 22, 1935,
     pp. 406-409; Baukloh and H. Guthmann, Archs. Eisenhüttenw,
     Vol. 9, 1935/36, pp. 201-202.

favorable proportion of the alloying metal (about 0.9% Cr) and
reduced it again with higher additions, and that with increasing
carbon content the stability of the chromium steels increase 8/.
As a result Baukloh failed to discover neither in the chromium
steels nor in the other alloys studied by him any connection
between the decarburization behavior and the phase diagram; he
does not ascribe deciding influence upon the decarburization
stability to the stability of the carbides formed but to the per-
meability of the alloys by hydrogen.

      We will investigate below whether any relationship exists
between the hydrogen resistance of chromium steels and their por-
tion in the 3-component system, iron-chromium-carbon. Fig. 4
shows a horizontal cross section at 20°C through the iron corner
of this system, according to W. Tofaute, C. Kuttner and A. Butt-
ing 9/. They have found there a pure alpha region and three vari-
able areas which differed in the form of the carbides present. In
the first area only iron carbide is present, which dissolves in-
creasing amounts of chromium as the chromium content increases;
chromium carbide Cr_7C_3 exists in the second area, in addition to
the iron carbide, and it acts as a solvent for the iron; in the
third area exists only the special carbide containing iron car-
bide. The alloys investigated have been plotted in the diagram
and we may note up to what temperature they are resistant to hydro-
gen under 300 atm pressure. Considering first the alloys with 0.1% C,

8/ Baukloh and H. Guthmann, Z. Metallkde, Vol. 28, 1936, pp. 36-40.
9/ Arch. Eisenhutten., Vol. 9, 1935-36, pp. 607-617.

we may see that the steels with 1.02 and 1.97% Cr, show a slight improvement in their hydrogen stability, and they still contain iron carbide, while the most stable steels with 3.11-4.95% Cr are already in the area of the special carbide, or more precisely where the iron carbide is disappearing. The high stability of alloys with over 3% Cr is therefore doubtlessly to be attributed to the great chemical stability of the chromium carbide, while the steady increase in the stability before the formation of the special carbide is to be explained by the increasing solution of chromium in the iron carbide. Conversely, the lower stability of the carbon-rich alloys is caused by the reappearance of iron carbide in them, the chromium content of which is decreased with increasing carbon content. In contradiction to the results of W. Baukloh, there is a clear connection between the hydrogen stability of chromium steels and the carbide phases present in the 3-component diagram iron-chromium-carbon.

Effect of Tungsten and Molybdenum

The effect of tungsten and molybdenum was studied on two steels with 1 and 2% W and three steels with 0.6, 1.2 and 1.8% Mo (Table 2). The steels were tempered in water; in addition, one series was always annealed at 950° and slowly cooled in the furnace to overcome the harmful influence of long heating upon the notched bar strength. Fig. 5 shows the connection between the reduction of area of tempered samples and the temperature of the test.

The steel with 1% W was still stable at 450° and was only attacked at 500°C, behaving thus exactly like a steel with 2% Cr.

The addition of 2% W increased the stability to over 500°C. The annealed and tempered samples behaved alike.

The annealed sample with 0.6% Mo was attacked at 500°C, while the tempered was yet undamaged at this temperature. The two steels with 1.2 and 1.8% Mo were stable at 500°C, but both were attacked at 600°. Molybdenum improves the hydrogen resistance still more than tungsten. The effect is particularly great with small additions.

Tungsten and molybdenum also belong to the carbide forming elements. The structure of the iron-tungsten-carbon and iron-molybdenum-carbon alloys has not yet been fully explained, but it may be assumed that both elements present in small amounts form no special carbides, but dissolve in appreciable amounts in the iron carbide, like chromium and manganese 3/. The effect of tungsten and molybdenum might accordingly depend on the stabilizing action upon the iron carbide. H. L. Maxwell 10/ has reached the same conclusion and also found that the molybdenum and tungsten alloy steels were particularly well suited to meet the requirements of the ammonia synthesis.

It must be mentioned in this connection that pure powdered tungsten carbide, available from the preparation of the high speed tool steel, was not decomposed after 100 hours of heating in hydrogen at 600 atm and 600°C, and had the composition WC with 6.1% C.

Hydrogen Resistant Chrome-molybdenum Steels

According to the above, a combination of chromium + molybdenum should furnish a particularly suitable basis for the compounding

10/Trans. Amer. Soc. Met., Vol. 24, 1936, pp. 213-224.

of hydrogen resistant steels, the more so that the chrome-molybde-
num steels have a good hot strength and would be best suited for
the especially strenuous mechanical requirements of the high
pressure installations. The firm, Fried. Krupp A.-G., has brought
out a series of hydrogen resistant special steels on this alloy
basis, and of these steels, those with 3 and 6% Cr have been widely
used for years in the chemical industry 11/. Figures 6-10 show the
stability diagrams for a series of chrome-molybdenum alloys of this
kind. They deal with alloys containing 1, 2, 3 and 6% Cr and about
0.4% Mo. The carbon content is 0.10-0.15%. Added to this is a
steel with 3% Cr and 0.25% C, and for comparison an unalloyed steel
with 0.11% C. Hydrogen pressure was systematically changed in these
tests. The tests lasted 100 hours. The experimental results are
valid only for that length of heating.

As before, in the unalloyed steels decarburization may
assume two different forms, one of them the result of the hydrogen
attack, the other as edge decarburization. The edge decarburiza-
tion differs from the hydrogen attack in that it leaves no struc-
tural disturbances and does not accordingly affect the ductility
of the test pieces. Figs. 6-10 show the hydrogen attack in solid
lines and the edge decarburization in broken lines. Both curves
apparently proceed entirely independently from each other. In the
unalloyed steels the hydrogen attack begins at 350°C at pressures
of 50 atm, while in the chrome-molybdenum steels with 1% Cr only
at 200 atm and 600°C and in the steel with 2% Cr only at 300 atm
and 600°C. Only the steel with the higher carbon content was

11/ M. Pier, Chem. Fabrik., Vol. 8, 1935, pp. 45-54.

attacked among steels with 3% Cr in this range, and only at 300
atm pressure and 700°C, while the carbon-poorer steels were
entirely unattacked. Steel with 6% Cr was not at all attacked.
While the hydrogen attack requires a high pressure, the pressure
has to be the higher the richer the alloys are in chromium, but
the edge decarburization of all the steels starts already at
atmospheric pressure, in the unalloyed steel at 650°, in steel
with 1 and 2% Cr at 700°C and with a steel at 3% Cr at 750°C, and
in the steel with 6% Cr at 800°C. With increasing pressures the
edge decarburization becomes displaced towards lower temperatures.

The hydrogen stability increases with increasing chromium
content to a much greater extent than the resistance to edge decar-
burization, as can be seen from the comparison of curves in Figs.
11 and 12. The hydrogen attack is therefore the result of entirely
different conditions than the edge decarburization, in particular
since it is much more strongly dependent on the hydrogen pressure
and the chromium content of the steel.

The progress of the edge decarburization depends evidently
upon other factors than the hydrogen attack in its relationship to
temperature and pressure. The hydrogen attack progresses immediately
very deeply into the inside of the sample as soon as some limiting
temperature and a definite limiting pressure have been exceeded,
while the depth of the edge decarburization progresses relatively
slowly and steadily with increasing temperature and increasing
pressure as shown in Figs. 13 and 14 for the two steels with 3% Cr.
The curves are fundamentally different than for the hydrogen attack,

especially for the temperature relationship (compare curves, Fig.
21 in the earlier work 1/) and similar to the curves determined by
W. Baukloh and H. Guthmann 8/ in their decarburization studies. It
is remarkable, moreover, that in this range steels with the higher
carbon content are decarburized more slowly than those with less
carbon. This again is different with the hydrogen attacks, as may
be seen on the steel with 0.25% C in the strong increase of the
depth of decarburization between 650 and 700° and between 200 and
500 atm pressure. Fig. 33, Plate 1, shows that the decarburization
proceeds in the previously observed branched form down to the middle
of the test piece. The uniform and stronger decarburization with
less loosening up of the structure occurs in the edge zone as a
result of a combination of surface action of the edge decarburiza-
tion changes with the progressive hydrogen attack (Fig. 34, Plate 1).

The differences in the formation and forms of manifesta-
tions of the two kinds of decarburization have been explained pre-
viously 1/ by saying that the edge decarburization was not the result
of the action of hydrogen but of the water vapors present in the
hydrogen used. This was caused by oxide formation in the struc-
ture of the test pieces with edge decarburization. Figs. 35 and 36
(Plate 2) give the edge structure of such a test piece from chrome-
molybdenum steel with 6% Cr. This viewpoint is confirmed by a num-
ber of investigators, who show that very dry hydrogen under atmos-
pheric pressure does not at all decarburize, or only very slowly
at the low temperatures as used in these tests, while moist hydro-
gen decarburizes very strongly.

The following decarburization tests permitted drawing
the same conclusion: two square rods with 10mm edge from unalloyed
steel with 0.11% C and the 3% chrome-molybdenum steel with 0.10% C
were heated for 100 hours in hydrogen at atmospheric pressure to
750°C, with the hydrogen in one case carefully purified and dried,
and in the other one passed through a tube with water at 80°C. The
test piece of unalloyed steel was decarburized to the center in
moist hydrogen, and the test piece from the chrome-molybdenum steel
was completely decarburized to a depth of 1.2mm, while the pieces
heated in dry hydrogen had a decarburization extending only 0.07
and 0.03mm in depth. Figs. 37-40 (Table 2) show sections of the
chrome-molybdenum steel test pieces. The samples decarburized in
moist hydrogen show distinctly the formation of fine oxides in the
edge zone consisting of columnar ferrite crystals, a structure
which has been found by J. E. Stead 12/ only in decarburization with
oxidizing agents, and such oxides can also be recognized in the other
test pieces, which leads one to conclude that even in those cases
the slight decarburization was caused by an incomplete elimination
of traces of water vapors.

The small depth of the edge decarburization is therefore
probably caused by the slow diffusion of oxygen, and the absence of
changes in the decarburized structure by the formation during the
decarburization reaction of a gas capable of diffusion, namely car-
bon monoxide. The solid curves in the Figs. 6-10 show, in agreement

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12/ J. Iron Steel Inst., Vol. 53, 1898, pp. 145-205.

with this conception, the limiting conditions under which the
hydrogen attack begins, and the broken lines the conditions in
which the oxygen decarburization or diffusion starts in. The
course of the broken curves could naturally not be determined
experimentally with the unalloyed steel, because the edge decar-
burization to be expected at higher temperatures is covered up in
the region of higher pressures by the attack with hydrogen, and
was drawn approximately parallel to the other broken lines from
the few known points at atmospheric pressure.

It is very difficult, according to experience, to remove
the last traces of moisture from hydrogen, and one must always
count on complications resulting from oxygen in the decarburization
tests with hydrogen. It is impossible to follow up the decarburi-
zation process purely analytically and distinguish between the
action of hydrogen and of oxygen. Results obtained in decarburi-
zation tests with filings are to be treated with care. It s pre-
ferable to use compact test pieces which can be investigated metallo-
graphically or, better still, mechanically.

Such a series of chrome-molybdenum steels, occasionally
with addition of other alloying elements which improve th mechani-
cal properties, permit meeting the demands of different hydro-
genation processes upon the structural material of the containers.
It must be mentioned, in addition, that these steels possess an
increased resistance against the sulfur-containing oils and the
hydrogen sulfide produced from the coal. In special cases, there
are available high alloy steels of the non-rusting and heat-resis-
tant kind. Thus, e.g. an austenitic chrome-nickel steel with the

greatest creep strength can be used for reactors in the ammonia synthesis by the Claude method where both mechanical and chemical strains are particularly strong.

Hydrogen Diffusion Tests

It has already been mentioned, that the opinion has been expressed that the capacity of resistance of iron alloys against hydrogen decarburization was determined by the degree of their hydrogen permeability. It has already been stated that this does not apply to all the chromium steels. Those connections were more fully clarified by preparing a series of unalloyed and chrome alloyed steels of a composition shown in Table 3 and using them in diffusion tests.

Table 3

THE COMPOSITION OF THE STEELS USED FOR
HYDROGEN DIFFUSION TESTS

%C	% Si	% Mn	% Cr	% Mo	% Ti
0.10	Trace	0.48	n.d. *	n.d.	n.d.
0.34	0.33	0.55	n.d.	n.d.	n.d.
0.64	0.14	0.56	n.d.	n.d.	n.d.
0.09	0.30	0.68	n.d.	n.d.	0.52
0.13	0.32	0.33	0.87	0.51	n.d.
0.11	0.18	0.32	3.02	0.35	n.d.
0.19	0.17	0.33	5.60	0.40	n.d.
0.11	0.24	0.40	13.30	n.d.	n.d.
0.11	0.70	0.40	17.40	n.d.	n.d.

* not determined

A low alloy titanium steel which should have been expected
to have the same permeability as the unalloyed steel was added to
that series, but it had, as subsequently found, a high hydrogen
resistance, permitting the study of permeability of an unalloyed
steel at higher temperatures and pressures, than those at which
unalloyed steels would be suitable as a result of the attack with
hydrogen.

The experimental arrangement was as shown in Fig. 15. A
small plate of the material tested, originally 20mm thick, was
welded into a tube of non-rusting steel cut into two pieces. After
welding, the piece was heat treated (the unalloyed steel and the
titanium steel were normalized, the chrome-molybdenum steels with
1.5 and 6.5 Cr were tempered in the air and the steels with 13 and
17% Cr were soft annealed) and the drilling then was continued
from both sides, until a separating wall of 5mm thickness was left.
The drillings were then carefully cleaned and defatted. The tube
was introduced into an electrically heated tubular furnace; the
temperature was measured by an iron - constantan thermocouple intro-
duced close to the small plate. Hydrogen was compressed in 1/2 of
the tube, the second half was evacuated. The introduction of hydro-
gen was so timed that the small plate could become saturated with
hydrogen before the beginning of measurements. The test lasted 12
hours; during the test the evacuated side was evacuated every 1/2
hour. The gas was collected, measured and analyzed, in order to be
sure to consist of nothing but hydrogen, and not of mixtures caused
by leaks or by decarburization reactions. The small plate was sepa-
rated after the conclusion of each series of tests, accurately

measured and studied metallographically. The small variations
in the wall thickness and area were taken into consideration during
the recalculation to mls/cm^2, h.

The results are shown in Fig. 16 for a pressure of 300 atm
and also for 1,000 atm for the unalloyed steel with 0.10% C, in
relationship to the temperature. The logarithms of the amount of
hydrogen diffused were plotted against the reciprocals of the abso-
lute temperature. The exponential temperature relationship of
diffusion 13/ should in this case be expressed in straight lines.
Such was actually the case; only at lower temperatures, below 200°C
lower values were occasionally found than corresponded to the straight
lines. Fig. 17 gives the values found for unalloyed steel and for
the titanium steel in relationship to the hydrogen pressure. The
amount diffused increases linearly with the square root of the
pressure, which applies also, in contradiction to the results of
W. Baukloh and H. Guthmann 8/, to pressure in excess of 150 atm.
The only deviation from the $\sqrt{p}$ consists in that the lines do not
pass through the 0 point. G. Borelius 13/ has, however, observed
similar deviations at lower temperatures.

Fig. 30 shows that the hydrogen permeability decreases with
increasing chromium content; the reduction in the permeability is
not, however, in any way related to the increase in stability caused
by the chromium content. E.g. the unalloyed steel with 0.1% C under
300 atm pressure at the limit of its stability of 360° permits 1 ml

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13/ G. Borelius and S. Lindblom Ann. Phys., Vol. 82, 1927, pp. 201-
226; G. Borelius, Ann. Phys., Vol. 83, 1927, pp. 121-136; G.
Borelius, Metallwirtsch, Vol. 8, 1929, pp. 105-108.

of hydrogen to pass through a unit surface/hour. The same amount
diffuses through steel with 1% Cr at 350° and through steel with
3% Cr at 410°; yet the first steel, with 1% Cr, is resistant to
hydrogen to 560° and the one with 3% to 700°. To put it differ-
ently: steel with 1% Cr at 550° is still resistant to hydrogen
although it transmits more than three times the amount transmitted
by the unalloyed steel, and the steel with 3% at 700°C is still
resistant although it already transmits five times the amount of
hydrogen transmitted by the unalloyed steel at the limit of its
stability. The permeability to hydrogen of the unalloyed steel
is reduced with increasing carbon content (Fig. 17, 300° curve)
without raising its stability as has been shown previously 1/.
Unalloyed steel with 0.64% C has about the same permeability as
the 3% chrome-molybdenum steel, and yet the latter is stable about
700°C, while the former is already attacked at 400°.

As will be shown later, titanium steel has a high perme-
ability and transmits exactly the same amount of hydrogen as the
unalloyed steels of the same carbon content. This juxtaposition
shows perfectly clearly that the hydrogen resistance of steels does
not depend on their permeability to hydrogen but on the stability
of their carbides.

Effect of Vanadium

It must therefore appear promising to add elements to
steel which form even in low concentrations more stable special
carbides than the carbide-formers discussed heretofore. Such is
the case with vanadium and titanium. Tests with chrome-vanadium

steels of similar amount of alloying have, however, not possessed
the expected properties. Such steels behaved even appreciably
less well than the highly alloyed chrome-molybdenum steels. J. S.
Vanick, W. W. de Sveshnikoff and J. G. Thompson 4/ have found no
appreciable improvement in hydrogen resistance by the addition of
vanadium in their tests with chrome-vanadium steels. This, at
first unexpected behavior, was explained through the following
tests with pure vanadium steels in which both the vanadium and the
carbon content were changed systematically. The composition of the
alloys used (made in 50 kg castings in the arc furnace) are shown
in Table 4. All steels were normalized and tested after tempering.
The hydrogen pressure was 300 atm and the experiments lasted 100
hours and only the temperature was altered. Changes of the reduc-
tion in area in relationship to the experimental temperature are
shown again in Figs. 18 and 19, as a criterion for the behavior
of these steels.

Table 4

THE STABILITY OF VANADIUM, COLUMBIUM AND TITANIUM STEEL
AGAINST HYDROGEN AT 300 ATM-PRESSURE (100 HOUR TEST)

%C	%Si	%Mn	%V	%Cb	%Ta			Treatment	Beginning of Attack °C
0.12	0.35	0.42	0.26			V:C =	2.2	Normalized Tempered	400-500 400-450
0.13	0.40	0.45	0.53	-	-	V:C =	4.0	Normalized Tempered	400-500 400-450
0.10	0.70	0.58	0.59	-	-	V:C =	5.9	Normalized Tempered	400-500 >600
0.12	0.31	0.51	0.79	-	-	V:C =	6.6	Normalized Tempered	>600 >600
0.10	0.34	0.43	0.76	-	-	V:C =	7.6	Normalized Tempered	>600 >600

(Table 4 cont'd.)

%C	%Si	%Mn	%V	%Cb	%Ta			Treatment	Beginning of Attack °C
0.10	0.28	0.45	0.99	-	-	V:C =	9.9	Normalized	>600
								Tempered	>600
0.05	0.11	0.28	0.55	-	-	V:C =	11.0	Normalized	>600
								Tempered	>600
0.19	0.42	0.46	0.79	-	-	V:C =	4.2	Normalized	400-500
								Tempered	400-450
0.19	0.44	0.46	1.52	-	-	V:C =	8.0	Normalized	>600
								Tempered	>600
0.30	0.25	0.54	0.60	-	-	V:C =	2.0	Normalized	400-500
								Tempered	400-450
0.36	0.27	0.43	1.52	-	-	V:C =	4.2	Normalized	400-500
								Tempered	400-450
0.28	0.34	0.52	1.82	-	-	V:C =	6.5	Normalized	>600
								Tempered	>600
0.12	0.33	0.55	-	0.10	0.17	Cb:C =	3.3	Untreated	400-500
0.10	0.22	0.45	-	0.87	0.09	Cb:C =	8.7	Untreated	>600
0.11	0.26	0.49	-	0.04	0.94	Ta:C =	8.5	Untreated	350-400
0.09	0.25	0.43	-	0.04	1.70	Ta:C =	18.9	Untreated	>600

Among the steels with 0.1% C, the steel with 0.28% V was
stable at 400°C and was only attacked at 450°. The steel with
0.52% V behaved no better. The steel with 0.59% V showed some in-
dications of attack in the annealed state at 500°C still, but was
stable in the tempered state at 600°C. The steels with 0.78, 0.79
and 0.99% V, as well as steels with 0.05% C and 0.55% V are stable
up to 600°C even in the annealed state. Of the steels with 0.20% C,
the one with 0.79% V was already attacked at 450°, while the steel
with 1.52% V remained stable even at 600°. In the series with
0.30% C, the two steels with 0.60 and 1.52% V were already attacked

at 450°; the steel with 1.82% V remained, however, unattacked even at 600°.

It is therefore characteristic of the behavior of vanadium steels, that the stability does not rise uniformly in the beginning, as it does with chromium, tungsten and molybdenum steels, but increases suddenly only with a certain amount of the alloying metal. This vanadium content is about 0.60% V with a C content of 0.10%, between 0.79% V and 1.52% V for 0.20% C, and between 1.52% and 1.82% V for 0.30% C, i.e. it increases with increasing carbon content in a certain definite relationship with it.

Such behavior of vanadium steels is explained by its structure. According to E. Maurer [14], vanadium forms a special carbide in steel, V_4C_3. According to H. Hougardy [15] this carbide is formed immediately in the steel, without previous solution of vanadium in the iron carbide, so that vanadium steels contain at first both pure carbides Fe_3C and V_4C_3 side by side, until the vanadium content is high enough to combine with all the carbon. Such is the case when V:C (% by weight) are in a proportion of 5.7:1. Steels containing more vanadium than 5.7 times the carbon content consist accordingly at room temperature only of alpha iron and of vanadium carbide. The hydrogen stability of an alloy in which two carbides are present will have the stability of the least stable carbide, which is the iron carbide according to Hougardy, and the stability will not increase until the iron carbide

14/ Stahl und Eisen, Vol. 45, 1925, pp. 1629-1632.
15/ Arch. Eisenhuttenw. Vol. 4, 1930/31, pp. 497-503.

has disappeared. Vanadium steels in which the proportion $V:C < 5.7$ can therefore not resist hydrogen any better than unalloyed steel with the corresponding small carbon content. On the other hand, the vanadium carbide is very stable and one might expect a high stability in alloys where the $V:C \geq 5.7$.

This is almost exactly what does happen as shown in a comparison of experimental results with V:C values in Table 1. Only the steel with 0.10% C and 0.59% V, which is close to the limiting value, forms an exception, because it still is attacked by hydrogen in the annealed state. Nor do even the unstable steels behave quite as poorly as the unalloyed steels, but are always stable to within a temperature of 50° higher than the latter. We may conclude therefore that there remains a slight solubility of vanadium in iron carbide. In agreement with this, the phase diagram of the iron-vanadium-carbon system constructed by R. Vogel and E. Martin [16] and M. Oya [17] shows a region of coexistence of alpha iron + Fe_3C.

P. Wever, A. Rose and H. Eggers [18] showed that the limits of this region were lower than given by Vogel and Martin. The tests described above seem to indicate that the value of 0.2 to 0.3% V given by Wever, Rose and Eggers is still too high. E. Houdremont, H. Bennek and H. Schrader [19] showed that on annealing tempered steels with 0.1% V to 500 and 700°C the hardness drop became slower which was a result of the separation of vanadium carbide. Fig. 20

16/ Ibid. Vol. 4, 1930/31, pp. 487-495.
17/ Sci. Rep. Tohoku Univ., Vol. 19, 1930, pp. 331-364, and 419-472.
18/ Mitt. K.-Wilh-Inst. Eisenf. Vol. 18, 1936, pp. 239-246.
19/ The Arch. Eisenhuttenw, Vol. 6, 1932/33, pp. 24-34.

shows a horizontal section at room temperature through the iron
corner of the phase diagram of the system iron-vanadium-carbon,
where the boundary of the alpha iron + Fe_3C is assumed to be with
0.10% V. It shows that all the unstable vanadium steels, includ-
ing the steel with 0.10% and 0.59% V, are in the area of alpha iron +
Fe_3C + V_4C_3 and all the stable steels in the area alpha iron + V_4C_3.

The different behavior of the two carbides can be definitely
proven in the structure of the annealed samples. The unstable steels
contain iron carbide in the form of perlite, side by side with the
finely dispersed vanadium carbide (Fig. 41, Plate 3). The perlite
disappears completely when heating in hydrogen, while the vanadium
carbide remains (Fig. 43). On the other hand, the structure of the
stable steels is free from perlite (Fig. 42) and remains unchanged
after heating in hydrogen (Fig. 44).

The Effect of Columbium and Tantalum

One may expect that the elements Cb and Ta, which are
closely related to vanadium behave similarly to the latter. To
prove this, two samples each of Cb and Ta steels of the composition
shown in Table 4 have been prepared. The alloys were made of such
a composition that assuming the existence of the carbides CbC and
TaC, one of the steels would be in the area of iron carbide + the
special carbide and the other in the area with the pure special
carbide (Cb:C $\sim$ 8 and Ta:C $\sim$ 15). The samples were not heat treated.

The steel with 0.40% Cb was again stable up to 400°C (Fig.
21), the steel with 0.94% Ta was only stable up to 350°C like an
unalloyed steel. The tantalum doesn't seem to dissolve at all in

the iron carbide. The highly alloyed steels were both attacked
at 600°C. The structure (Figs. 45-48, Plate 3) shows the lower
steels to contain the special carbides as well as perlite which is
eliminated by the action of hydrogen, while the higher alloyed con-
tain only the resistant special carbides. The conditions are there-
fore exactly the same as with vanadium; but columbium and tantalum
have higher atomic weights and require correspondingly higher addi-
tions to combine with the carbon.

Effect of Titanium, Zirconium and Thorium

Titanium and the two elements closely related to it, zir-
conium and thorium, are also strong carbide-formers. Titanium
steels have been again investigated. Table 5 gives the composition
of the steels studied (25-50 kg castings). They are arranged in
four series with 0.1, 0.2, 0.4 and 0.8% C. The melts were in general
made with alumino-thermally reduced ferro-titanium and for that
reason contained some aluminum. Only the steel with 0.10% C and
0.50% Ti were made with pure titaniummetal and is therefore alumi-
num free. All steels, excepting those with 0.8% C which was soft
annealed, were tested in the forged condition; some of the steels
with 0.1% C (Table 5) have been tempered.

Table 5 and Fig. 22 show that steels with 0.1% C and 0.11
and 0.26% Ti are only stable to 400°, while with 0.42% and over of
titanium are stable to above 600°, which refers to the untreated
as well as the tempered samples. With steels with 0.20% C the
sudden change in stability occurred between 0.61 and 1.04% Ti, with
0.35% C above 1.09% Ti and with 0.80% C only between 1.59 and 3.70% Ti.

Table 5

STABILITY AGAINST HYDROGEN AT 300 ATM PRESSURE OF TITANIUM, ZIRCONIUM AND THORIUM STEELS (100 HOUR TEST)

% C	% Si	% Mn	% Al	% Ti	% Zr	% Th		Treatment	Beginning of Attack °C
0.12	0.30	0.60	0.04	0.11	-	-	Ti:C = 0.9	Untreated	400-500
0.11	0.45	0.62	0.08	0.26	-	-	Ti:C = 2.4	Untreated	400-500
0.09	0.23	0.50	0.13	0.42	-	-	Ti:C = 4.7	Untreated	>600
								Tempered	>600
0.10	0.28	0.47	0.00	0.60	-	-	Ti:C = 6.0	Untreated	>600
								Tempered	>600
0.10	0.31	0.63	0.19	0.33	-	-	Ti:C = 9.8	Untreated	>600
								Tempered	>600
0.24	0.19	0.68	0.13	0.57	-	-	Ti:C = 2.4	Untreated	400-500
0.20	0.46	0.72	0.17	0.61	-	-	Ti:C = 3.1	Untreated	400-500
0.20	0.37	0.64	0.22	1.04	-	-	Ti:C = 5.2	Untreated	>600
0.42	0.32	0.73	0.16	0.50	-	-	Ti:C = 1.2	Untreated	400-500
0.35	0.25	0.58	0.27	1.09	-	-	Ti:C = 3.1	Untreated	400-500
1.05	0.45	0.74	0.16	0.92	-	-	Ti:C = 0.9	Soft Annealed	400-500
0.80	0.53	0.72	0.31	1.59	-	-	Ti:C = 2.0	Soft Annealed	400-500
0.80	0.46	0.76	0.58	3.70	-	-	Ti:C = 4.6	Soft Annealed	>600
0.12	0.52	0.52	-	-	0.42	-	Zr:C = 3.5	Untreated	400-500
0.07	0.70	0.56	-	-	0.36	-	Zr:C = 5.2	Untreated	400-500
0.13	0.49	0.23	-	-	1.37	-	Zr:C = 10.5	Untreated	>600
0.10	0.31	0.60	-	-	2.26	-	Zr:C = 22.6	Untreated	>600
0.05	0.02	0.10	-	-	-	1.90	Th:C = 38.0	Untreated	>600

W. Tofaute and A. Buttinghaus [20] have prepared a phase diagram
of the iron-titanium-carbon alloys, and a comparison of the
behavior of the steels and their position in the phase diagram
shows again, that all steels are unstable in which titanium car-
bide still contains iron carbide, and all those consisting of
only alpha iron and titanium carbide are stable. The course of
the boundary line between the two areas corresponds approximately
to the relationship Ti:C = 4:1, and we may say that the titanium
steel, when it contains more than four times as much titanium as
carbon, is hydrogen resistant.

The section again shows the attack upon perlite in the
unstable steels and its disappearance (Figs. 49-56, Plate 4),
while the finer dispersed titanium carbide remains.

The processes have also been followed up analytically by
taking very fine milling filings from several steels and heating
them for 100 hours in hydrogen under 300 atm pressure at 500 and
600°C. The filings were analyzed before and after the test (Table
6). Fig. 24 shows that all the carbon present as Fe_3C is elimi-
nated by hydrogen, while the carbon in combination with titanium
is quantitively retained.

Pure powdered titanium carbide was also found to be com-
pletely unaffected by hydrogen when heated for 100 hours at 600°C
under a pressure of 300 atm. The initial carbon content was
17.8%, and after 100 hours heating it was 18.3%.

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[20] Techn. Mitt. Krupp Forsch.-Ber., 1938 pp. 67-78.

Table 6

RESULTS OF DECARBURIZATION TESTS WITH TITANIUM STEEL FILINGS (100 HOURS HEATED IN HYDROGEN UNDER 300 ATM PRESSURE)

Initial Material		Carbon Content after Heating to	
C %	Ti %	500° %	600° %
0.12	0.11	0.03	0.03
0.09	0.42	0.09	0.09
0.22	0.43	0.10	0.11
0.16	0.81	0.16	0.16
0.42	0.50	0.13	0.13
0.35	1.05	0.25	0.25
0.32	2.10	0.33	0.35
1.05	0.92	0.24	0.24
0.80	1.59	0.39	0.40
0.80	3.70	0.80	0.80

The effect of zirconium was studied on four steels containing about 0.10% C, and in addition a single thorium steel was tested, alloyed in a way to make it presumably hydrogen resistant (Table 5, Fig. 25). The samples were not heat treated. Both zirconium steels with 0.36 and 0.42% Zr were attacked at temperatures above 400°, while the steels with 1.37 and 2.26% were stable at 600°C and the same was true of the thorium steel. The sudden change in stability of the zirconium steels must have corresponded to the composition of the carbide ZrC with the proportion of Zr:C of about 7.6; it actually has been found to be in the interval between 5.2 and 10.5.

Summary

Fig. 26 shows the brief summary of the principal results of the work. Elements not forming carbides, - silicon, nickel and

copper - have no effect upon the hydrogen stability. Manganese forms no special carbide in steel, but is dissolved by the iron carbide to an appreciable extent, but affects the stability but little. Chromium, tungsten and molybdenum produce a strong and progressive increase in the hydrogen stability. These elements dissolve at first as readily as the iron carbide, and their action unquestionably depends upon a stabilization of the iron carbides. In case of the chromium steel there is a further known continuous increase in the stability after a certain chromium content is reached which depends on the carbon content. It has been shown that this phenomenon is connected with the formation of the special carbide $(Cr,Fe)_7C_3$, or more precisely with the disappearance of the iron carbide $(Fe,Cr)_3C$. Decarburizations (edge decarburization) could still be observed in the range of the hydrogen stable chromium steels within the chromium carbide range, but they are harmless, because the ductility of the material is not affected by it. This edge decarburization might be explained as an effect of the water vapors present in hydrogen.

Vanadium, titanium, zirconium and columbium cause at first a slight increase in the hydrogen stability, but do not show any further improvements and are in this respect excelled by tungsten and molybdenum. Only after the additions exceed a certain amount depending on the carbon content, do these elements produce a sudden and extraordinarily great resistance to the hydrogen stability. A comparison with the phase diagram permitted the following explanation. The original increase in stability must be attributed to a solution of the elements in the iron carbide. The solubility is,

however, very slight, and even if the specific effect of the
additives upon the stability of the iron carbide is evidently
large, no important improvement in the stability could be found
in this area. When the alloying metal content is still further
increased and exceeds the solubility limits of the iron carbide
for the alloying elements, the special carbides of these elements
saturated with iron carbide were formed. The hydrogen stability
of the steels depends on the stability of the least stable car-
bide, in this case the iron carbide, and as a result no further
improvement is obtained in this range with a quantitative increase
in the amounts of the special carbides. Only after iron carbide
has completely disappeared, and only the carbide of the addition
metals is present, is the stability suddenly increased because the
carbides of these elements are very stable and impart extraordinar-
ily high resistance.

A consideration of these relationships permit the produc-
tion of hydrogen resistant materials with these alloying elements.
The amount of additions may be relatively small, and the smaller,
the lower the atomic weight of the corresponding element. E.g.
steels with 0.1% C and with 0.5% Ti or 0.6% V are more stable than
a steel with 3% Cr and the same amount of carbon, and is even more
stable when taking into consideration the edge decarburization of
the chromium steels than the 5% chrome steel. It must, however, be
noticed that the applicability of these alloys, e.g. in the pro-
duction of liquid fuels, is limited by their not producing an in-
creased resistance to hydrogen sulfide, similar to that of the

chrome alloy steels, and they are not suited for the production

of thick walled forged pieces.

Discussions

W. Baukloh, Berlin

I would like first of all to warn against the statement

that methane is not capable of diffusing through iron. The fact

that the ferritic edge zones appear in the decarburization of steel

is a proof that the gaseous product of the reaction, in this case

methane, can diffuse through the iron layer. The scientific formu-

lation of Mr. Naumann's statement should be that methane cannot

diffuse through the iron lattice, which is in agreement with the

general conception of the diffusion properties of gas through

metals.

The recarburization of the edge zone with hydrogen-methane

mixtures would be explained by the equilibrium diagram of carbon-

hydrogen-iron, which would lead us too far afield.

Moreover, the edge decarburization with the hydrogen treat-

ment of steel does not occur only when the hydrogen contains a

certain amount of water vapors, according to our experimental re-

sults. Moreover, this could be derived from the fact that we are

dealing in this case with a heterogenous reaction in which the

diffusion ability of some of the reacting substances has, in most

cases, a deciding influence upon the total course of the reaction.

Myself and my collaborators have been able to observe a visible

edge decarburization with hydrogen most carefully freed from water.

The effect of carbon upon the rate of decarburization can be seen
in Fig. 57 8/, which shows that at 700°C the decarburization is
reduced with increasing carbon content, while conditions are re-
versed at 900 and 1,000°C. In the latter case the total decar-
burization increases with increasing carbon content. To find an
explanation for this, we have to make certain that we are dealing
in this case with a heterogenous reaction as has already been
explained. We have here two opposing processes: (1) the ability
to remove carbon by hydrogen and (2) the reverse ability of car-
bon to return to the edge layers of the steel. If the rate of
the removal of carbon by hydrogen is greater than the return ve-
locity of carbon to the edge layers, ferritic edge layers will
always be observed. When, however, the relationship is reversed,
the decarburization proceeds uniformly over the whole cross sec-
tion. The first case is preferentially the process of decarburi-
zation at relatively low temperatures and high pressures, while
the second phenomenon can be observed chiefly during decarburi-
zations at high temperatures. The more precise data are being
published in a work by W. Baukloh and B. Knapp.

Those two manifestations of decarburization must naturally
affect the rate of decarburization, and the results of the tests
shown in Fig. 57 must be explained in their light. The rate of
migration of carbon is still small at 700°C in comparison with the
possibility of removal of carbon by hydrogen. The rate of decar-
burization is therefore largely determined by the possibility of
supplying hydrogen to the decarburization zone or of removing me-
thane from the decarburization zone to the outside. W. Baukloh

and H. Guthmann 8/ have shown that the diffusion rate of hydrogen
is reduced with increasing carbon content of steels, as has also
been confirmed by Mr. Naumann. This diffusion-interfering effect
is therefore of deciding importance for the course of the reaction
and therefore the reason for the shape of the decarburization curve
for 700°C in Fig. 57. On the other hand the rate of migration of
carbon at 900 and 1,000°C is already so large that the carbon sup-
plied from the surface of the test piece of steel can at any moment
be redissolved in inner parts of the steel sample. Under such con-
ditions the transformation by the carbon and hydrogen is only ob-
servable on the surface of the steel test piece, and the diffusion
ability of the gaseous products of reaction play practically no
role. The reaction velocity is now determined only by the concen-
tration of the hydrogen and the carbon, i.e. it must become larger
with increasing carbon content, as may be seen in Fig. 57. These
conditions are not only for pure iron-carbon alloys but for the
alloyed steels as well, as shown in Fig. 58.

I would like to refute here a statement by Mr. Naumann
that contrary to my opinion no relationship exists between the
rate of decarburization and the rate of diffusion of the reaction
component participating in the decarburization. Quite aside from
the fact that this relationship can no longer be doubted today
from the picture of the mechanism of heterogenous reactions, Mr.
Naumann is trying to deny the importance of these tests in which
he alloys carbide-formers to convert the carbon into a more stable
form, which reduces the possibility of the reaction between hydro-
gen and carbon to such an extent, as to force them into the back-
ground right from the start.

My own and my collaborators' investigations on the hydro-
gen decarburization of steel had for their main purpose To contri-
bute to our knowledge of the reaction possibilities between gase-
ous and solid substances. They could not therefore be kept within
the narrow program of experiments such as the finding of hydrogen
resistant steels, and had to extend over temperature and pressure
ranges which may not be of particular practical interest today but
are of great importance for the scientific answer to these questions.

O. Knapp, Berlin

I would like to report on some tests in connection with
the discussions by Mr. Baukloh which I have performed in the Eisen-
hüttenmännischen Institut of the Technical High School in Berlin.

A complete agreement with W. Baukloh and W. v Kronenfels [21]
was found in the decarburization tests with filings of pure iron-
carbon alloys in the relationship of decarburization to the carbon
content. The decarburization decreases between 800 and 850°C with
increasing carbon content up to 0.9%, and remains there then approxi-
mately uniform. Conditions are fundamentally different between 900
and 1,000°C, where the decarburization increases with increasing
carbon content. One might say that the introduction of the concept
"percentage decarburization" ($\frac{\% \text{ C at start} - \% \text{ C at end}}{\% \text{ C at the start}} \times 100$)
makes the relationship less understandable. This, however, is not
the case as can be proven by drawing the curves on the carbon removal
in grams from 1 gram of the initial alloy. These curves show the

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21/ Arch. Eisenhüttenw, Vol. 11, 1937-38, pp. 145-156.

reduction of the amount of carbon removed with increasing carbon
content below 850°C in alloys from 0.1 - 0.9% C, and increased
amount at higher temperatures. It is furthermore remarkable that
not only the decarburization of filings but also the edge decar-
burization of cubes of pure iron-carbon alloys possess a similar
relationship. The cubes were exposed to the action of a stream of
hydrogen under pressure. The decarburisation, expressed in terms of
the thickness of the ferritic edge layer formed, decreases with
increasing carbon content at 600 and 700°C. The amount of carbon
remaining in the ferritic zone of a 0.88% C remaining at 700°C is
only 50% of that of the 0.32% C steel at 700°C. It may be worth
mentioning that at increasing temperatures the ferritic edge zone
finally disappears, with formation of edge layers with decreasing
C content from the inside to the outside. This is caused by the
equilibrium relationship in the iron-carbon-hydrogen system, the
discussion of which would lead us too far afield here. At 800°C,
and still higher, the relationships are such that a reaction be-
tween hydrogen and carbon proceeds on the surface of the piece.
The migration velocity of carbon is now so great that enough car-
bon always enters the outside surface. No edge layers are observed
any longer, and one is in the range of uniform decarburization over
the whole cross section.

F. Eisenstecken, Dortmund

Mr. Haumann's experiments show a certain relationship to
the corrosion tests. That raises the question whether the short
duration tests of Mr. Haumann could be confirmed in extended tests.

It would otherwise be possible that a difference exists between
the results found in hydrogen diffusion tests and the actual
hydrogen stability in operations.

K. Naumann, Essen

Mr. Baukloh has undertaken the study of such temperature
ranges in the interest of science which are but of limited impor-
tance from a practical standpoint and is therefore unquestionably
to be congratulated. One naturally should avoid to draw conclusions
from such tests on the behavior of steels under operating conditions
of the high pressure processes. One might possibly arrive at the
opinion from the study of the work of Mr. Baukloh that a steel with
0.0% Cr is more hydrogen resistant under conditions of hydrogenation
of coal or of the ammonia synthesis than is steel with 3 or 5% Cr,
or that steel with a 6% Cr and 0.05% C is just as stable as a steel
with 3.5% Cr and 0.18% C, which actually does not in any way corres-
pond to facts. It is also known from the industrial application of
such steels.

The fact that ferritic edge zones are formed at atmospheric
pressure and relatively low temperatures by hydrogen decarburization
of steel, and not at high temperature, has been known for a long
time as well as the explanation advanced by Messrs. Baukloh and
Krekeler for these phenomena 22/. In contradiction to Mr. Bauk-
loh's opinion but in agreement with Mr. E. H. Schulz and W. Huls-
bruch, as well as C. L. Austin 23/, I have failed to observe the for-
mation of such ferritic edges when using carefully dried and purified

22/ E. H. Schulz and W. Hulsbruch, Arch. Eisenhuttenw, Vol. 1,
    1927/28, pp. 225-240.
23/ Trans. Amer. Soc. Met., Vol. 22, 1934, pp. 31-67.

hydrogen, from which I have concluded that these ferritic zones
were not the result of decarburization with hydrogen but of the
action of water vapors or oxygen.

It appears to me therefore that the formation of a ferri-
tic edge layer is no proof that methane can diffuse in iron, but
rather a proof that the hydrogen used was not completely free from
water vapors or oxygen. I have already mentioned that it is exceed-
ingly difficult to remove the last traces of water vapors from
hydrogen.

I have not claimed the existence of a relationship between
the decarburization velocity and diffusion velocity of the reaction
agent participating in the decarburization, and have merely stated
that no relationship between the hydrogen stability of the differ-
ent steels and their permeability to hydrogen has been observed but
that the small decarburization rate during the "edge decarbuniza-
tion" can be definitely traced to the slow oxygen diffusion. When
Mr. Büchholz made note that these relationships are driven that which
which would by the addition of carbide-formers, he probably adopted
my opinion about the retarding effect upon the hydrogen stability
of the combination of carbon.

I would like to reply to Mr. Aisenstephen's question by
saying that the tests occasionally were extended to 2,000 hours'
duration, and that the steels behaved under long-time operating
stresses fundamentally in the same way as during the short-term
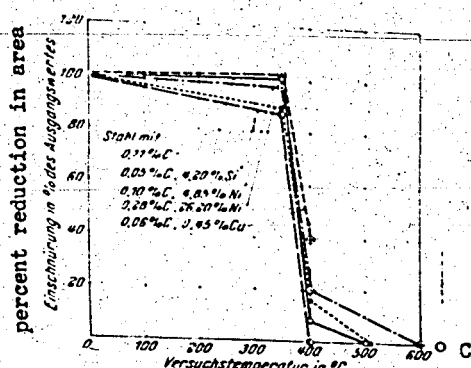tests.

Fig.1. Effect of Si, Ni and Cu on the reduction in area after heating in H$_2$
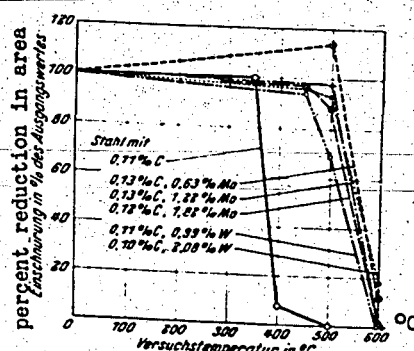
Fig.5. Effect of Mo and W on the reduction in area after heating in H$_2$
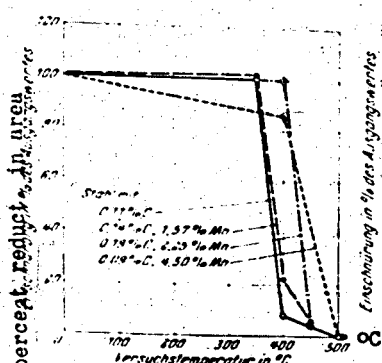
Fig.2. Effect of Mn on the reduction in area after heating in H$_2$
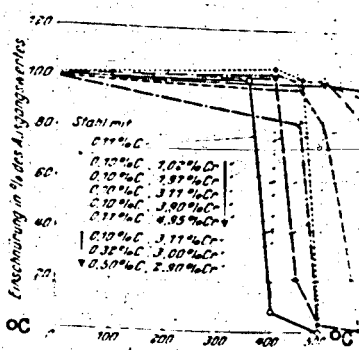
Fig.3. Effect of Cr on reduction in area after heating in H$_2$

unstable
stable
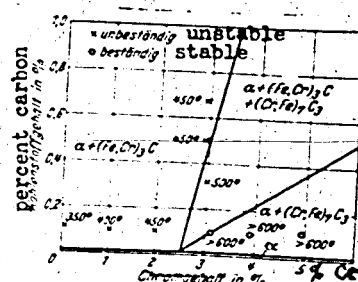
Fig.4. Hydrogen stability of Fe-Cr-C, in relation to equilibrium diagram

no action   edge decarb. H$_2$ attack
unalloyed

only for steel with 0.25% C
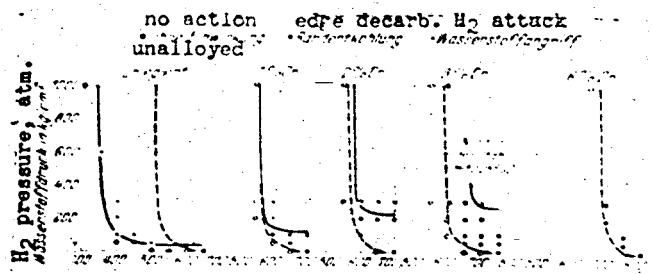
Figs 6-10 limits of stability of Cr-Mo steels.

hydrogen attack | edge decarbur.
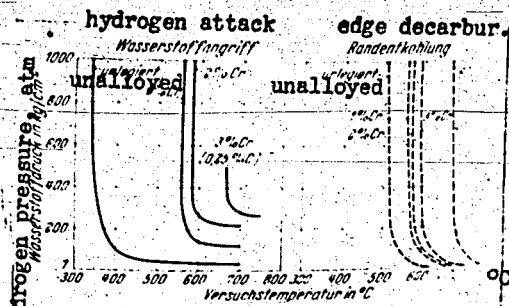
Figs 11 and 12 limits of stability of Cr-Mo steels
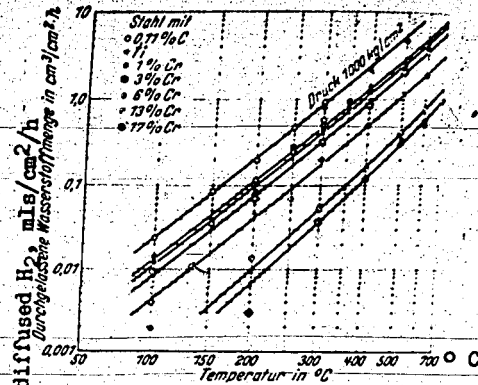
Fig. 16 Temp. relat. of H2 diffusion
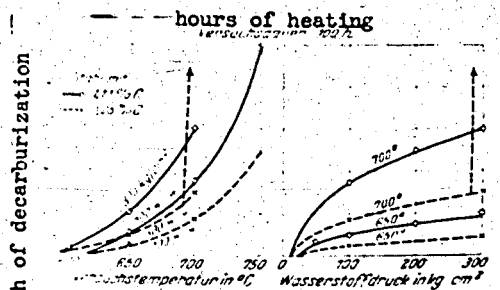
hours of heating

Figs. 13 and 14. depthe of decarbur. against temp and H2 pressure, Cr-Mo steel

Material
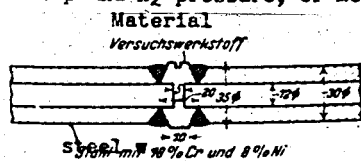
Fig. 15. Apparatus for study of H2 diffusion
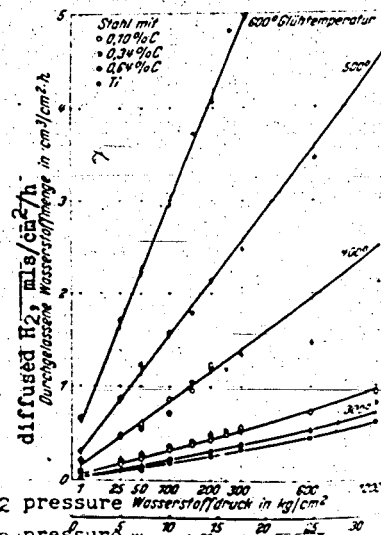
H2 pressure

H2 pressure

Fig. 17. Pressure relationship of hydrogen diffusion
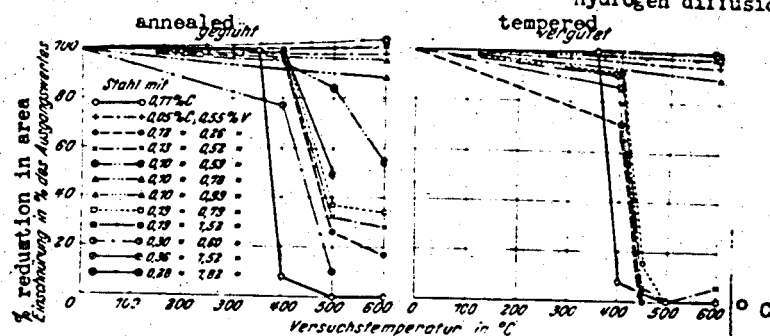
annealed

tempered

Fig. 18 and 19. Effects of V on redustion in area after heating in hydrogen (300 atm, 100 h.)
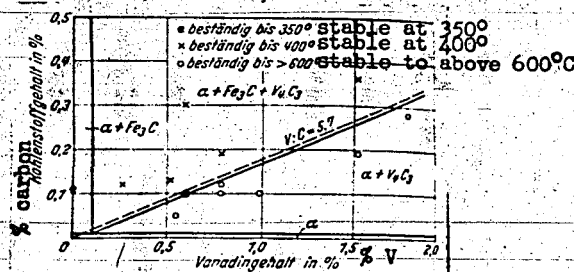
Fig. 20. Relation between resistance to hydrogen and the Fe-V-C equilibrium diagram
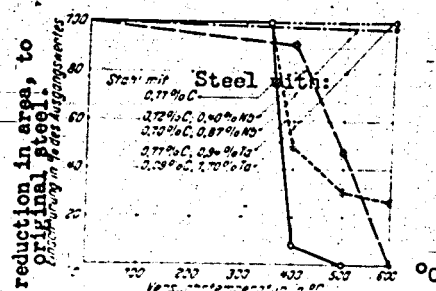
Fig. 21. Effects of columbium and tantalum upon the reduction in area after heat. in H_2 (300 atm, 100 h.)

Fig. 24. Decaeburization tests with titanium steel filings (300 atm., 600°C, 100 h.

Fig. 25. Effect of zirconium on the reduction in area after heating in H_2 (300 atm., 100 h.)
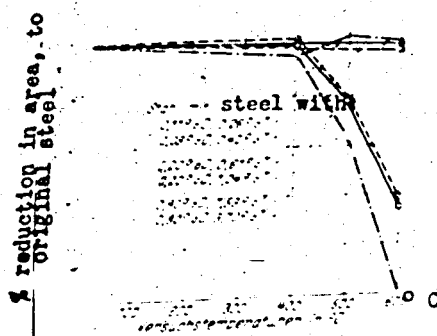
Fig. 22. Effect of Ti on the reduction in area after heating in hydrogen (300atm)
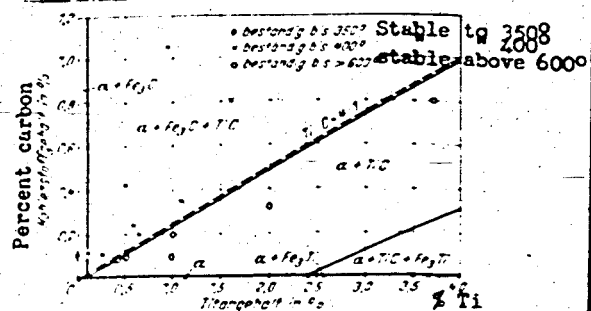
Fig. 2 . Connection between resistance to H_2 and the Fe-Ti-C equilibrium diagram
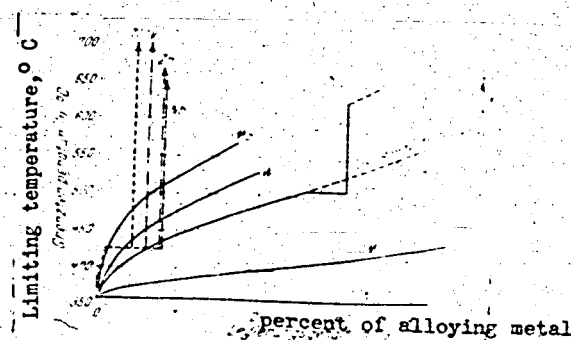
Fig 26. Effect of alloying metal on the hydrogen resistance of steels with 0.1% C (300 atm, 100 h)
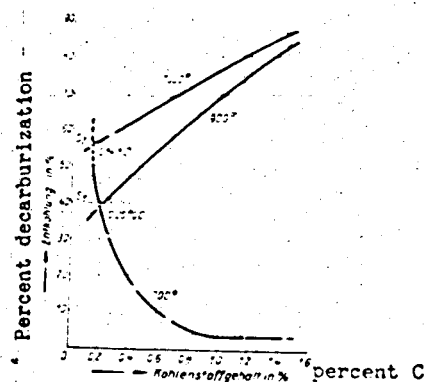
Fig. 57. Hydrogen decarburization Fe-C alloys (Baukloh and Guthmann)
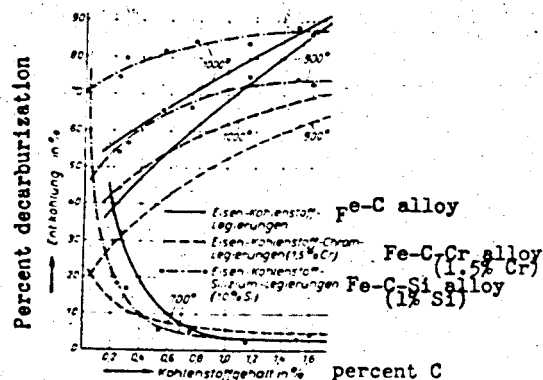
Fig. 58. Hydrogen decarburization of alloyed and unalloyed steels at different temperature, in relation to carbon content.

F. K. Naumann:

Der Einfluß von Legierungszusätzen auf die Beständigkeit von Stahl gegen Wasserstoff unter hohem Druck.

Initial struct.   300 atm, 400°C, 100 h   300 atm. 600°C, 100 h.
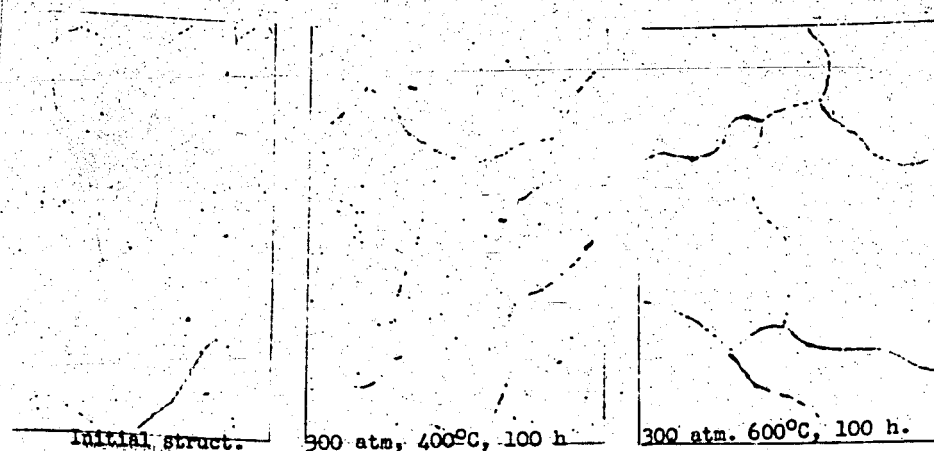
Bilder 27 bis 29. Gefügeänderung des Stahles mit 0.09% C und 4.20% Si

Figs 27 - 29. Changes in structure of steel with 0.09% C and 4.20% Si

Initial struct.
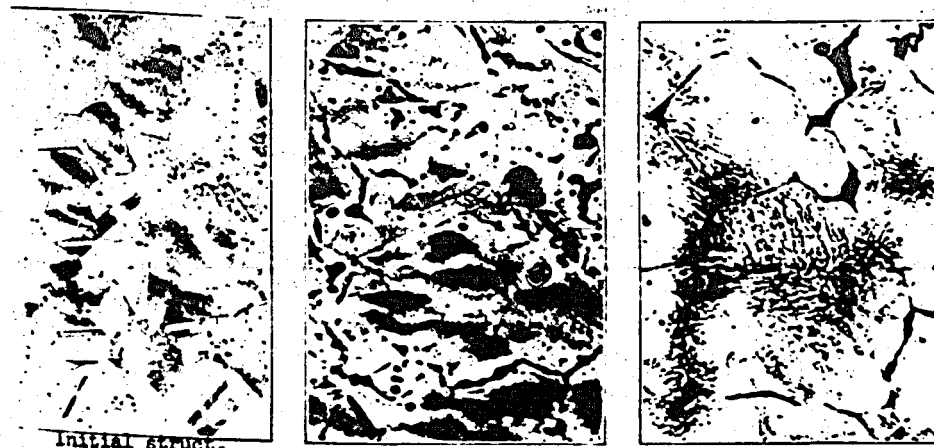
Bilder 30 bis 32. Gefügeänderung des Stahles mit 0.28% C und 26.2% Ni durch Wasserstoffeinwirkung

Figs. 30 - 32. Changes in structure of steel with 0.28% C and 26.2% Ni

Bild 33 und 34. Struktur von Chrom-Molybdän Stahl

Figs. 33, 34. Structure of chrome-molybdenum steel after attack by hydrogen.
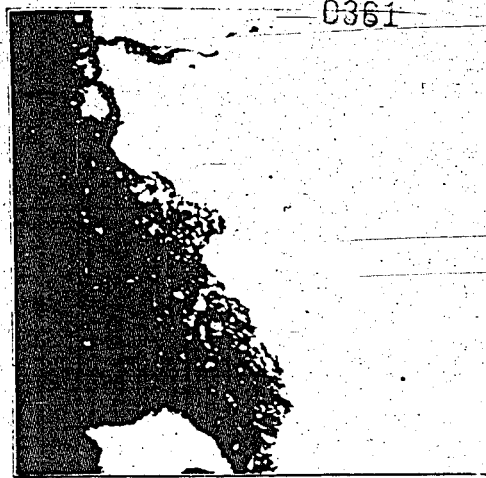
not etched   etched with picric acid

Figs 35, 36. Oxide deposition in edge decarburis. of Cr-Mo steel
structure in dry H_2 structure in moist H_2
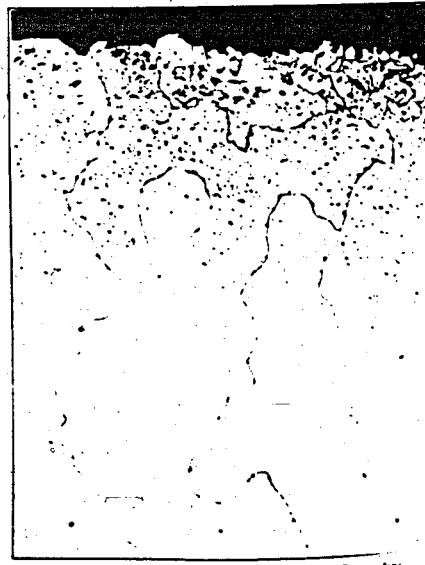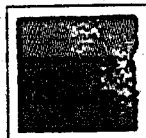
Figs 37 - 40. Effect of moisture on heating Cr-Mo steel (1 atm, 750° C
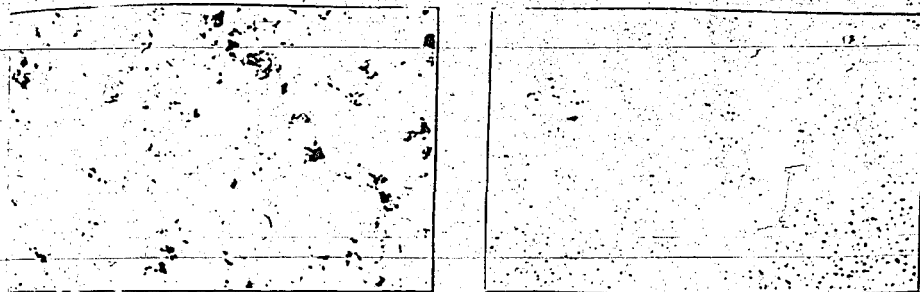
Initial structure (normalized)
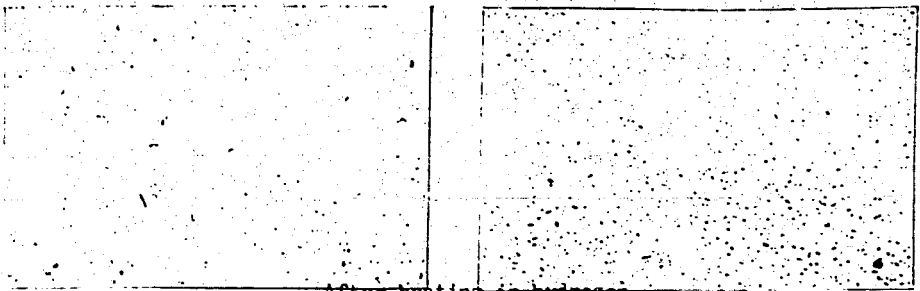
After heating in hydrogen

Figs 41-44. Changes in structure of V steels after heating in H_2

Initial structure (untreated)
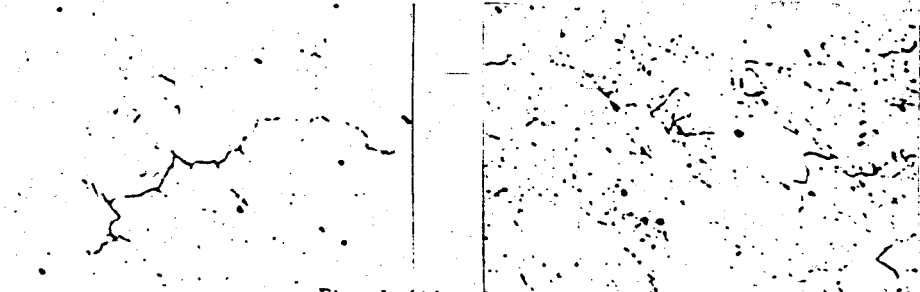
After heating in hydrogen

Figs 45-48. Unstable and stable Cb steel before and after heating in H_2
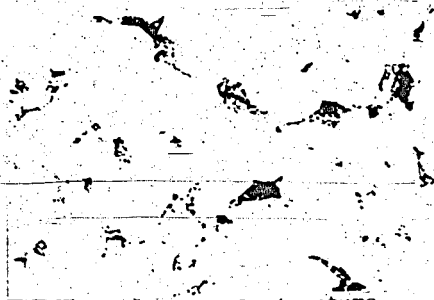
Initial structure.   (not treated)

After hydrogen attack (300 atm, 600° C, 100 h)

Figs 49 - 52. Titanium steels, before and after heating in H_2

Initial structure. (untreated)

After hydrogen attack

Figs. 53 - 56. Ti steel, before and after heating in H_2 (300 atm, 600°
100 hours

(2)

Sinclair Oil Refining Company Translations

Cracking of shale tars with aluminum chloride

by

N. I. Zelenin and N. N. Kosheleva

Anhydrous aluminum chloride began to play an important role in the chemical industry during recent years. We are perfectly aware of the importance of aluminum chloride for the chemical engineering problems. It is a universal agent, by means of which a great number of reactions can be catalyzed. It is principally used in organic chemistry for producing various kinds of syntheses.

Of special interest is the well-known property of aluminum chloride to dissociate hydrocarbons at medium temperatures (up to 300° C.), using the usual cracking methods.

Cracking with aluminum chloride is distinguished by a greater yield of benzine, whatever the cracking process applied. The benzine produced in its presence is completely stable and suitable for consumption as finished product, without additional working up and cleaning.

Aluminum chloride desulfurizes also the cracked oil. Thus the process is considerably simplified: the charge is cracked, stabilized and desulfurized, all at the same time.

When we are using aluminum chloride as a cracking agent, we may expect that all these properties may yield more or less satisfactory results also in the processing of shale tar.

Shale tar is a product of the decomposition of oil shales. The tars contain a large amount of unsaturated compounds, and when they are subjected to some kind of further thermal processing, they may in an emergency give more or less satisfactorily marketable light fractions. All the residua, with the exception of the gas produced, are waste products, which can be used only at the place of production.

With aluminum chloride, however, we may not only expect benzine to be produced but also an improvement in the working-up of the entire stock.

We do not understand exactly the mechanism of the action of Al Cl₃. On the basis of the literature [1] we may assume that cracking with aluminum chloride represents an intricate complex of reactions, characterized by the most divergent tendencies. The ultimate course of the various reactions depends obviously to a large extent upon the quantity of Al Cl₃ present and on the nature of the charging stock.

The role played by the stock determines from the very beginning what basic reactions will take place. The main types of reactions are: (1) isomerization, (2) polymerization, and (3) splitting.

_____

(1) Pictet & Zerczynska, Bull. Soc. Chem. 1916
    Zelinskij, Petroleum Economy (USSR), 1920

These types of reactions are generally characteristic of all pyrogenic reactions. In the present case, the process comprises the active saturation of the molecules with hydrogen. And this feature distinguishes the aluminum-chloride process from analogous methods.

The specific course of the reaction within one of the main trands in question, depends in the first line upon the nature of the charging stock, or rather, upon the nature of the hydrocarbons present in the individual stock. However, the influence of the material is so prominent only at the start of the process, thereafter, the course of the reaction becomes more and more uniform, independent of the starting material, but it does not become independent of the quantity of Al Cl_3 present.

For the cracking process, polymerization and splitting reactions are of great interest. In the presence of unsaturated compounds polymerization phenomena will occur already at a temperature of from 20 – 100° C.; and the products of this process are high-molecular saturated bodies. A splitting reaction will start at about 200° C., that is, the two processes are separated by a considerable difference in temperature, a fact which is of importance for controlling the nature of the final products.

Aluminum chloride is not a catalyst in the usual meaning of this word. It is rather an agent which reacts with the hydrocarbons in a definite proportion. For this reason, the intensity (lit. depth) of the process depends essentially upon the quantity of aluminum chloride present.

When the amount of Al Cl_3 is small in proportion to the saturated hydrocarbons, the yield of benzine is uninportant; but, on the other hand, when we introduce a large amount of aluminum chloride, we attain very great yields. When such a proportion of aluminum chloride to saturated hydrocarbons is used, we shall expect at first a polymerization reaction to take place. If more aluminum chloride is introduced, the polymerized molecules are cracked, so that the production of benzine is a secondary conversion reaction from the polymers. Shale tars are a conglomerate of all kinds of unsaturated hydrocarbons and of a small portion of saturated hydrocarbons (excluding heterocyclic compounds), consequently, they exhibit the scheme in question.

If cracking follows immediately after polymerization, it can not yield an important quantity of benzine, because unsaturated compounds give comparatively little benzine. It is difficult to get out of such a limited quantity a satisfactory hydrogen balance, which is necessary for obtaining higher yields of benzine. Therefore, we must not expect high yields of benzine but rather a mixture of fully saturated light end-products and viscous products, and several types of oil.

Under these conditions, cracking becomes a method of working up shale oils to marketable products of high-boiling motor fuels and lubricating oils.

A distillate up to 250 – 270° C. is drawn off, cleansed from Al Cl by means of alkali, and separated into two fractions, the first up to 200° C. benzine, the second, one above that – kerosene I. The cracking residue is drawn off from the still and likewise separated into 2 fractions; the first, up to 300° C. — kerosene II and the second above 300° C., oil.

A series of preliminary experiments with various types of tar indicated that the tars ought to be freed of phenol before being worked up (Fig. 5).

This phenomenon may be explained in the following manner. Aluminum chloride does not only split the molecules but promotes also a hydrogenating reaction at the expense of the hydrogen residue (in the flask remains a highly polymerized, asphalt-like substance); therefore, we may expect that the oxygen containing compounds will give off water, which will paralyze the action of $Al\,Cl_3$.

For our principal experiments, we cut out a medium fraction from Shale tar, 200 - 300° C., dephenolizing it in the normal fashion. It had the following characteristic numbers:

Spec. gravity	0.8564
Sulfur	1.39%
Boiling start	175°
up to 200°	3.0 volume percent
200°- 210°	4.8 " "
210 - 220°	12.2 " "
220 - 230°	6.0 " "
230 - 240°	14.0 " "
240 - 250°	9.5 " "
250 - 260°	13.5 " "
260 - 270°	7.0 " "
270 - 280°	2.0 " "
280 - 290°	8.0 " "
above 290° etc.	13.0 " "

The first series of experiments demonstrated the effect of varying ratios of $Al\,Cl_3$ on the yield and nature of the products. We see with unusual clarity that approximately up to 10%, the $AlCl_3$ is consumed preeminently in a polymerization reaction. Under these conditions, the yields of benzine will not exceed 9% (confer Table I.)

Unimportant changes observed in the yields of benzine (from 5.9 to 9%) when the proportion of $Al\,Cl_3$ is altered from 3 to 10%, stress this relationship still more, since with a 3% addition the polymerization is not yet of sufficient intensity — only 13% of the fractions have their boiling points above 300° C. (Table 2).

At 15% occurs a break — an intensive increase in the yields of benzine begins to take place, reaching 27.6% in presence of 25% of $Al\,Cl_3$, while the yields of polymer products decrease at the same time — in the presence of 25% of $Al\,Cl_3$ there is practically no fraction above 300° C. present.

Those fractions which have a boiling point of more than 300° C. increase intensively when the amount of $Al\,Cl_3$ is increased up to 10%, reaching as much as 25.8%.

Kerosene I exhibits an interesting development. In the first stage of our experiments its quantity would always decrease, giving polymers, on the one hand, and a certain part of benzine, on the other hand. When the ration of 14% of $Al\,Cl_3$ is reached, the yields of kerosene drop to a minimum, at the expense of a higher conversion rate for benzine; but after this point is passed, the proportion of this

fraction begins to grow, in agreement with the decrease in the amount of polymers formed; Kerosene I is produced.

When the amount of aluminum chloride is further increased, the porportional amount of kerosene I will always drop, obviously, because benzine and polymers are formed in its stead; with 15% Al Cl₃ this decrease will stop, but a slight decomposition of the residue will occur; but thereafter the decrease will start once more, and when the proportion of aluminum chloride has reached 25%, there is next to no kerosene II formed any more.

The period, during which the formation of polymers takes place, is also distinguished by the phenomenon that very little gas is formed, no more than 3 litres per 400 g of raw material. The formation of benzine is connected with the formation of gas.

Benzine, Kerosene I & II may be reckoned as finished products (confer their characteristics below). The total yields of these fractions, which we call light products, are given in Table 3.

Table 3

Yield of light products

Number of tests	Al Cl₃ %	Benzine %	Kerosene %	Total %
15	3	5.9	67.9	73.8
14	5	5.7	57.8	65.5
11	10	9.0	39.1	48.1
7	15	18.2	29.3	47.5
8	20	23.3	23.3	46.6
13	25	27.6	18.7	46.3

From this entire series of experiments we may draw the following conclusion:

Small ratios of aluminum chloride give preeminently polymers and an unsatisfactory amount of light products; that means, up to a ratio of 5% of Al Cl₃, we obtain very little benzine, and both kinds of kerosene appear to be only the slightly altered starting material with all its properties.

A high percentage of Al Cl₃ yields highly satisfactory light products, but at the expense of the elimination of polymers and of high losses in raw material (confer the column for losses by gas and complex formation on Table 2), since, the more aluminum chloride enters into the reaction, the more hydrocarbons enter into an irreversible association with Al Cl₃, contributing to the formation of an asphalt-like body, at the expense of an enormous consumption of the "catalyst". We think that it is most suitable to introduce 10% of Al Cl₃ into the reaction. In this case, we obtain a maximum yield of oils — 25% — along with a satisfactory yield of light products of good quality, up to 50%. The losses amount in this case to 20 - 25%. The amount of aluminum chloride lost when the ratio is 10%, is quite tolerable.

When the ratio of aluminum chloride is 5%, we obtain entirely satisfactory yields of tar oils and of light products, but the amounts are considerably lower than with 10% of Al Cl$_3$. At any rate, when tar oils are to be cracked with aluminum chloride in large-scale operation, it is necessary to check the loss of Al Cl$_3$ for proportions of from 5 to 10%.

According to the literature, it is clear that the intensity of cracking with aluminum chloride depends to a large extent upon the continued heating or, on the other hand, upon the speedy removal of the distillates. Such an interrelation with the time, is very noticeable in all characteristic details of the process. The nature of the products is not only a function of the amount of aluminum chloride entered, but also of the length of time for cracking. In our case, the effect of the time is very hard to evaluate, since it is not a typical case of cracking and a much more intricate process. It is also difficult to draw any definite conclusions concerning the effect of the time on theprocess for the very reason that our tests failed to register any noticeable effect when the period of removing the distillate was more protracted.

We have carried out tests with 15% of Al Cl$_3$, changing the duration of the process from 37 to 1,200 minutes. Table 4 shows that, with the exception of Test No. 17 all the other experiments were more or less of the same type. No. 17 differs from the rest not only insofar as the yield of benzine is lower, but also insofar as the quantity of polymers was low. In the subsequent tests, this amount of polymers becomes stable. This goes to demonstrate that polymerization like decomposition is dependent upon time. We may assume, in view of the fact that the yield of polymers had been stabilized at 70 - 150 minutes (as against 37 minutes), that the velocity of polymerization in Test 17 is substantially higher than the velocity of cracking. At the same time it was found in Test 17 that the longer the residence period in cracking, the greater the changes benzine undergoes with respect to its yields and nature.

In our experiments we did not find a substantial change in the quantity of benzine. This may be seen by the consumption of Al Cl$_3$, mainly during the polymerization; the residual amount of Al Cl$_3$ which enters into crackin; can not effect a sensible change in the yields and in the nature of benzine.

We have shown in the previous discussion that the preliminary tests had shown how difficult becomes the cracking of tars with Al Cl$_3$, if the phenols have not been removed. Here we shall illustrate this case from the quantitative viewpoint for Gdov tars. At the same time, we shall discuss the results of cracking tests made with Kashpir tars which had not been dephenolized. By selecting the starting material in this fashion, we shall be in the position to obtain some preliminary indications for the interaction of these stable constituents of tar oil (oxygen and sulfur) with Al Cl$_3$.

In Table 5 we see the paralyzing action of oxygen-containing compounds upon the cracking reaction and at the same time the enormous losses in raw material (more than 40%). Aluminum chloride is a desulfurizing agent. This may be explained by its character which effects an active hydrogenization in cracking

Table 5 indicates that with large amounts of hydrogenous compounds or in the presence of a large amount of sulfur (about 7%) practically no cracking takes place. The problem of how polymerization proceeds under such conditions will be treated in a separate study.

Some information about the change in the sulfur content is given in Table 6.

Table 6

Starting material	Sulfur content in feed stock %	Sulfur in benzine %	Sulfur in Kerosene I %	Sulfur in Kerosene II %
Tar from Glov	1.39	0.38	0.42	0.28
Tar from Kashpir	6.23	2.2 (x)	not determined	

The products from cracking with aluminum chloride

The quantity of gas evolved in cracking averages 2% and does not exceed 6%. When the first cracking studies started, it has been found that the cracking gas consisted of more or less pure butane. All the subsequent investigations carroborated this fact. A large cracking test was made in order to obtain more detailed information concerning the composition of the gas (2.5 kg feed stock and 15% Al Cl$_3$).

The gas was sampled at the beginning, middle and end of the process. All the three samples were identical. When we disregard the fact that some H$_2$S and H Cl were found in the gas, we may say that the rest consisted exclusively of butane.

There are no olefins, no methane. In this respect, the cracking gas from shale tars does not differ from that obtained when petroleum products are treated.

Benzine

From all experiments of this series, an amount of 900 cm^3 of benzine was collected. The benzine had the following characteristics: spec. grav. 0.7588, sulfur 0.38, iodine number 9.01.

The benzine was perfectly stable, colorless, of a specific odor, by no means like the usual shale benzines.

_____

(x) It is of interest to note that on cracking crude shale tar with Al Cl$_3$ in the laboratory, Zelenen, Levina and Furova (Chemistry of solid fuels, No. 6, 1931) yields of 24% by weight of benzine (b.p. 70-200° C.) with a sulfur content of 2.2%, had been obtained. This product was refined with 92% sulfuric acid and yielded 21% of benzine (calculated on the basis of the crude tar) free from unsaturated compounds (their were about 0.02% present in the benzine).

-7-

On cracking various petroleum products with aluminum chloride [1] it had been found that the composition of the benzine is independent of the starting material and can be roughly divided into two types: up to 100° -- paraffinic hydrocarbons; and above 100° -- naphthenic hydrocarbons. In order to verify this observation the benzine was subjected to a fractional distillation in 10° fractions in a column. The specific gravities of the fractions have been determined:

Table 7

(40 - 150° is calculated as 100%)

Fraction	Volume %	Specific gravity
40 - 50°	3.8	0.6443
50 - 60°	2.3	0.6637
60 - 70°	1.8	0.6838
70 - 80°	8.5	0.6945
80 - 90°	5.4	0.7069
90 - 100°	11.8	0.7283
100 - 110°	5.4	0.7439
110 - 120°	15.7	0.7532
120 - 130°	21.4	0.7651
130 - 140°	15.4	0.7739
140 - 150°	9.0	0.7817

To judge from the specific gravity and the percentile distribution of the fractions, the structure of the benzine is like that of petroleum products which have been manufactured by cracking with aluminum chloride. In the fractions up to 100°C. paraffinic hydrocarbons prevail, in higher-boiling fractions, naphthenic.

Kerosenes

There are two types of kerosenes. One of them is the cracking residue, (boiling point above 200°), the other, a distillate prepared from the cracking residue after removing aluminum chloride. In general, the boiling range of both kerosenes is from 200 - 500°. Kerosene I has a range of from 200 to 250 - 260°, Kerosene II of from 240 - 250 - 300°. This division has been worked out in the course of operation. The main characteristics of the kerosene are tabulated in Table 8.

Table 8

Kerosene	Spec. Grav.	% sulfur	Iodine number
I	0.8125	0.12	7.49
II	0.8418	0.28	6.67

---

(1) A. F. Dobranskij and H. Zelenin, Cracking with aluminum chloride.

Oils

By the term "oils" we denote all fractions the initial boiling point of which is higher than 300°. The starting material does not contain any such fractions. Consequently, we must presume that they have been formed in the course of the cracking process and, in particular, during the first stage of this process.

In view of the fact that the preparation of shale tars and lubricants by a working-up process is of great interest, we are planning to study all possibilities for preparing oils from shale tars of different proveniences. Now we are going to give the characteristic data for the oils obtained in the course of this process.

The residue (b.p. above 300°) is in fact already a lubricant (confer the viscosity curve) but it is not sufficiently viscous. By distilling off some fraction from it, a fraction of much higher viscosity may be obtained.

The 300 - 350° fractions have been distilled off from the residue in the vacuum (on conversion from a 15 mm to a 760 mm pressure). This fraction is of a specific gravity of 0.8694, apparently similar to kerosene II. The yields of this fraction amounts to about 1/5 of the volume of the entire residue. The residue of more than 350° b.p. was the subject of a more detailed investigation (Table 9).

Table 9

Properties of the oil

Specific gravity	0.9521
Flash point (Brenken)	193°
Volatility in 1 hr. at 110° C.	0.04%
" " 3 " " 110° C.	0.17%
Freezing point	-15
Viscosity at E_{50}	718°
Ashes	0.19%
Acidity	0.75° mg KOH
Iodine number	19.0

The oils resemble machine oils. The rather high degree of acidity and the presence of ashes may be explained by the assumption that in these tests the oil was not washed sufficiently so as to remove all traces of aluminum chloride. The presence of ashes means that there is some $Al Cl_3$ in the oil.

We are giving the viscosity curves pretaining to two of these oils and to some petroleum oils. They how that our oils are to a certain extent capable of replacing similar petroleum oils.

The curves on the graph mean: (1) petroleum spindle oil, (2) heavy machine oil, (3) our oil with an initial boiling point of 300°, (4) ditto, with an initial boiling point of 350°.

Conclusions

(1) The cracking of shale tars with aluminum chloride consists of two processes: polymerization and splitting. The possiblility of promoting one of these processes rather than the other depends from the amount of aluminum chloride which has been introduced.

(2) The first stage of the process, polymerization, will, therefore, go over into a process where ploymers are decomposed, in the course of time as well as when aluminum chloride is added. In the ploymerization, time does not play an important role (at the test temperatures).

(3) When aluminum chloride is used in quantities of not more than 10%, the process will yield 50% of light products (benzine and kerosene) and about 25% lubricating oils.

(4) When the percentage of aluminum chloride is as high as 15-25%, a considerable amount of benzene is obtained (up to 28%) but the yield of other products is correspondingly lower.

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Table 1

The Relationship between the Yield of Products and the Quantity of AlCl3

No. of Experiment	Quantity of Starting Material	Quantity of AlCl3 %	Duration of Experiment hour min.	Gas litre	Residue Gram	Residue %	Residue Spec. Grav.	Distillate Gram	Distillate %	Distillate Spec. Grav.	Fraction up to 200° Gram	Fraction up to 200° %	Fraction up to 200° Spec. Grav.	Fraction above 200° (from distillate) Gram	Fraction above 200° %	Fraction above 200° Spec. Grav.
15	400	3	3.00	-	191.0	47.7	0.8916	179.5	44.8	0.8404	23.8	5.9	0.8151	141.6	35.4	0.8356
14	400	5	4.00	1.5	189.9	47.4	0.8976	164.7	41.2	0.8344	30.9	7.7	0.8109	126.5	31.6	0.8330
11	400	10	3.55	3.0	168.0	42.0	0.9095	143.8	35.9	0.8261	36.0	9.0	0.7928	95.0	23.7	0.8242
7	400	15	4.00	8.0	160.6	40.2	-	114.5	28.6	0.7806	72.6	18.2	0.7673	30.0	7.5	0.8484
8	400	20	4.00	12.	73.0	18.2	0.8630	173.1	43.2	0.7709	93.0	23.3	0.7578	55.7	13.9	0.8121
13	400	25	3.55	15.	21.5	5.3	-	199.7	49.9	0.7737	110.5	27.6	0.7507	75.0	18.7	0.8076

Table 2

Properties of the Residue in relation to AlCl3

No. of Experiment	AlCl3 %	Fraction up to 300° (from residue) Gram	Fraction up to 300° %	Fraction up to 300° Spec. Grav.	Residue above 300° Gram	Residue above 300° %	Residue above 300° Spec. Grav.	Losses from gas and complexes %
15	3	130.5	32.5	0.8604	54.0	13.5	0.9546	7.5
14	5	104.8	26.2	0.8578	83.0	20.8	0.9451	11.4
11	10	61.4	15.4	0.8523	103.8	25.9	0.8447	22.1
7	15	87.0	21.8	0.8326	73.6	18.4	0.9190	31.2
8	20	37.7	9.4	0.8330	33.5	8.4	0.8077	30.6
3	25	-	-	-	-	-	-	44.8

Table 3

The Effect of the Heating Time

No. of Experiment	Duration Min.	Gas l	Distillate %	Distillate Spec. Grav.	Up to 200° %	Up to 200° Spec. Grav.	Above 200° %	Above 200° Spec. Grav.	Residue %	Residue Spec. Grav.	Up to 300° (from residue) %	Up to 300° Spec. Grav.	Above 300° %	Above 300° Spec. Grav.
17	37	3.0	52.0	0.8066	13.4	0.7719	28.8	0.8192	24.0	0.8936	13.4	0.8457	10.5	0.9329
18	70	3.5	47.0	0.8006	15.2	0.7672	24.0	0.8178	31.8	0.8929	13.4	0.8719	17.4	0.9328
19	150	4.2	40.5	0.7965	14.9	0.7616	19.4	0.8174	31.2	0.8915	11.4	0.8440	19.6	0.9205
20	300	2.8	40.7	0.7935	16.8	0.7702	15.1	0.8152	34.2	0.8905	12.0	0.8437	16.1	0.9253
28	1200	6.0	29.0	0.7882	14.6	0.7711	9.0	-	42.0	0.8725	22.7	0.8326	19.1	0.9252

(Table 5 following page)

Table 5

The influence of the starting material, sulfuric acid and oxygen-containing compounds

No. of Experiment	Starting Material	Quantity AlCl3 %	Duration Hrs. Min.	Gas Litre	Distillate %	Spec. Grav.	Up to 200° %	Spec. Grav.	Above 200° %	Spec. Grav.	Residue %	Spec. Grav.
27	Not dephenolized from Glov	10	4.00	0.75	28.3	0.8409	2.1	-	15.6	-	42.6	-
23	" " "	15	4.00	1.5	27.0	0.8892	4.3	-	15.1	0.8267	26.5	0.9362
25	Dephenolized from Kaehplr	10	4.00	-	37.0	0.9126	3.4	-	26.0	-	12	-
24	" " "	15	4.00	3.3	28.8	0.8920	8.3	-	15.5	-	24.5	-
26	" " "	25	4.00	5.5	48.0	0.8424	13.4	0.7925	23.5	0.8607	nothing	

MBiop.

Cracking and Hydrogenation of Esthonian and Kashpirian shale tars

N.D. Tilicheyev & G.N. Sledzhiev

(Conclusion) (1)

In cracking Kashpirian shale tar we shall be confronted with a still more substantial formation of coke than in cracking Esthonian oil shales (confer Table 12).

The total output of benzine being 7% (corrected value) about 4% of carboids are formed. An output of 10% of benzine (corrected value) goes with the formation of a huge quantity of carboids, indeed, about 20%. The cracking products consist of a heterogenous mixture of liquid and cokelike particles. This phenomenon shows that the cracking of Kashpirian shale tars by the usual methods is an extremely tedious affair, since the coke formed will fill the entire apparatus in a short time.

For the benzine-cracking experiment No. 11, the sulfur content has been determined with about 5.68%. This enormous sulfur content (Confer this Journal vol. 2 No. 1. (1931 Translation Book 212) in the cracking benzine made from Kashpirian shale tar, aggravates the prospects for a successful commercial cracking of Kashpirian tar.

In order to determine the maximum output of benzine which can be obtained by cracking Kashpirian shale tar, a cracking run, complete to a solid coke residue, was made of this tar; the following data were obtained in this test:

Gaseous products and losses	23.3 %	—
Cracking benzine (plus distillation losses)	27.0 %	0.820
Cracking fraction 200 - 300°	5.3 %	0.961
Residue above 300°	8.2 %	
Coke	35.3 %	

When we take into consideration that in Kashpirian shale tar there are 11.5% of heavy ligroin fraction, then we obtain a scheme of cracking products as follows, whereby we include into the "residue" the fractions of more than 200°, giving the values in round numbers:

Gaseous produces and losses	26 %
Cracking benzine	18 %
Cracking bottoms	15 %
Coke	41 %

The cracking benzine from Kashpirian shale tar has a specific gravity (at 15° C.) of 0.819 and consists of following fractions (Engler).

Initial b.p.	—	54° C.	—		Distill. up to 160° C.	77%
Distillate up to	+ 60	"	1%		"	"	"	18° "	93%
"	"	"	80	"	6%		"	"	"	193 "	98%
"	"	"	100	"	18%		Residue	—	1%
"	"	"	120	"	34%		Losses	—	1%
"	"	"	140	"	55%				

The fractional composition of cracking benzine from Kashpirian shale tars satisfies the standard specifications for heavy export benzine. There is only an unimportant inadequacy in the fractions up to 100° C. (18% instead of 20%). However, we must keep in mind that the cracking benzine which we obtained has a somewhat obnoxious fractional composition, since it contains a certain amount of heavy ligroin fractions practically all of which go over with the benzine. When Kashpirian tar would be subjected to cracking after all the fractions up to 200° C. have been removed, the fractional distribution of the cracking benzine would be considerably better.

Since the cracking of Kashpirian tar is accompanied by excessive coke formation, we studied also the cracking of the distillate, which had been obtained, when the distillation of the tar residue was continued to a solid coke. The distillation to a solid coke residue was carried out in an autoclave, and the following data have been obtained.

	Yields in % by weight	d_4^{15}
Gaseous products and losses in cracking	7.8	
Up to 200°	14.0	0.875
200 – 300°	31.2	0.948
Residue above 300°	30.7	1.023
Coke	14.4	—
Losses due to distillation	1.8	

After removing the fractions up to 200° C. from the coke distillate, the cracking operation was continued until coke was formed (Table 13).

The cracking of the distillate condensate gave considerably more satisfactory results than the immediate cracking of Kashpirian tar: the output is 17% of cracking benzine with a formation of 1% of carboids.

In order to investigate the possibility of obtaining soft asphalt from Kashpirian shale tar, this material has been distilled in the vacuum to varying rates of depth. For the soft asphalt products obtained in the residue, the chief constants have been determined and also what changes they underwent when heated to 163° C. for five hours (Table 14).

The data given in Table 14 show that by means of a simple distillation of an 80% distillate, a high-grade soft asphalt can be obtained from Kashpirian shale tar, fully in accord with the American standard specifications.

In order to investigate the possibility of producing a tractor fuel, or a broad fraction up to 300°, Kashpirian tar was cracked, up to solid coke formation, in an autoclave equipped with a column, under a pressure of 2 athmospheres. The following results have been obtained:

	%	d_4^{15}
Gaseous products and losses	14.8	—
Fraction up to 200° (incl distill. losses)	27.0	0.856
Fraction 200 - 300°	23.9	0.939
Residue above 300°	6.5	—
Coke	27.8	

The total output of fractions up to 300° is 51%.

Hydrogenation of Esthonian Shale Tar

The hydrogenation of Esthonian shale tar is carried out under an initial hydrogen pressure of 200 atm. in the average, at 390 atm. While the hydrogenation reaction took place, the pressure would quickly drop in the autoclave. This phenomenon indicates that the hydrogen addition took place with considerable intensity. Fig. 5 gives a typical graphic representation of the course temperature and pressure diring the hydrogenation process.

In another study it has been explained in detail [1] that it is impossible to obtain the maximum yield of benzine in one hydrogenation step, since the benzine which has been formed would undergo a decomposition to gaseous products, if it would be made to undergo the influence of a high temperature, for some length of time. If maximum yields of hydrogenation benzine are to be obtained, the hydrogenation must be carried out in two steps. It will give the following result: more than 30-35% of benzine is contained in the conversion product from the first hydrogenation reaction; the benzine fraction (up to 200°) is removed from the conversion product, and the residue of more than 200° is subjected to a second hydrogenation, and so on. The results obtained in three hydrogenation steps, with Esthonian shale tar, are given in Table 15.

In all experiments, a noticeable formation of coke took place. It is characteristic that the specific gravity of the residue above 300° was lower after each of the consecutive hydrogenation steps. This observation indicates that the hydrogenation of Esthonian shale tar can be carried to the end, that is, the end product will consist only of benzine and gas. The specific gravity of the benzine, on the other hand, goes up with every hydrogenation, and that means that there is an increase in the gravity of the/Kerosene fraction (200 - 300) remains practically unchanged.
　　　　　benzine fraction while that of the
The yield of hydrogenation products obtained from Esthonian shale tar, calculated on basis of the tar feed, are given in Table 16.

After three hydrogenation steps 58% of benzine (up to 200°) and about 15% of a residue above 200° C. had been obtained from Esthonian shale tar. If the residue is re-hydrogenated, it yields as much as 8% of benzine (calculated on the basis of the tar). Moreover, we must keep in mind that where the graph says "Gaseous Products and Losses," this figure includes also the losses suffered in the grinding process and by leakage of the apparatus, and these items amount to one fifth of the total amount for "gaseous products and losses." If we take this fact into consideration,

(1) Confer the article of Sakhalova & Tilikheyeva, Hydrogenation of petroleum products in the anthology of articles "Cracking and Hydrogenation" Moscow, 1931.

the output of benzine is 4% higher. After making these corrections, the yields of hydrogenation products made from Esthonian shale tar, are as follows (in round numbers):

Table 17

Products	%
Water	6
Gaseous products and losses	24
Benzine up to 200°	70

The fractional composition of the benzine which we obtained in the first and second hydrogenation steps is given in Table 18:

Table 18

Product	Benzine produced in the first hydrogenation of Esthonian shale tar	Benzine produced in the second hydrogenation of Esthonian shale tar
Specific gravity	0.742	0.782
Initial b.p.	46° C.	55° C.
up to 60° C.	4 %	2 %
" " 80 "	19 %	12 %
" " 100 "	35 %	20 %
" " 120 "	53 %	21 %
" " 140 "	71 %	53 %
" " 160 "	80 %	67 %
" " 180 "	94 %	78 %
" " 200 "	94 %	89 %
" " 225 "	97 %	95 %
End b.p.	230° C. (98%)	249° C. (98%)
Residue	1 %	1 %
Losses	1 %	1 %

The fraction distribution of the benzine obtained in the first hydrogenation step is most satisfactory; the benzine contains a large quantity of the fractions up to 80° C. (19%) and up to 100° (35%). The fraction distribution of the benzine obtained in the second hydrogenation step is not quite as satisfactory, but this benzine, too, is in accord with the standard specifications for heavy export benzine.

Hydrogenation benzines form Esthonian shale tars have a very low sulfur content; in the various tests it varied between 0.01 and 0.04 % (lamp method). The latter circumstance is of supreme importance, since Esthonian shale tars yield benzines with a sulfur content of as much as 0.56% when they are cracked in the usual fashion. But by the hydrogenation method it is easy to obtain benzines which are practically free from sulfur compounds.

The Hydrogenation of Kashpirian Shale Tar

The hydrogenation of Kashpirian shale tar has been carried out under the same conditions as the hydrogenation of Esthonian tar. In both of these cases, the course of the reaction was nearly identical. Table 19 gives the results of the re-hydrogenation of Kashpirian shale tar.

Table 20

Output of rehydrogenation products made from Kashpirian shale tar, calculated on the basis of the tar charge.

No. of tests	Index number of hydrogenations	Yield of hydrogenation products, in weight %			
		Water	Gas & Loss	Fract. -200 + dist. loss	Residue above 200°
21-22	First	2.4	22.0	32.6	(48.0)
23	Second	0.9	4.5	10.7	27.0
	Total	3.3	26.5	43.3	27.0

43.3% of benzine and 27% of residue were obtained in the two hydrogenation steps. If the residue is rehydrated once more, it may give 70% of benzine or 19% of benzine, calculated on the basis of the tar charge. Further more, it may be pointed out that the figure given in the item "Gaseous Products and Losses" includes the grinding losses, which amount to as much as 20% of the total amount of this item. When the hydrogenation of Kashpirian shale tar is repeated once more, a sum total of 65 - 70% of benzine may be recovered, the rest will be made up of 5 - 6% of water, and gaseous products.

The fractional composition of the benzine which was produced in the first hydrogenation is as follows:

Spec. weight	0.760	Goes over up to 180°	91 cm^3
Initial b.p.	52°	" 200°	95 "
goes over up to	60°	2 cm^3	" 225°	97 "
" " " "	80°	19 "	End boiling point 232°	98 "
" " " "	100°	37 "	Residue	1 "
" " " "	120°	55 "	Losses	1 "
" " " "	140°	70 "		
" " " "	160°	83 "		

The fractional composition of the benzine obtained in the first hydrogenation of Kashpirian shale tar is most satisfactory. It is distinguished by a large content of the light fractions (up to 80° - 19 %, and up to 100° - 37 %). In this relation, these benzines are much superior to the majority of the ordinary benzines which are produced by straight distillation and cracking.

The sulfur content in first-hydrogenation benzines made from Kashpirian shale tar, amounts to 0.36%.

This low sulfur content is most satisfactory. When Kashpirian shale tar is treated by cracking, the sulfur content will be as high as 6.5 - 7.0 %; it almost fails to meet the specifications if treated by the ordinary methods. But when the very same tars are hydrogenated, the benzine will have a total sulfur content of about 0.36%. Without any doubt, by changing the hydrogenation conditions or by rehydrogenating the benzine, the sulfur content can be reduced still further, so that it meets American standard specifications (not more than 0.1%).

Table 21 gives an analysis of the gases obtained by the hydrogenation of shale tar.

Table 22

Hydrogen consumption in relation to the benzine output

No. of tests	Name of shale tars	Yield of hydrogenation benzine (Weight %)	Hydrogen consumption Weight %
18	Esthonian	22.8	2.9
22	Kashpirian	34.4	2.9
24	Kashpirian	28.6	2.6

The residual gases contained altogether 30 - 40 % of hydrogen, that is, the hydrogen partial pressure amounted to 90 - 100 atm. For this reason, we may hope that in a commercial plant adapted to a continuous process, where high hydrogen concentrations are comparatively easy to obtain, an operating pressure of 150 atm. and even 200 atm. will entirely sufficient.

Considerable losses (Table 21) are mainly occurring because of the spreading (???) of the product.

Table 22 shows the consumption of hydrogen in relation to the formation of benzine.

On the basis of these data, we may understand that for the total benzine output from the hydrogenation of shale tar (about 70%), the hydrogen consumption will reach approx. 6-7%.

It is not necessary to stress the importance of the low H_2S - content in the gases. It is possible that a considerable part of the sulfur has been combined with the oxygen of the nickel, forming nickel sulfide. This compound, like cobalt sulfide, is also catalytically active, according to the data given in the scientific literature. If necessary, the nickel oxide would be easy to regenerate by roasting the nickel sulfide in the presence of oxygen.

In the experimental part of this investigation, we were supported by the entire research collective of the cracking division of the research institute "GROZNEFTI."

Conclusions.

1.) Cracking of Esthonian and Kashpirian shale tar is accompanied by a high rate of coke formation.

2.) When cracking is continued to a solid coke residue, 24% of gaseous products and losses, 26% cracking benzine, 14% cracking gasoil and 36% coke were obtained from Esthonian shale tar. The sulfur-content of the benzine was 0.56%.

3.) It is most expedient to crack the lighter fractions of the Esthonian tar and to work up the residual heavy fractions to asphalt.

4.) Cracking of Esthonian tar for the purpose of obtaining "tractor fuel" (a broad fraction up to 300°) yields 3% of water, 10% gaseous products, and 50% of the fraction up to 300°, 8% of cracking gasoil and 29% of coke.

5.) Cracking to a solid coke residue carried out with Kashpirian shale tar, yielded 26% of gaseous products and losses, 18% of cracking benzine, 15% of

cracking gasoil, and 41% of coke. The sulfur content of the cracking benzine was 5.88%. The low yield of benzine and the excessive sulfur content of the benzine make it very improbable that the cracking of Kashpirian shale tar can be made economically profitable.

6.) When about 80% of distillate have been removed from Kashpirian shale tar, a residue is left which is a high-grade asphalt.

7.) The hydrogenation of Esthonian and Kashpirian shale tars yields about 24% of gaseous products, 6% of water and 70% of benzine. The sulfur content of benzine made from Esthonian tar was 0.01 to 0.04% of sulfur, and that of Kashpirian tar was 0.26%.

8.) For the complete output of benzine (70%), a hydrogen consumption of 6-7% (on the basis of the intake tar) was necessary.

9.) By hydrogenating the shale tars in question, it is possible to obtain a special brand of stable aviation benzine, and also aromatics.

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Table 12

The Coke Formation at the Cracking of Kashpirian Shale Tar

No. of Experi- ments	Cracking Conditions			Output at the Cracking in Weight %					d_4^{15}	
	Temperature °C	Pressure atm.	Duration Min.	Gaseous Pro- ducts & Losses	Fraction up to 200°	200-300°	Carboids	Corr. Output fr. -200°C	up to 200°	200-300°
11	425	36	10	5.0	15.2	26.0	0.83	4.2	0.850	0.947
12	425	40	29	10.6	17.6	26.4	3.83	6.9	0.851	0.965
13	425	40	64	17.5	20.6	11.9	19.9	10.3	0.920	0.954

Table 13

Cracking of the Distillate Obtained in a Distillation Procedure Carried up to Coke (after isolating the fraction up to 200°C, of Kashpirian Shale Tar, Spec. Grav. 0.992

No. of Experi- ments	Cracking Conditions			Yield of Cracking Products at Weight %					d_4^{15}	
	Temperature °C	Pressure atm.	Duration Min.	Gas & Loss	Fraction up to 200°+	200-300°	Carboid	Dist. Loss	Up to 200°	200-300°
14	425	20	30	6.1	17.0	34.2	1.14	17.0	0.824	0.953

Table 14

Nature of Soft Asphalt Obtained from Kashpirian Shale Tar

No. of Experi- ments	Amount of isolated distillate in wt.%	d_4^{15}	Properties of soft asphalt on being heated		Properties of soft asphalt after being heated to 163°C for 6 hours		Losses at heating wt.%
			Temperature of Softening °C	Penetrometer Ductilimeter At 25°C	Softening Temp. °C	Penetrometer Ductilimeter at 25°C	
1	74.6	1.07	26	141 <116	26-26	93-96 <116	0.34
2	78.8	1.101	41	26 >115	45-46	19-21 <110	0.00
3	89.5	-	88	-	-	-	

Table 15

Rehydrogenation of Esthonian Shale Tar

Operating Conditions: 450° (corr. 425°) 200 atm. initial hydrogen pressure, 10% nickel oxide

No. of Experi- ments	Number of Hydrogenation Runs	Duration		Yield of hydrogenization product in wt.%					d_4^{15}				
		Hours	Min.	Water	Gas & Loss	Fraction-200° and distill loss	200-300°	Residue >300°	Up to 200°	200-300°	Residue 300°	Products before Hydrogena- tion	Hydro- gena- tion Products
17 First	3		08	1.9	14.8	30.6	26.0	26.7	0.741	0.905	1.057	0.999	0.869
19 Second	6		08	3.4	11.6	26.7	37.3	21.0	0.784	0.907	1.033	0.969	0.867
20 Third	6		01	3.4	4.6	14.3	33.1	14.6	0.826	0.701	0.996	0.984	0.933

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Table 19

Rehydrogenation of Kashpirian Shale Tar

Operating conditions: 450° (corr. 425°) 200 atm. initial hydrogen pressure, 10% nickel oxide

No. of Experiment	Number of Hydrogenation	Duration		Water	Yield of hydrogenation products in wt. %				-200°	200-300°	Product Before Hydrogenation	Product After Hydrogenation
		Hours	Mins.		Gas & Loss	Fraction -200° + dist.loss	200-300°	Residue 300°				
21-22	First	3	01	2.4	22.0	32.6	22.0	21.0	0.760	0.947	1.015	0.890
23	Second	6	05	2.1	10.4	24.8	40.8	21.9	0.838	0.946	0.984	0.935

Table 21
Analysis of the Shale Tar Hydrogenization Gases (450°) and Hydrogen Consumption: 200 atm. initial hydrogen pressure; 3 hours, in the presence of 10% nickel oxide

Number	Designation of Starting Material	Final Pressure Atm.	Gas m³	Average Spec. Gravity of gas	Composition of the gas vol.%				Balance of hydrogenation					After the reaction			Hydrogen balance in wt. %		
					CO₂ + H₂S	Unsaturated	Oxygen	Methane	Before the reaction Start. Material	H₂	Catalyst	Total output	Reaction Products	Catalyst + tar sludge	Gas	Loss	Weight of H₂ intake	Weight of left-over H₂	Weight of added H₂
18	Esthonian Shale Tar	282	96.5	0.512	5.0	0.1	0.0	64.5	100.0	3.3	10.0	113.3	73.8	14.2	9.7	15.6	3.3	0.4	2.9
22	Kashpirian Shale Tar	280	90.5	0.664	2.4	0.1	0.9	61.7	100.0	3.4	10.0	113.4	74.2	14.2	12.3	12.7	3.4	0.5	2.9
24	Residue >200° of Kashpir Tar	283	111.0	0.475	1.0	0.4	1.4	55.0	100.0	3.4	10.0	113.4	73.0	16.4	13.6	10.4	3.4	0.8	2.6

Table 23
Cracking of Esthonian Shale Tar

No. of Exp.	Designation of Starting Material (tar)	Cracking Operating Conditions				Yields in weight % of cracking products								d₄¹⁵			Properties of the residue >300°			Sulfur Content in Benzin %t.%
		Temp. °C	Pressure atm.	Duration Hours	Min.	Water	Gas & Loss	Up to 200°	200-300°	Residue >300°	Coke	Carboid	Distill. Loss	Up to 200°	200-300°	d₄¹⁵	Solid Point °C	E100	
1	Esthonian Shale Tar	-475	0	4	-	-	8.0	9.6	-	61.2	19.9	-	0.9	0.798	0.962		-	-	-
2	" " "	470	2	4	10	2.8	10.6	17.6	-	(Res.>200) 8.1	29.2	-	2.3	0.764	0.890	Residue>200	-	-	-
3	" " "	425	40	-	20	0.1	4.9	11.2	29.4	63.3	-	1.12	0.5	0.778	0.898	>1.0	-	-	-
4	" " "	425	40	-	23	-	6.?	13.2	19.3	51.0	-	1.87	1.4	0.768	0.916	>1.0	+22	7.8	-
5	Residue >200° exp.No. 1 Spec.Grav. 0.962	425	40	-	30	-	8.9	12.7	20.4	53.8	-	3.14	1.4	0.799	0.887	>1.0	+25	21.9	-
6	"	425	35	-	30	-	5.8	8.5	20.5	54.5	-	0.25	1.4	0.765	0.897	>1.0	+24	16.9	-
7	"	425	40	1	01	-	7.6	14.7	30.3	46.4	-	1.05	0.4	0.785	0.901	>1.0	-	-	-
8	Esthonian shale tar	350-475	20	3	50	-	23.6	25.9	30.5	6.2	35.2	-	2.8	0.762	-	>1.0	-	-	-
9	Kashpirian shale tar	425	0	4	-	0.8	6.3	14.3	6.9	62.6 (sic)15.3	-	-	0.7	0.764	-	>20°	-	-	0.56
10	" " "	425	2	4	10	-	14.5	25.8	-	(Residue>200) 27.8	-	-	1.2	0.856	0.939	0.992	-	-	-
11	" " "	425	36	-	10	-	5.0	15.0	23.9	6.5	-	0.83	0.2	0.850	0.947	>1	-	7.7	-
12	" " "	425	40	-	29	-	10.6	16.4	26.4	53.0	-	3.83	1.2	0.851	0.965	>1	+22°	-	6.86
13	Residue >200° exp. 9. spec.grav. 0.992	425	40	1	04	-	17.5	19.2	14.9	41.6	-	19.9	1.4	0.820	0.954	>1	-	-	-
14	Kashpirian shale tar	425	20	-	30	-	6.?	16.6	34.2	27.1	-	1.14	0.4	0.824	0.953	>1	-	-	-
15		350-460	20	3	-	-	24.?	24.1	5.3?	41.6	35.3	-	2.9	0.820	0.961	-	-	-	-
										8.2									

Table 24
Hydrogenization of Esthonian and Kashpirian Shale Tar in the Presence of 10% Nickel Oxide

No. of Exp.	Designation of starting Material	Hydrogenization conditions						Duration		Water	Gas & Loss	Up to 200°	200-300	Residue >300°	Distill.Loss	d₄¹⁵			Products at Hydrogen	Products after Hydrogen	Amount feed g
		Temp. °C	Hydrogen pressure, atm.					Hrs.	Min.							Up to 200°	200-300°	Residue 300°			
			Initial	Maximum	Terminal	Condensation															
16	Esthonian Shale Tar	450(2)	200	395	210	60		3	-	-	16.5	26.0	26.0	27.3	4.2	0.738	0.904	1.059	0.959	0.871	600
17	" " "	450	200	390	209	56		3	-	-3.3	18.2	26.8	26.0	26.0	4.2	0.744	0.907	1.054	0.999	0.867	500
18	" " "	450	200	401	232	66		3	01	4.3	15.8	25.1	25.0	26.1	2.7	0.743	0.912	1.073	0.999	0.871	500
19	Residue >200° exp. 1-2	450	200	448	310	117		6	-	3.4	11.6	25.3	37.2	21.0	1.5	0.784	0.907	1.003	0.969	0.837	410
20	" >200° exp. 3	450	200	438	312	145		6	-	3.4	4.6	43.0	33.1	14.6	1.3	0.826	0.910	0.996	0.923	0.871	175
21	Kashpir Shale Tar	450	200	390	257	73		3	-	1.9	22.3	27.3	27.1	23.3	3.5	0.763	0.940	1.137	1.015	0.897	600
22	" " "	450	200	405	230	60		3	-	-	21.7	31.0	22.7	21.2	3.4	0.752	0.940	1.074	1.015	0.872	600
23	Residue >200° exp. 5-6	450	200	362	253	87		6	-	2.1	10.4	22.3	40.3	21.9	2.5	0.839	0.946	1.074	0.984	0.936	230
24	Kashpir shale tar without light fraction C₁	450	200	398	283	80		3	-	2.8	18.8	25.9	25.6	25.2	2.7	0.750	0.913	1.061	1.039	0.885	-
25	" " " " "	450	200	408	300	90		2	57	3.6	16.6	26.5	25.7	23.5	4.1	0.758	0.935	1.036	1.039	0.859	-

(1) In tests No. 24 and 25, Kashpir tar has been reacted after the fraction up to 200° had been carefully withdrawn in a copper flask with column.........

(2) The actual temperature in all tests was about 425°C.

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Thermal Decomposition of Gdov Shales under Hydrogen Pressure

by V. P. Tsybasov, S. A. Dymshits and I.S. Levit

Prior studies on the Berginization of Kashpir shales and shales from Obsheye Sirta have demonstrated the fact that thermal decomposition under hydrogen pressure does not only provide higher yields of liquid products with less sulfur-compounds, but alters the character of the decomposition of the organic material[1].

The effect of the hydrogen on the decomposition of Volga shales is distinguished by the feature that the organic substance becomes susceptible of bituminization and is converted at a 95% rate into a benzol-soluble asphalt-like product — bitumen — at a temperature of 360-370°C.

The thermal working-up of Kashpir shales, before Berginization, makes it possible to obtain as much as 20% of shale tar with a sulfur content of 1.54%, whereas the usual distillation methods in the Fischer retort give 10-11% of tar with a sulfur content of 6.5%.

The decomposition of shales of a given provenience entails a considerable consumption of hydrogen. With shales from Obsheye Sirta, we need 6% and with Kashpir shales 8.4%, calculated on the basis of the amount of organic substance.

The large consumption of hydrogen is connected with the chemical constitution of the organic substances, which are of a humus-like, sapropelic structure, with a predominance of the humus part.

The studies made in the field of the destructive hydrogenation of humic coals, demonstrate that these coals are very hard to liquefy and consume a great amount of hydrogen.

Gdov shales, the organic matter of which is rather of a sapropelic-humic constitution, with a predominance of the sapropelic type, will probably be decomposed in the same manner as sapropelic coal, which responds exceptionally well to the Berginization process and is characterized by rich yields of fuel oils.[2]

The experiments described in the following text have been carried out by varying the temperature conditions, for the purpose of elucidating the effect of hydrogen on the organic substance in the course of the thermal decomposition of Gdov shales.

(1) Journal of Chemical Engineering (Kh.T.T.) No. 3, 1933, Ephramov Tsibasov;
    Oil Shales, No. 2, 1934, Ephramov Tsibasov.

(2) Journal of Chemical Engineering (Kh.T.T.), No. 4, 1932, A.Orlov and
    N.I.Ignatovich.