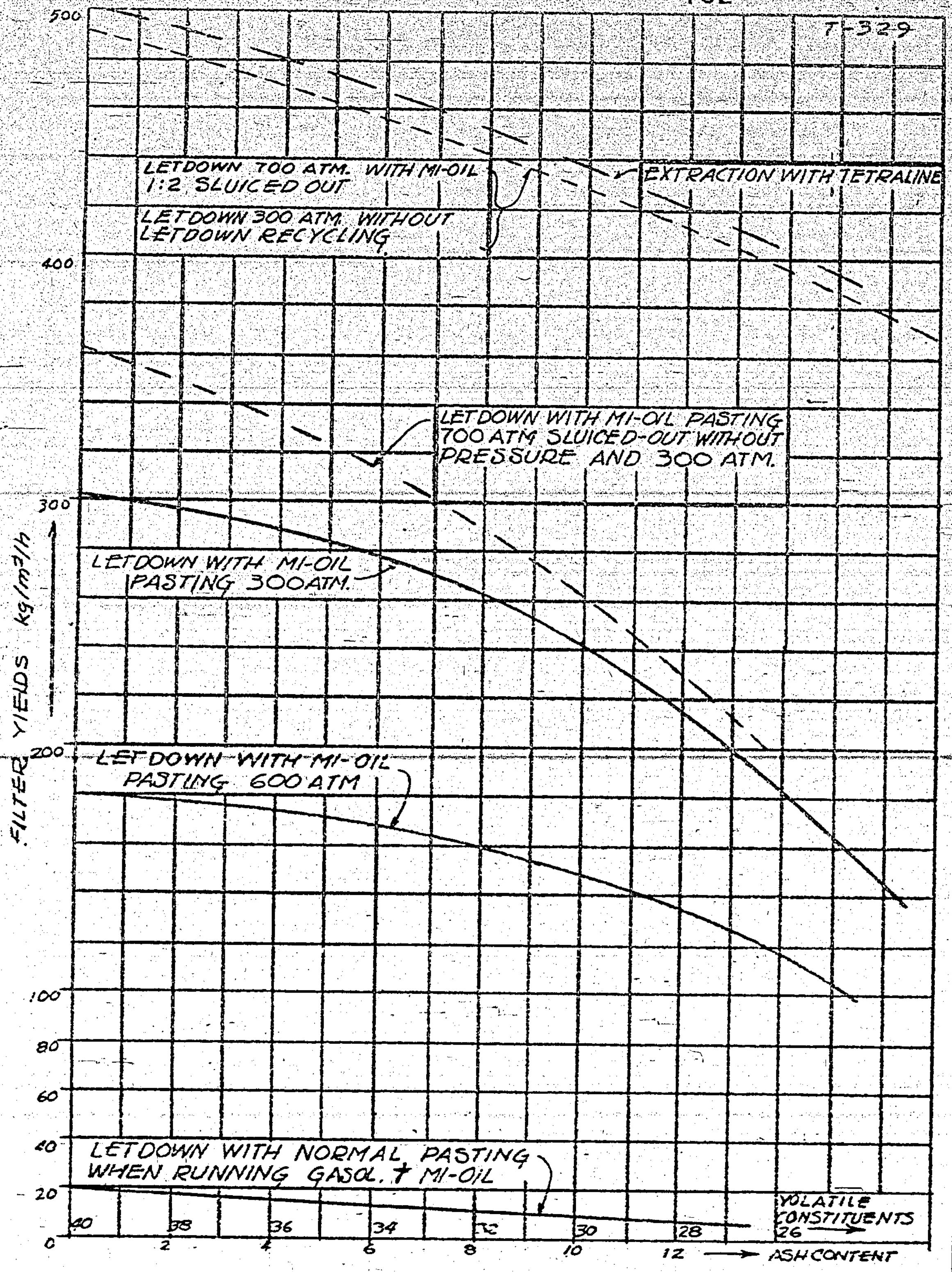
to 1:1.25 middle oil pasting, the filtrability drops correspondingly at 300 atm. At 700 atm, the drop is even greater, which, however, is due only to the strong dispersion and colloiding of the residual constituents in passing thru the letdown valves. If this post-disintegration is eliminated by sluicing as done by Uhde, or by the use of alternately operated sluicing vessels, the filtrability is greatly increased, and the differences between 300 and 700 atm are practically eliminated. Normal letdown with centrifuge oil recycling is roughly 10 times worse in filtrability, though the knowledge gained herewith will probably also lead to progress there.

/pkl

T-329


500
400
300
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40
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FILTER YIELDS kg/m²/h
LETDOWN 700 ATM. WITH MI-OIL 1:2 SLUICED OUT
LETDOWN 300 ATM. WITHOUT LETDOWN RECYCLING
EXTRACTION WITH TETRALINE
LETDOWN WITH MI-OIL PASTING 700 ATM SLUICED-OUT WITHOUT PRESSURE AND 300 ATM.
LETDOWN WITH MI-OIL PASTING 300ATM.
LETDOWN WITH MI-OIL PASTING 600 ATM
LETDOWN WITH NORMAL PASTING WHEN RUNNING GASOL. + MI-OIL
40
38
36
34
32
30
28
26
VOLATILE CONSTITUENTS
2
4
6
8
10
12
ASH CONTENT

DR. STORCH

U. S. BUREAU OF MINES 793 T-330
HYDRO. DEMON. PLANT DIV.

KCBraun/kp
4-22-47

BINDERS AND THEIR COMPOSITION

By Rank, Ludwigshafen, 29 Jan. 1943

Results of experiments by various authors have shown that the principal carrier of the binding power in briquetting and binding media is to be found in those substances which are soluble in benzol or insoluble in gasoline, such as s-asphalt, B-pitch or solid bitumen. Due to too high softening points of these substances and the simultaneous presence of inert benzol solids, suitable briquetting media must contain larger or smaller quantities of oil.

The realization that the softening point alone is not a sufficient criterion of the binding power and suitability of a binding or briquetting medium, led to a number of experiments in which the substances mentioned were decomposed by means of solvents.

In the following discussion I refer to the most important results of these experiments:

H. Broche & H. Nedelmann: "Characteristics and composition of briquetting pitch." (Glückauf 69, 1933).

W. Demann: "Extraction of bituminous coal tar pitches." (Brennstoff-chemie, Vol. 14, 1933).

Neukirch: "Investigations into coal binders." (Untersuchungen über das Bindemittel der Kohlenfabrication) (I. G. Bitterfeld, Report #395, 1933).

The solvent used in these experiments was benzol and normal gasoline or petroleum ether, so that good comparisons are possible with our usual methods of making analyses. The classes of substances obtained in the decomposition are named differently by the different authors:

TABLE I -- DESIGNATION

Experiments by	Broche & Nedelmann; Demann	Neukirch, Bitterfeld	Ludwigshafen
Benzol insolubles	A-Pitch 1)	Residue	Benzol solids
Benzol solubles, but gasol. or petrol. ether insolubles	B-Pitch	Solid bitumen	S-Asphalt
Benzol & gasoline solubles	G-Pitch	Oil bitumen	Oil

Note: - 1) A-, B-, G-Pitch = Alpha-, beta-, gamma- respectively, wherever referred to herein.

The substances corresponding to each other are listed horizontally. While Broche, Nedelmann and Demann investigated briquetting media, Neukirch confined himself principally to electrode binders.

It should first be noted that briquetting pitches may have varying characteristics, in spite of the same softening points. The decomposition of such pitches by means of benzol and normal gasoline offers an explanation for this:

TABLE II

No. & Kind of Pitch	% A-Pitch	% B-Pitch	% G-Pitch	Softening Point	Bending Strength[2]
1 - good normal pitch	25.0	38.3	36.7	68.5° C	18.1 kg/cm²
2 - good blister pitch	26.0	35.4	38.6	64.5	16.0 "
3 - poor pitch	31.0	26.6	42.4	68.5	12.6 "
4 - poor blister pitch	28.5	28.8	42.7	68.5	10.3 "

[2] as a measure of binding power.

The various pitches are composed of different constituents of A-, B- and G-pitch, in spite of the same softening point.

A-, B-, and G-pitches were isolated and are characterized as follows by Broche and Nedelmann:

A-Pitch: (benzol solids) is a blackish-brown powder, consisting of substances similar to coal. The A-constituents of good pitches act somewhat differently from, e.g. the A-constituents of poorly blistered pitches. With good pitches, the A-pitch melts (sinters) between 400-500° C, while still showing tar separation. Molten and blistered coke is obtained from it when it is coked. With poor blister pitches, the A-constituents are practically unmeltable and produce only baked or sintered coke. The ability to absorb oils is greater with the A-constituents of poor pitches than with the A-constituents of good pitches.

The A-pitch not only has no binding power itself, but influences the binding power of the other pitch constituents as well. This is shown in Table III. Briquetts were made with (B+G)-pitches alone and also with additions of A-pitch as briquetting media. The percentage of briquetting medium is so proportioned that equal quantities of (B+G)-pitches are always present in the briquetts.

TABLE III

% Binder	Briquetting Media % A-Pitch	% (B+G)-Pitch	°C Soft. Point	Bending Strength (Binding Power)
5.7	0	100.0	38	18.6 kg/cm²
6.3	9.5	90.5	54	17.9 "
7.0	19.0	81.0	64.5	17.9 "
7.9	28.5	71.5	83.5	11.9 "
9.2	38.0	62.0	99	7.2 "
7.0	Normal Pitch		66	17.8 kg/cm²

The table visualizes the strong effect of the A-pitch addition. The softening point is raised, the A-consitituent absorbs (B+G)-constituents and thus takes these away from the coal to be bound together. Even increased additions of briquetting media can not counteract the deteriorating influence.

When A-pitch was extracted with tetraline, 29% solubles could still be found. The remaining 71% had completely lost its baking and blistering properties in coking.

B-Pitch: is an almost black, brittle hard pitch, with high softening point (+80°C) and good grinding properties. Because of its high melting point, it has little binding power in itself.

G-Pitch: represents the lowest molecular portion of pitch and is a soft, brown mass (oils and crystals) or a resinous substance. In itself, this constituent also has little binding power (too low softening point). Its binding power is all the better, the higher molecular it is (pitch content in distillation).

The binding medium in the pitch is rather the mixture of B- and G-pitches. It has been found that their proportion in good pitches is approximately 1:1, Table II, items 1 and 2, corresponding to a soft pitch with a softening point of about 30-40° C. In poor pitches, the proportion of B:G is about 1:1.5, corresponding to a soft pitch with a softening point of 10-20°C.

Poor pitches, with a necessary softening point of 20°C, contain much A- and G-pitch, Table II, items 3 and 4.

Poor blistering augments A-pitch by strong decomposition of (B+G)-pitch and dehydrogenation (93% of O_2, separated as H_2O, 7% as CO_2), which changes the proportion of B:G with a definite softening point.

Good grades of pitch contain:

19 - 26% A-pitch
35 - 43% B-pitch
36 - 41% G-pitch.

W. Demann gets similar results. He finds great variations in the composition of various pitches:

18 - 32% A-pitch
14 - 27% B-pitch
47 - 66% G-pitch.

The analyses of A-, B- and G- pitches from various pitches closely agree with each other:

TABLE IV. PITCH ANALYSES

Ash-free Substance	A-Pitch	B-Pitch	G-Pitch
%C	89.27	89.20	91.0
%H	4.60	5.35	6.4
%O	3.61	3.04	1.0
%N	1.44	1.62	0.7
%S	1.08	0.29	0.87

G-pitch has the highest H_2 and lowest O_2 content.

Coking @ 1000°C:

A-pitch: 7.6 - 11.5% volatils, coke not baked, like fused coke.
B-pitch: 41.4 - 52.9% " , " strongly swelled and molten.
G-pitch: 87.7 - 94.5% " , " molten.

Baking property @ 900°C with sand (Damm):

A-pitch:	baking property	0
B-pitch:	" "	52-65
G-pitch:	" "	0

Baking property @ 400°C with sand:

A-pitch: baking property 0
G-pitch has better baking properties than B-pitch. After cooling, cake is hard with B-pitch, soft with G-pitch.

B-pitch: turns brown in heating, swells strongly, becomes partly insoluble in benzol, decomposes @ 400°C, bakes at 400°C and above, characteristics of bitumen.

G-pitch: its binding power depends on the softening point, liquefies in heating, at first without appreciable decomposition, at higher temperature most of it (90%) is distilled, @ 900°C it loses its baking property. G-pitch possibly has softening properties for the surface of the coal, hydrocarbon character.

TABLE V

Product Investigated	From Bit Coal			From Brown Coal			From Petrol.
	Rashig Tar	Soft Pitch	Hard Pitch	Tar Pitch	Fresol Pitch	Montan Pitch	Petrol. Pitch
Soft. Point, °C	<20	45	78	76	82	78	97
Decomposed into:							
% Residue (A-pitch)	5.5	21	23	12	12	--	--
% Solid bitum. (B- ")	32	37	35	28	42	--	--
% Oil bitumen (G- ")	62.5	42	42	60	46	100	100
Residue (A-pitch):							
Soft. Point, °C	>210	>210	>210	>210	>210	--	
% Coke	83	79	81	73	66	--	
% Volatile	17	21	19	27	34	--	
Solid bitum. (B-pitch):							
Soft. Point, °C	73	92	107	158	130	--	
% Coke	58	64	67	58	50	--	
% Volatile	42	36	33	42	50	--	
Oil bitumen (G-pitch):							
Soft. Point, °C	<-30	-18	16	31	22	77	85 ?
% Coke	18	32	38	31	29	22	30
% Volatile	82	68	62	69	71	78	70

In a similar manner, Neukirch investigated a number of binders of various origin, under consideration for the manufacture of electrodes.

Table V shows that the melting points (softening points) of the B and G constituents from brown coal products are higher than for the corresponding products from bituminous coal.

In order to determine the suitability of the individual pitch constituents for the production of electrode carbons, briquettes were made from bituminous coal pitch coke with A-, B- and G-pitch from Griesheim bituminous coal soft pitch. The amount of binder used was 15%, the briquette press pressure 500 atm. The pressing temperature was a maximum @ 150°C, or at least 20°C above the melting point of the binder. The briquettes were then burnt at a maximum temperature of 1000°C.

Table VI gives the results of these experiments.

TABLE VI

Production of Electrodes from Pitch Coke and Griesheim Coal Tar Soft Pitch
(Addition of Binder = 15% in each case)

Binder					Unburnt Briquettes		Burnt Briquettes		
% A-Pitch	% B-Pitch	% G-Pitch	Melting Point °C	% Coke Residue	Kind	Density	Kind	Density	Electrical Resistance ohms/m/mm²
100	--	--	>210	79	Breaks up under light pressure	1.28	Breaks up	1.21	Impossible to measure
40	60	--	144	72	Breakable by hand	1.60	Strong, some cracks	1.50	101
20	80	--	124	69	Strong	1.62	Strong	1.52	91
--	100	--	92	64	Very strong, cannot be deformed	1.63	Very strong	1.53	96
--	80	20	74	62	"	1.63	"	1.51	93
--	60	40	40	55	Strong	1.63	"	1.50	106
--	40	60	<20	48	Not very strong, can be deformed	1.59	Still strong	1.46	125
--	20	80	<20	37	Soft	1.58	Breakable by hand	1.44	145
--	--	100	-18	32	Breaks up under light pressure	1.58	Easily breakable	1.40	158
20	--	80	<20	42	Soft	1.57	Breakable by hand	1.44	180
40	--	60	<20	51	Breakable by hand	1.53	"	1.43	215
60	--	80	64	64	"	1.56	"	1.47	148
80	--	20	177	75	Breaks up under light pressure	1.36	Can be broken very readily	1.31	257

The following conclusions were drawn from these experiments:

A-pitch is suitable as binder for neither burnt nor unburnt coal; it decomposes before reaching the melting point.

B-pitch is the proper and practically the only carrier of binding properties and gives the best results for unburnt as well as burnt coal. It first melts in the burning of the coal, does not distill off, but decomposes and forms binding coke.

G-pitch has practically no binding power for unburnt carbon. For burnt coal it has little binding power. It first melts, but distills off, largely undecomposed, in further heating and forms only little binder coke.

Mixtures of A- and G-pitch are bad. B-pitch still produces good briquettes when 20% A-pitch or 40% G-pitch is added. Smaller additions of B- and G-pitch are favorable because the softening point is lowered.

Considering that binders containing A-pitch will probably always be used in practice and that considerable quantities of G-pitch must then be present to reduce the softening point, Neukirch's results agree very well with the experiences of Broche and Demann.

Further experiments by Neukirch showed that A-, B- and G-pitch from different bituminous coal products are practically identical, respectively, in their behavior as binders.

Briquette Binder from Scholven Letdown.

Discussion at Scholven, April 16, 1943. (Abstract)

Dr. Urban said that the thruput thru the ball kiln (Kugelofen) in the topping of letdown for the production of briquette binder had been increased from 5.5 m^3 to 8 m^3 injection per hour by removing the balls and attaching overflow plates. The briquette binder production at the time was about 100 to 120 t/day. After enlarging the cooler and granulating equipment, the production is to be increased to the proposed 150 t/day. The coal thruput in hydrogenation could be increased 10%, increasing the gasoline yield by about 3 to 4% above the former normal yield, even though the oil remaining in the binder is lost to hydrogenation. Thus, the desired condition in the production of briquette binder in hydrogenation, whereby the oil losses sustained in the production of briquette binder should be equalized by a correspondingly increased thruput in residue processing, has been reached.

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

KCBraun
4-23-47

Operating Experiences at Pölitz
(Reg. Valve, Converters, Temperatures, Water Inj, Cold C.P.)

By Bastian, Ludwigshafen
12 March 1943

(Discussion held in Ludwigshafen, 4 March 1943)

Regulating Valve

Pölitz desires better regulation in its gas inlet valve to the stall for the purpose of providing reserve pressure for cold gas distribution. The present main valve is 80 mm with a 30 mm bypass. Pölitz proposes a 45 mm main valve with a 16 mm bypass. I. G. considers it more appropriate to use regulating valves with "Regulier-schwanz" (possibly an elongated cone or needle).

The 30 mm cold gas valves should eventually also be similarly rebuilt.

Pölitz does not consider a regulating cone necessary for the 16 mm air valves.

Exchange of Converter 5 for Converter 3

To provide for the interchanging of the various long converters Pölitz has provided a movable concrete base for the short converters.

With respect to the position of the 10 m converter, the following has been determined:

Stettin exchanges converter 5 for converter 3. No cold gas inlet to the catalyst space will then be provided.

Operating Temperatures

The maximum permissible operating temperature in pipe lines will be reduced from 570 to 550°C.

D. I. Schappert will get in touch with the individual plants for the purpose of determining a uniform measurement of the wall temperatures in hairpin tubes (570°C).

Water and Lye Injection

No decision was reached on the quantities of lye and/or the dimensions of the pumps, containers, etc.

Dr. Burian will check this item and get an early decision in agreement with Dr. Donath.

With regard to the pipe arrangement itself, the following agreement was reached: Separate lines will be used for soda solution and pure water to the stalls.

Each stall will be provided with a pH apparatus and a valve group with 2 meters for dosing the quantities. Depending upon the most favorable operating conditions, water and lye will either be mixed on the way to the stall, suggested by Ludwigshafen, or injected separately into the circulating line between heat exchanger 3 and the cooler, suggested by Pölitz.

Inclination of the Product Catchpot

The slope of the product catchpot is to be 1%. The suction and pressure separators will have a slope of 4%.

/pkl

Wiley

U. S. BUREAU OF MINES
COAL TO OIL DEMONSTRATION DIV.

TOM Reel 163, frames 288-289 802 T-332

High Pressure Experiments,
Leuna, 558

TEA
10/19/42

SOLID AROMATIC SUBSTANCES IN HYDROGENATION SLUDGES
(New Summary)

I. Kind.

The solid aromatics obtained in today's industrial processes are characterized by their particularly symmetrical structure. When hydrogenating under pressure and at high temperatures there is dehydrogenation in addition to the cracking of the hydrogenated rings.

These hydrocarbons are principally: pyrene, corenene; also homologues of pyrene, carbazol and benzperylene.

II. Occurence.

The above mentioned hydrocarbons are formed in particular during the pressure hydrogenation of bituminous coal, coal tar, somewhat less in the hydrogenation of brown coal, in still smaller amounts in the hydrogenation of petroleum residues.

III. The more accurate information has been found in the large scale test K 804 and at the Hydrogenation Works Scholven. According to these sources, the amounts are as follows:

	In Kiln Oil	Referred to 1000 te Pure Coal	
Carbazol	abt. 1%	abt. 1.7 t	With con-
Pyrene	abt. 8 - 10%	abt. 14 - 27 t	tinous
Pyrene homologues	abt. 1 - 2%	abt. 1.7 - 3.4	removal
Benzperylene	abt. 0.1%	abt. 0.2 t.	possibly
Coronene	abt. 0.5 - 1%	abt 0.8-1.7t	1/5-1/10 parts

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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

803

TOM Reel No. 164, Frame 545

T - 333
W. M. Sternberg

High Pressure Experiments

Lu. 558

June 17, 1940

SOLUBILITY OF CORONENE AND BENZPERYLENE AT 20°

		Coronene	Benzperylene
		g dissolved in 100 g. saturated solution	
Solvent:	Benzol	0.02	0.620
	Toluol	-	0.114
	Xylol	0.01	0.110
	Cyclohexane	0.004	0.110
	CS_3	0.134	3.45
	Methyl naphthaline	0.046	1.48
	Prod. converter 322 [1/]		
	Fraction -180°	-	1.22
	Fraction 275 - 330°	0.096	1.24
	Heavy oil, + 325°	0.0003	0.66

/s/ Hölscher

1/ The operations in converter 322 were as follows (Dr. Peters): The heavy oil from bituminous coal liquefaction (silesian coal) was filtered, hydrogenated over the Welheim catalyst at 600 atm, 24. mv.

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LOUISIANA, MISSOURI

TOM Reel No. 164, Frame 784 804 T-334

W. M. Sternberg

High Pressure Experiments March 22, 1943

Lu. 558

ISOLATION AND DETERMINATION OF CORONENE IN THE HYDROGENATION RESIDUES

The identification of small amounts of coronene in the hydrogenation residues is made difficult by the distillation range of coronene being inside of those of the resins and asphalts.

The isolation of coronene as molecular compounds, e.g. as a picrate, which is very little soluble in the pure state, is almost impossible, because resins and asphalts prevent the crystallization.

The coronene is best determined by distilling the solid-free hydrogenation residues in a vacuum of about 1 mm (Kp_{760} = abt. 400°). A reddish resin distills first, and at Kp = abt. 330° a fraction is obtained when coronene is present, which in part crystallizes. When this fraction is ground with benzol or acetone, coronene separates out almost quantitatively.

One may occasionally get along without distillation, by a refining hydrogenation at about 400°. The high molecular weight hydrocarbons present with the coronene will then be hydrogenated. The coronene will remain in the non-hydrogenated form, and is almost quantitatively precipitated in the hydrogen-rich reaction product, especially after dilution with a 7-fold amount of cyclohexane.

The hydrogenation residues, which contain coronene and no "asphalts", deposit coronene by simple dilution with gasoline.

/s/ Boente.

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TOM Reel No. 5, pp. 542 - 547 806 T-335

W. M Sternberg

CORONENE

By Dr. Boente, I.G. Farbenindustrie A. G. Ludwigshafen

(A reprint of a magazine article, magazine and year not given)

Coronene, or, in other designation, hexa benzobenzene or dibenzperylene is a highly condensed hydrocarbon with 7 rings, and has always created great interest. This hydrocarbon, with its exceptionally symmetrical structure, offered particular attraction for study. Several investigators have attempted in the past to obtain coronene by synthesis, e.g. J.v. Braun and K. Weissbach in 1931 1/, E. Clar and J.D. Wallenstein 2/. R. Scholl and K. Meyer have succeeded in 1932 to synthetize this hydrocarbon by a very complicated synthesis, starting with molecules of anthracene and xylene 3/.

Synthesis of coronene (schematic)

Scholl and Meyer

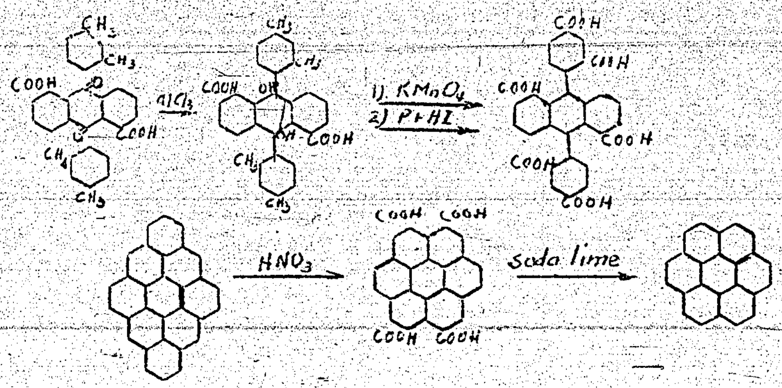

Figure 1.

This synthesis proceeds over 14 intermediate products. The individual reaction steps of the synthesis ~~are here indicated very briefly (figure 1). The~~ starting materials were anthraquinone 1, 5 - dicarboxylic acid chloride and 2 molecules of m-xylene. By interaction with aluminum chloride 9,10 di-m-xylene

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1/ Ber., vol 64, 1931, p. 1787

2/ Ber. " 64, 1931, p. 2076

3/ Ber. " 65, 1932, p. 902.

9,10 dioxy-9,10 dihydroanthracene - 1,5 dicarboxylic acid is first obtained. Oxydation followed by reduction produces the hexacarboxylic acid. A few more reactions lead to the closing of the rings, etc, and to anti-peri-dibenzcoronene. Finally, passing by way of oxydation to the tetracarboxylic acid of coronene, we get coronene.

The organic laboratory of the high pressure experiments of the I.G. Farbenindustrie A.G. at Ludwigshafen-Oppau succeeded in 1935 in isolating for the first time coronene from pressure hydrogenation products, i.e. a product obtained industrially. In this way, this interesting product, which has originally cost several thousand marks a gram, could now be obtained in larger quantities industrially.

The physical and chemical properties of coronene were primarily of interest to us within the limitations of our work on hydrogenation, at first principally the question of hydrogenation of coronene, and later in the study of the composition of hydrogenation products.

We will first, however, describe in greater detail the hydrocarbon itself, and repeat briefly its physical and chemical properties, as far as they are known. Coronene crystallizes in pale yellow, extremely fine long needles, m.p. 432° (corr.). The b.p. is 525°

at 760 mm pressure, and the hydrocarbon can be distilled without decomposition at this temperature. The solubility in most of the common organic solvents, such as toluene, xylene, etc., is exceedingly limited in the cold, about 0.1 percent. The solubility in the boiling solvents is somewhat greater, and coronene may be crystallized from boiling ~~xylene,~~ or better still, from o-dichloro benzene.

The easy sublimation of coronene is striking. This property of the hydrocarbon may readily lead to trouble industrially. Conditions are here similar as with naphthalene, which is readily carried over with gases because of the ease of its sublimation, and later becomes deposited on the walls of the gas pipe lines. Coronene sublimes similarly with light oil vapors during the distillation of the hydrogenation products. Because of its low solubility, coronene may readily crystallize in the distillate and this may lead to plugging up.

Because of its high boiling point and high molecular weight, coronene extends into the field of the asphalts, and does behave in certain respects similar to these substances. Thus, a heavy oil obtained in the coal liquefaction deposited 1.1 percent "asphalt" with benzol, and 25 percent of it consisted of coronene. The power of adsorption of coronene by active materials, like animal charcoal or bleaching earth, is almost equal to that of the asphalts.

The technically produced coronene is colored deep yellow. This coloration is in part due to accompanying substances, the so-called chrysogen of the hydrocarbon. The nature of this chrysogen is unknown. It may be an intensely colored hydrocarbon, similar to naphthacene, which is known as a chrysogen of anthracene and chrysene, and colors these hydrocarbons yellow. It is extremely difficult to remove the traces of the chrysogen from coronene. Chrysogen is destroyed by hydrogenation followed by dehydrogenation.

Coronene fluoresces in the ultra-violet light, with a strong yellowish green fluorescence in the solid states, and blue in solution. We may add to the known chemistry of coronene, that it can be sulfonated with strong sulfuric acid. Halogen products are formed by the action of the halogens. Oxidation produces quinone-like substances. Dyes prepared from coronene as an intermediate are characterized by exceptionally great stability.

The constitution of the hydrocarbon will be discussed first in connection with the hydrogenation products. (figure 2)

Constitutional formula of coronene

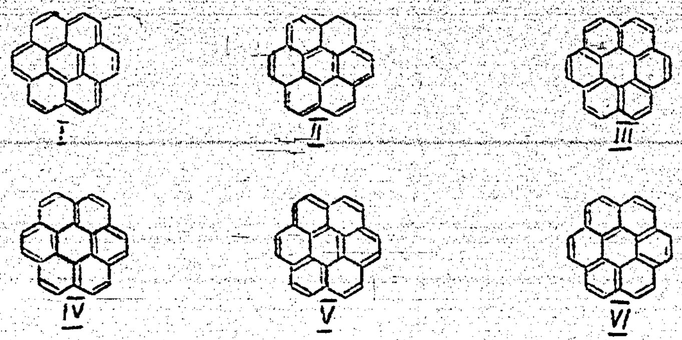


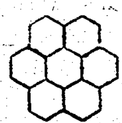
Figure 2.

We can construct a number of formulas to represent the compound $C_{24}H_{12}$. An inside ring is surrounded by an outer, and the two are interconnected by some kind of spokes. In I and II they are single, in III they are double; in IV to VI they are of mixed types. All the formulas differ from each other by the arrangement of the bonds, i.e. of the pairs of electrons (each bond is a pair of electronos). We know now, that in every case, when many formulas can be drawn, which differ from each other only in the distribution of electrons, but in which the sequence of the atoms is the same, no concrete meaning can be attached to any of the formulas, i.e, there are no real isomers I to VI, but only a uniform coronene, and that the above formula are nothing more than symbols which limit the actual combination state of the coronene.

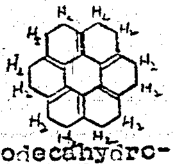
We speak here of course of a quantum-mechanical resonance, or mesomerism between the limiting cases, which may be pictures as a very rapid oscilation. Such mesomeric systems are of lower energy content than computed for each individual formula. The limiting formulas may however occur as reaction formulas. It is therefore entirely possible that one or another formula may appear "in the form of one of its reaction product", without proving in this way anything about the correctness of the formula. If then the dodeca hydro compound be obtained by careful hydrogenation of coronene, and the formula for the hydrogenated compound is as represented in figure 3, we must assume that coronene had reacted according to formula III. It is however to be suspected, that formula III does not generally represent all the properties of coronene. Formulas I and II with simple spokes and a circle of conjugated double bonds may be the favored two. In agreement with this, intermediate stages are very difficult to obtain in the hydrogenation of coronene; one gets essentially immediately a perhydrogenation, similarly to the symmetrically constructed benzol, which does not produce by direct hydrogenation with hydrogen under pressure the di and tetrahydro benzols, and the hexahydrobenzene is alone obtained.

The perhydrogenation of coronene was accordingly performed first. The low solubility of the hydrocarbon is here unfavorable. We choose a suspension of coronene in a five fold amount of decalene. Tungsten sulfide was used as a catalyst. The partial pressure of hydrogen was 300 or 600atmthe temperature 270° C. (Naturally at 450° and above, even under a high partial pressure of hydrogen there are simultaneously reactions of hydrogenation and dehydrogenation of the hydrogenated coronene).

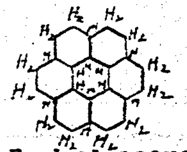
Such perhydrogenated coronene prepared in a single step crystallizes from benzene in long, fine, white



Coronene
M.P. 432°
(corr.)



Dodecahydrocoronene
M.P. 363°
(corr.)



Perhydrocoronene
Isomers: 1) M.P. 370
2) " 203

Figure 3

needles, m.p. 370° (corr.). It boils at 430° and is unaffected by hot sulfuric acid. Heating with selenium to 360° results in the back formation of coronene.

Numerous isomers of perhydrogenated coronene are possible (figure 3). Thus, the mother liquor of the hydrogenation products of coronene contained an isomeric perhydrocoronene. It is considerably more soluble in benzene than the principal product. It also forms white needles, but more mat in appearance. M.p. 203°, This product as well was dehydrogenated by selenium. The proportion in which the two isomeric perhydrocoronenes, m.p. 370° and 203° are formed is about 1 : 10. A somewhat higher proportion of the lower melting isomer is obtained with a nickel-containing catalyst.*).

Attempts first made of producing partially hydrogenated coronene were unsuccessful. All we obtained

*). In the hydrogenation of polycyclic aromatic compounds with Ni as catalyst, the isomer with the lower melting point appears to be preferentially formed. This is particularly well shown in the perhydrogenation of pyrene. The Ammoniakwerke Mersoburg used Ni as catalyst; there is in addition the work of Ituo Kagehira (C. 1932, I,p. 1359). A liquid perhydrated product is here principally obtained, b.p.$_{760}$ = 290 - 310°; and in addition small amounts of a solid perhydropyrene, m.p. 88 - 89°. When, however, pyrene is hydrogenated with a tungsten sulfide catalyst, we obtained a new isomer, as the almost exclusive solid product, glass clear prismatic crystals, m.p. 104°, with a trace of some other isomer, mat-whiteneedles, m.p. 67°.

was a mixture of the unaltered and the perhydrogenated coronene. A partially hydrogenated product was first obtained with a mixed sulfide catalyst, the ultimate analysis of which agreed with the formula for hydrocoronene $C_{24}H_{24}$. It crystallizes in small yellow quadratic platelets, m.p. 353° (corr.). It forms no picrate. Coronene dissolves in hot sulfuric acid with the formation of a beautiful green solution with a blue fluorescence, dodecahydrocoronene forms a blood red solution with red fluorescence. This dodecahydrocoronene is only present, to-gether with the unaltered and perhydrogenated coronene, in exceedingly small proportion in the reaction product. When examining the formula for dodecahydrocoronene shown in figure 3, the product appears rather unstable. It apparently is very readily hydrogenated further.

Properties of Coronene and its Hydrogenation Products

	Formula	M.p. (corr)	b.p. 760 mm	picrate	hot H_2SO_4
coronene	$C_{24}H_{12}$	432°	525°	308°	green; red fluorescence
dodeca-hydro-coronene	$C_{24}H_{24}$	353°		no picrate	red; red fluorescence
Perhydro-coronene	$C_{24}H_{36}$	370°	500°	---	unattacked

	Formula	M.p. (corr)	b.p. 760 mm	picrate	hot H_2SO_4
Isomeric hydrocoronene	$C_{24}H_{36}$	204°	500°	--	-
Molecular compound: Coronene + hydrocoronene	$C_{24}C_{24}$	428°		-	-

Figure 4 shows the properties of coronene and the hydrogenation products discussed here, as well as a molecular compound, about which more will be told below.

Perhydrocoronene forms a stable molecular compound with coronene. Mixing the two components in the proportion 1 : 1, and crystallizing from xylene, the molecular compound is deposited forming needles, m.p. 406 - 408. This molecular compound is so stable, that coronene, which forms an exceedingly insoluble picrate, can not be extracted from this compound with picric acid. When therefore some unaltered coronene and perhydrogenated coronene are present in the reaction mixture from the hydrogenation of coronene, there must also be some of the molecular compound, and one may be readily misled into believing in the existence of dodecahydrocoronene, because the analysis gives the exact values for it.

This molecular compound can also be very clearly recognized from an examination of the (uncorrected) melting point diagram of the components (figure 4). The curve of the melting points of mixture of coronene and perhydrocoronene (m.p. 412 and 350° , resp.)

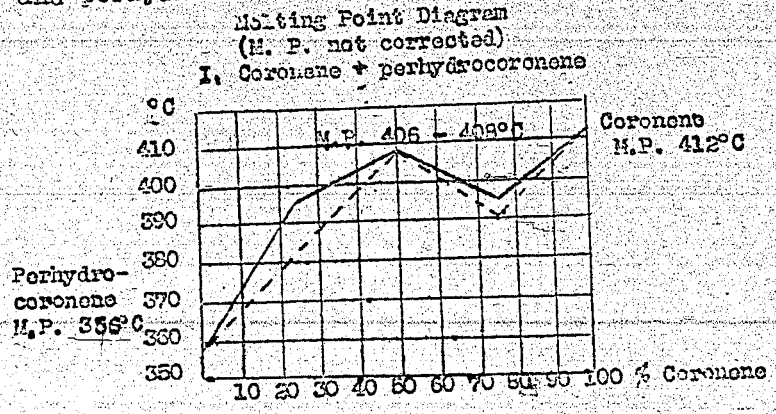


Figure 4

shows a distinct maximum between 406 and 408°, with a proportion of 1 : 1, i.e. at the composition of the molecular compound. This mixture produces minima of melting points in the usual way with the two individual components. *).

An other peculiarity of the perhydrogenated coronene is the strong phosphorescence it exhibits with about 2 percent coronene, i.e. it emits a strong orange yellow glow after a short illumination with

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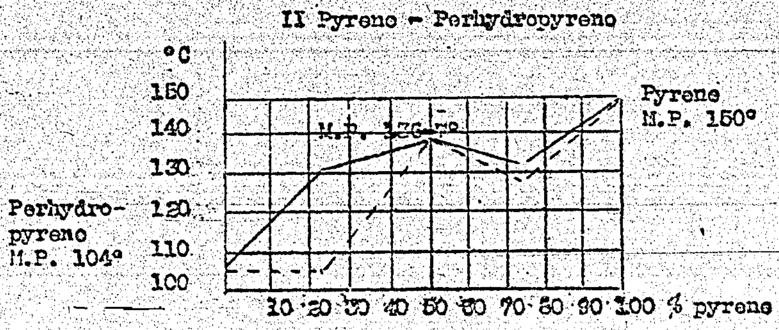
*) Pyrene behaves quite similarly. Its melting point is 150°, a mixture with hydrogenated pyrene melts at 104° . The melting point diagram (figure 5) indicates here as well the existence of an undoubted molecular compound, m.p. 136-137°. This complex decomposes however very readily back into its components.

ultra-violet, daylight or artificial light. The phenomenon is entirely similar to that seen with other crystalline phosphorus, e.g. zinc sulfide.

In the phosphorescent sulfides traces of other heavy metal sulfides must be intercalated. The phosphorescence of the hydrogenated coronene contaminated with coronene must be connected with the crystalline state: the two substances are permitted to crystallize to-gether from solutions or from the molten state. This compound is of further interest in that it fluoresces in a short-wave blue light, but phosphoresces with an orange-yellow color. When the substance is heated, the color of the phosphorescence changes reversibly to blue at 74°, evidently as a result of a change of modification. The illumination lasts about 1 to 2 minutes, a long time for the phosphorescence of an organic substance.

The two phenomena just mentioned, the relatively stable molecular combination and the phosphorescence is possibly caused by the hydrogen atoms in the inside of the hydrogenated molecule, in coronene on the inner benzol ring, in pyrene at the inner double bond (hydrogen bridges)

Figure 5.


II Pyrene - Perhydropyrene
°C
150
140
130
120
110
100
M.P. 136-138
Pyrene
M.P. 150°
Perhydro-
pyrene
M.P. 104°
10 20 30 40 50 60 70 80 90 100 % pyrene

Wiley

820

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUELS
LOUISIANA, MISSOURI

TOM Reel No. 162, Frames 423 - 426 T-336

W.M. Sternberg

High Pressure Experiments

Lu. 558 Feb. 9, 1943

PRODUCTION OF PYRIDINE FROM THE LIQUID PHASE PRODUCTS FROM BROWN COAL

Preliminary Experiments

Summary

Bases and phenols from brown coal liquefaction products were washed out in glass columns with 10 percent sulfuric acid and 10 percent sodium hydroxide. The bases were set free by neutralization with gaseous ammonia, separated, and pyridine determined in them analytically.

The amounts in the different products were as follows:

Liquid phase gasoline, - 165°, from Lu. Catchpot
0.012 - 0.014 percent pyridine

- 200°, from Rhenish brown coal
0.019 - 0.022 percent pyridine

Liquid phase middle oil, + 165°, Lu. Catchpot
0.042 - 0.056 percent pyridine

According to information in literature, pyridine forms compounds with the phenols present in solution, and it is to be suspected that it will be found in higher fractinns than corresponds to its boiling

point (116°). This fact seems to be confirmed in the higher percentage of pyridine content of the middle oil.

No reduction in quality of the products is to be feared from the removal of the bases. The experiments are being continued.

/s/ Botter

With Dr. Donath
Wittmann
Furst

Apparatus and Recovery of Bases (Phenols).

For the scrubbing of the liquid phase products from bases and phenols glass columns about 160 cm long (135 cm with Raschig rings about 3 x 6 mm) and 6 cm diameter were used. The products were fed from below counter currently to the 10 percent sulfuric acid or sodium hydroxide (fed dropwise from above). Between the two scrubbers and behind them was a water scrubber consisting of a 85 cm column, also filled with Raschig rings.

Attempts to distribute the feed as fine as possible by using fritted glass inlets were successful only with gasoline; with middle oil there was a plugging up.

At first the breaking up of the double compounds of phenols and pyridine was done by means of sodium hydroxide solution. Water scrubbing was followed with sulfuric acid wash, and then again with water. A thruput was maintained of 1000/g of the feed, 200 g 10 percent NaOH, 200 g water, 200 g 10 percent H_2SO_4 and 200 g water.

The total wash acid (the alkali was only studied once) was separated from the entrained oil in a separatory funnel, and distilled for the separation of alcohol, etc. Gaseous ammonia from a steel cylinder was fed under cooling (below 15°C) into the acid solution until the solution reacted alkaline. The liberated bases were recovered in part by separation in a separatory funnel and in part by extraction with ether.

Pyridine was determined by titration (Astruc, C.R. vol. 129, 1899, p. 1021) in the 70 - 160° fraction after distilling off the ether and fractionation, or by the precipitation method with cadmium chloride (Malatesta and Germain, Bull chim. et farm., vol. 53, 1914, p. 225).

Changes in the product are shown in table 1, the results of the determination of bases in table 2.

Table 1 shows that only the bases and the phenol contents have changed (no figures given). The washing has not however been sufficiently thorough to remove all the bases.

Table 2 shows that the crude base contents of the products was more reduced in the higher boiling point range, - about two to three times as much in the middle oil than in gasoline, - , and that the three products contained similar proportions of pyridine in the crude bases.

Table 1.

	Liquid phase gas. Leuna, P 1251 -165°		Liquid phase m.o. Leuna, P 1251 + 165°		Liquid phase gasoline from Rhenish brown coal K 229, -200°	
	before scrubbing	after scrubbing	before scrubbing	after scrubbing	before scrubbing	after scrubbing
Spec. grav, 20°	0.750	0.753	0.936	0.927	0.781	-
Aniline point, °C	26.5	27	9.5	12.5	18	-
Start. b.p.°C	53	66	178	158	70	-
percent - 100°	46	41.5-200°	4	7 -100°	19	-
- 150°	95	95.5-250°	52.5	61.5-150°	80	-
- 170°	-	—300°	90.0	83.5-170°	95	
Final b.p.	164/98	163/98.5	321/99	330/98	233/99	
Phenols	0.125	-	24.43	-	0.92	
Bases (mg NH_3/li)	984.0	56.6	978.0 (?)	76.5	168	40.8

Table 2.

Analyses of the recovered crude bases

	P1251, -165°C		P1251+165°		K 229 S gas. - 200°	
kg starting matter	95		18		80	
g crude bases, ether-free, moist,	135		194		189	
Decomposition of crude bases 70-160° fract,:						
upper layer, percent H_2O	66.3	(89.5)	39.0	(75.5)	77.0	(145.6)
percent pyridine (titrat.)	19.2	(26.0)	-		1.1	(2.0)
percent pyridine ($CdCl_2$)	14.5	(19.5)	61.0	(118.5)	21.8	(41.4)
Lower layer:						
percent pyridine (titr.)	3.7	(1.0)	-	-	9.0	(0.2)
g crude bases, dry		118.2		141.1		171.8
percent crude bases in orig. product	0.125		0.786		0.215	
g pyridine in crude bases after titration		12.8		10		17.2
after $CdCl_2$ pption		10.8		7.5		14.9
percent pyridine in crude bas.	9.1-10.8		5,3-7.1		8.7-10.0	
percent pyridine in original product	0,012-0.014		0.049-0.056		0.019-0.022	

825 T-337

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

KCBraun
4-24-47

De-ashing Experiments on Brüx Tar

(See also T-204)

By Lemme, Ludwigshafen
28 January 1942

Brüx tar (P 1397 original) has an ash content 0.05 to 0.065%. The possibility of an eventual separation of dissolved ash constituents in converter operation impelled us to experiment on separating the ash. We tried to accomplish this by chemical and physico-chemical means.

1). Chemical Deashing

Because we might have to deal with iron or possibly zinc-phenolate in case the ash was dissolved, the tar was intensively agitated for several hours with a 2% aqueous solution of equal parts of ammonium bicarbonate and ammonium sulfide @ about 60°C, then separated from the aqueous phase and freed of the adhering water by stirring @ 105°C. It was then filtered twice @ 100°C. The filtrate, practically free of solids, showed practically no change in its ash content, rather slight increase to 0.075%, which, however, is within the range of possible errors.

2) Physico-Chemical Deashing.

Here we tried to obtain some effect by means of adsorbents. In one case, 1/2% Grude, charge 12, (carbonization coke) was stirred with the tar @ 100°C and then filtered twice. In another case, the tar was similarly treated with 1/2% terrana. Here, also, the filtrates showed practically no change in ash content, 0.06% with Grude, 0.1% with terrana.

Apparently, both methods were inadequate to effect a deashing under the given conditions. Possibly similar treatments under pressure might be more successful. The microscopical examinations were very interesting. While the original tar shows a copious flake formation and no solid constituents, the filtrates show practically no solids. (?). It is further remarkable that in the tars treated the addition of benzol improved the separation of asphaltic substances, as compared with the untreated. The original tar contains 2% benzol solids, that treated with ammonium carbonate or sulfide 4.5%, that treated with Terrana 4.3%, and that treated with Grude 2.6%. In spite of these solids contents, the total ash values are practically the same. The copious flakes in the original tar are likewise of apparently asphaltic nature, since they do not increase the ash content either.

/pkl

DR. STORCH

T-338

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

826 KCBraun
4-24-47

Gasification in Aromatization at 250, 450 and 600 atm

By Peters & Wehm
Ludwigshafen
23 March 1941.

A. When Running to 50-50%/wt. Aromatics (Table 1)

The higher pressure reduces gasification by 1 to 2%. In comparison with catalyst 7019, 3 to 4%.

The C_4 constituent in the gas is the same at 250 and 450 atm. The iso-C_4 content in the butane is at 450 at least twice as high as at 250 atm.

B. When Running to 20 - 45% Aromatics (Table 2)

When operating to less than 50% aromatics in the gasoline, the high pressure reduces gasification by about 5%.

The butane content in gasification is increased at high pressure only when the concentration of aromatics in the gasoline is very low, e.g. 20%. The iso-butane content of the C_4-fraction is considerably higher at 450 and 600 atm. than at 250 atm. The residual gasoline is, therefor, also somewhat better at high than at low pressure.

The following tables contain individual values of the gas analyses and the C_4 and iso-C_4 determinations. However, the entire experimental data for the past year is being statistically checked by Dr. Günther in order to obtain reliable mean values.

/pkl

TABLE 1

Aromatization of Bit. Coal Liquefaction Middle Oil @ 250 & 450 atm. H_2-Pressure, with Reflux over 160°C run to 160° Gasoline with 50 - 55%/wt. Aromatics

	250 atm.		600 atm.	450 atm.	
Catalyst	7019	Act. Alum. 8 SiO_2 10 Cr_2O_3 2 Zn O 0.5 MoO_3	7019	Chromium silicate 2 MoO_3	Terrana 3 Cr_2O_3 0.1 MoO_3
160° Gasol. Yield	0.3	0.28	0.4	0.3	0.3
Wt.% Aromatics	56	52	55	54	49
Vol. % Aromatics (not corrected)	51	47	50	49	44
% Gasif/Gasol. + Gasif. (unstab)	21	18	18	16	16
" " + Gasif. (stab.)	23	20	20	19	19
% C_4 in Gas	20	ca 25	20	20	26
iso-C_4 in C_4	12	20	30 ?	35	40 ?
Yield % Gasol.	77	80	80	81	81
% Gasol. + C_4	81.6	85	84	85	86
Resid. Gasol. O. N.	58	68.5	57.5(calc)	55(calc)	58(calc)
Resid. Gasol. > 100 O. N.	48	54	-	-	-

TABLE 2

Aromatization of Bit. Coal Liquefaction Middle Oil @ 250 & 450 atm H_2 - Pressure, with Reflux over 160°C run to 160°-Gasoline with 20 - 35%/wt. Aromatics

Pressure	250 atm.		600	450	600	450	600
Catalyst	Act. Alum. 10 ZnO 4 MoO_3	Terrana 10 MgO 20 MgMolyb.	Terrana 1 % MoO_3 or 6434	6108 10 CrF_3 5 AlF_3 0.5 MoO_3	New Welheim	New Welheim	Old Welheim
160° Gasol. Yield	0.40	0.27	0.62	0.53	0.50	0.38	0.27
Wt. % Aromatics	35	43	21	35	35	37	38
Vol.-% Aromatics (not corrected)	32	39	19	31	31	33	34
% Gasif/Gasol + Gasif. (unstab)	18	15	19	12	10.5	11	14
% Gasif/Gasol + Gasif. (stab)	24	19	13	16	14	14	18
% C_4 in Gas	35	33	50	25	-	32	30
iso-C_4 in C_4	25	24	50	57	-	48	30
Yield % Gasol.	76	81	87	84	86	86	82
% Gasol. + C_4	84	87	93	88	90	90	87
Residual Gasol. O.N.	63	54.5(calc)	70		66.5(calc)	64.5(calc)	63.5
Residual Gasol. 100 O. N.	51	-	64		-	-	52.5
180° Gasol. Yield	0.51	0.34	0.70	0.66	0.60	0.47	0.34
% Gasif/Gasol + Gasif. (unstab)	14	13	8		8.5	9	11
% " " + Gasif. (stab)	20	15	11		11	11	14.7

Carbonization

DR. STORCH

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

829

T-339

KCBraun
4-24-47

PRODUCTION OF ELECTRODE COKE BY PRESSURE CARBONIZATION (L.T.C.)

By Pfirrmann, Ludwigshafen
27 Jan. 1942

(See also T-330)

A. Hydrogenation

Two cases are possible:

1) The filtrate obtained in filtering the letdown, which includes the pasting middle oil, is used as feed (Ausgangsmaterial). When pasting 1:1, therefor, at least 100 parts of middle oil must be evaporated for each 100 parts of bitumen.

2) The hot bitumen coming from distillation @ 200 - 250°C is used for injection.

The processing is as follows:

The filtrate from filtration or the molten bitumen is pumped, while still hot, into the pressure coking chamber, by way of a preheater heated to 400 - 475°C. The pressure in the coking chamber is maintained @ 4-15 atm. The coking temperature is about 460 - 500°C. To provide the necessary coking heat, an alternate quantity of flushing gas (Spülgas) or steam (0.3 - 2 m³/kg) is heated to a temperature of 500 - 600°C and mixed with the liquid L.T.C. Feed at its entrance into the coking chambers. There are several of the latter and these are alternately emptied after filling.

The coke, still containing 5 - 10% volatile constituents, is broken up and heated for about 2 - 3 hours to 1000 - 1150°C in a coke oven, then dumped into cooling cars and is now ready for shipment.

The distillate coming from the carbonization chambers together with the flushing gas is cooled under pressure and stored in supply tanks. The high temperature tar obtained in heating the carbonization coke, about 2 - 3% of the latter, is also stored there. Both are distilled together. From the fraction 200 - 300°C obtained in distillation, the amount required for pasting is recycled and the residual oil is utilized as fuel oil. All gas is freed of gasoline under pressure and recycled and the excess gas is decompressed after recovering the liquid gas components.

B. The Processing of Carbonization Tar.

This is about half way between the carbonization of filtrate and melted bitumen. The tar must first be filtered with filter aid, to reduce the ash to a maximum of 0.1%. In pressure carbonization it requires about

10 - 20° higher carbonization temperatures than primary bitumen. In appearance, the coke resembles that from bitumen, is possibly a little denser. The ash, up to now, has always been higher than in hydrogenation bitumen coke.

The following table contains the results obtained in carbonization:

Feed Material	L.T.C. Oil	Coke	Gas + Loss	Ash in coke	Mi-oil in L.T.C. oil
Bitumen filtrate, 23.5 mV, 300 atm	76.0	19.5	5.5	0.20	75.0
Bitumen, free of pasting oil, 23.5 mV, 300 atm.	41.5	49.0	9.5	0.1	25.0
Bitumen filtrate 25 mV, 700 atm.	76.0	17.0	7.0	0.15	75.0
Bitumen, free of pasting oil, 25 mV, 700 atm.	31.0	60.0	9.0	0.25	29.0
Flush. gas tar, filtered	63.0	30.5	6.5	0.6	45.0
Schlesag tar, filtered	64.0	28.0	8.0	0.5	52.0

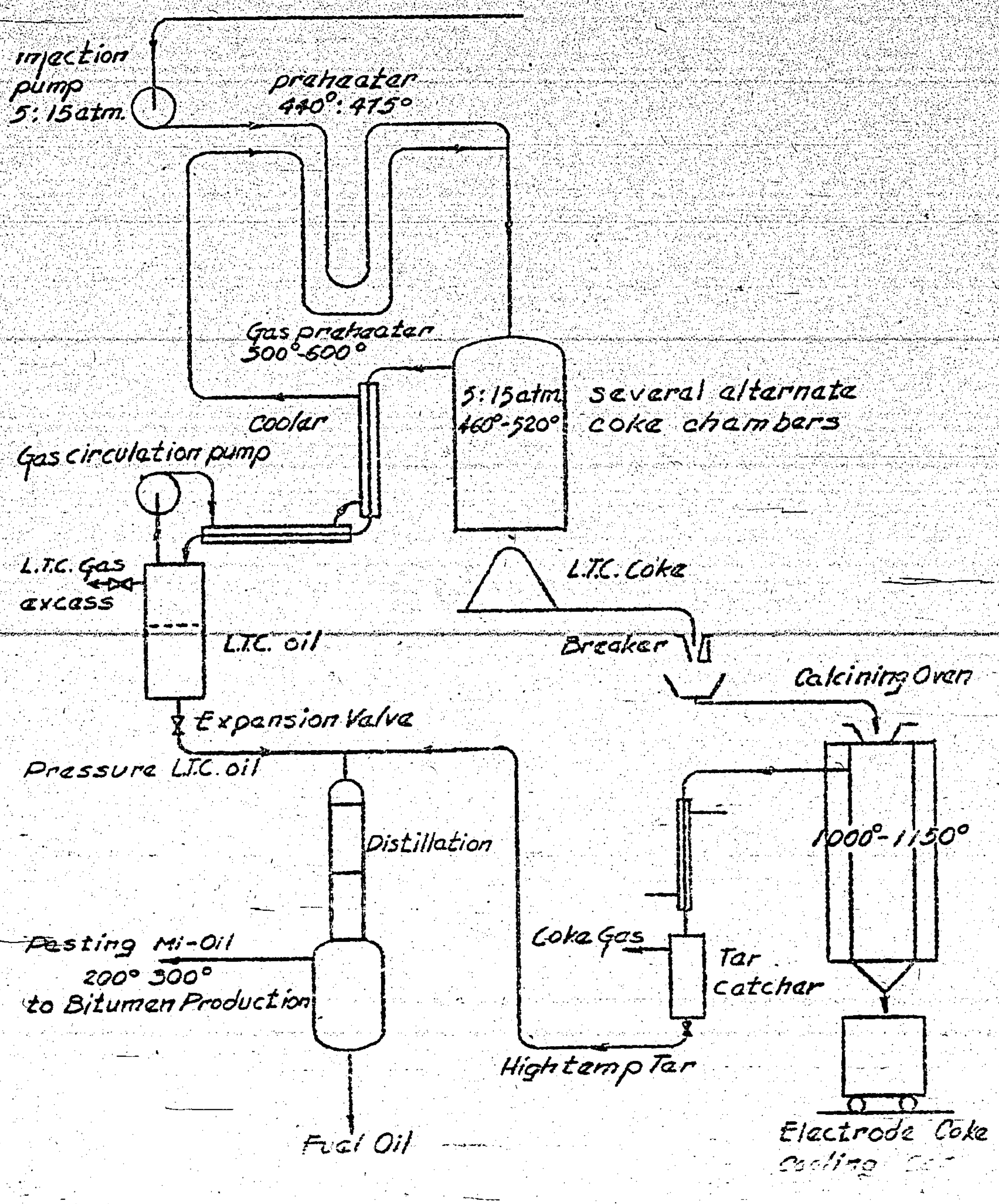
The results of the above experiments may vary with the carbonization conditions. The middle oil content, e.g. can be increased by higher temperature or pressure or less flushing gas, whereby the coke yield rises and the L.T.C. oil yield drops correspondingly. If, e.g. we figure on a yield in bitumen of 80% of the pure coal, we get 7 - 10% middle oil @ 325°C, based on pure coal, in the carbonization of this bitumen.

/pkl

Production of Electrode Coke

General Flow Sheet

Molten ash-free distillation residue or filterate



U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-340

KCBraun
4-25-47

Steps to be taken as a Result of the Explosion at Pölitz, June 26, 1942

Ludwigshafen, 2 July 1942
(See also T-307)

A. - Operation.

1) Emergency Letdown at Gas Failure.

The failure of coal stalls 15/16 again showed that the stalls are seriously endangered, even with partial gas failure. This is particularly true if the cold gas also fails at the same time. When this happens, the stalls in question should be emptied immediately (emergency letdown), without trying to force the gas to flow.

2) Course of Temperature Rise.

The temperature in Converter 2 rose from normal 25.0 mV to 27.0 mV in about 5 minutes. From here on the temperature rises to about 40 mV and above in another 3 to 5 minutes. Consequently, emergency expansion must be conducted so that the converters are largely emptied of liquids in about 5 minutes.

3) Cold oil connection to the top of the converters or the connecting lines. Oil reserve in accumulator to bridge over period till pumps can be started.

B. - Design.

1) Each stall should properly have a separate line to the emergency letdown tower. Also, the letdown nozzles (valves) at each converter should be of such a size that the 5 minute period can easily be met.

2) Automatic temperature control, even if only the most important elements.

3) The use of full-wall tubes for all rising lines even for old installations, as specified for new installations since the spring of 1941. The risers should not be insulated or should even be provided with fins.

4) Reinforcing the partition walls and increasing the height of the back wall of the stalls.

5) Fastening the connecting lines between the converters preferably at their highest point to prevent them from being hurled away.

6) Electrical ignition device at the top of the stalls. (To prevent accumulation of explosive gases by immediate ignition on their escape from converters or lines.)

7) Protection against flash flames of unprotected buildings in the vicinity.

8) In order to prevent liquid pockets in dead portions of circulating lines, a suitable by-pass between pressure and suction side should be provided so that there is some flow in these parts, e.g. 1000 m^3/h.

9) Provide separators at the ends of the circulating lines before the stalls.

10) Provide intermediate expansion with at least 3 valves between each 2 shut-off valves in circulating lines.

11) Since the circulating lines are not of equal length and, consequently, do not have equal flow thru them, the flow could be controlled by measuring the pressure differences, e.g. every 100 m in each circulating line.

/fkp

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

834

TOM Reel No. 162, Frame 370

T-341

W. M. Sternberg

High Pressure Experiments

Lu. 558

Feb. 18, 1943

CORONENE

The principal solid aromatic substances obtained during the industrial hydrogenation of coal and coal tar in Scholven and Pölitz are pyrene and coronene.

Amounts: pyrene abt. 1 - 2 percent
calculated to gasoline
coronene " 0.1 - 0.3 percent

Coronene: formerly only accessible in small amounts from complicated synthesis.

Properties: melting point 425° (corr.)
boiling point 550° (corr.) at 760 mm
mol. weight 300 ($C_{24}H_{12}$)

Uses of coronene:

1) In dye manufacture
   a) vat dyes (I. G. Lu., alizarine lab. patent)
   b) Sulfur dyes (I. G. Wolfen patent)

These dyes are distinguished by a particular light-fastness

2) for fluorescence (glow in ultra violet light) and phosphorescence (afterglow)

Coronene fluoresces yellowish-green does not phosphoresce Perhydrated coronene fluoresces blue, with 2 percent perhydrocoronene phosphoresces yellow.

The fluorescence and phosphorescence properties are occasionally found in other organic compounds, but are particularly strongly expressed in coronene. The phosphorescence lasts 1 - 2 minutes; is therefore at present only of scientific interest. (Inorganic phosphors are known which glow for many hours).

These values have been calculated from the present contents of the kiln oils. Nothing is known about the production of these aromatics if they are continuously extracted.

It must be observed that these amounts of the solid aromatic compounds are produced at 300 atm pressure, and that at 700 atm the amounts are greatly reduced. (At any rate, no crystals are formed in the fractionation distillation of the kiln oils, possibly because they are present in a partially hydrogenated form, or else because of the presence of other substances which interfere with the crystallization.)

More carbazol is found in the hydrogenation of tar (about the double amount, preformed in the tar), much less pyrene, and about half again as much of coronene (about 1.5 percent in the kiln oil).

IV Production.

Carbazol and pyrene are produced by the fractional distillation of kiln oil.

Coronene can be readily produced during the refining hydrogenation of kiln oil distillation residue at 400° and 760 mm pressure. The coronene may then be readily separated from the oil by filtration.

All these hydrocarbons are formed preferentially during the hydrogenation, and during their isolation their direct formation in a pure state after a single recrystallization offers a distinct advantage.

V Applications.

Carbazol: As polyvinyl carbazol (Lovican) plastic, I.G. Lu.

b) tetranitrocarbazol (Nitrozan) for pests control, I.G. Höchst. Pyrene. Generally in dye production. I. G. Höchst.

Coronene:

1) Technical: as intermediate in the production of lumogenes (fluorescing dyes)

b). in the manufacture of dyes:

Vat dyes; Alicarin Division, Lu.

Sulfur dyes, I. G. Wolfen; dye cotton khaki brown shades. The dyes posses, in addition to good stability, also a good light resistance.

2) Scientific:

Coronene has some interesting properties, such as:

a) Formation of phosphorescing compounds by the addition of coronene to perhydrogenated aromatic compounds (afterglow), with a strong and long phosphorescence (about 2 minutes), such as has been unknown so far in organic substances.

b) Strong tendency to formation of complexes with, e.g. perhydrocoronene)

c) As an intermediate for a large class of compounds, extending into the field of asphalts, coronene may assist in the studies of such compounds.

VI Properties of the principal aromatic compounds:

	crystalline form	melting point	boiling point
Carbazol	flakes	238°	338°
Pyrene	"	150°	270°
Coronene	needles	432° (corr)	550° (corr.)

VII Chrysene: In the dehydrogenation of vapor phase gasoline (160 - .190° fraction) over K 7360 some chrysene is formed, in amounts of the order 0.05 percent of the raw material. Chrysene is formed from 2 moles of indene, which is present in the 160 - 190° fraction.

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-342

839

KCBraun
4-25-47

Phenol Recovery with Liquid Ammonia

By Dr. Heilmann, Ludwigshafen, 3 August 1943

Summary.

The phenol recovery plant was completely destroyed by the explosion on July 27, 1943.

This article is a report on the results obtained to date, as far as this is possible without operating data, which were also destroyed.

From a hydrogenation middle oil from Gelsenberg containing 18% phenol, 86 to 96% concentrated raw phenol was obtained. Since the neutral oil obtained was free of phenol, and no phenol losses can occur in the process, e.g. thru oxidation, dehydroxidation, etc., we may assume that the yield was quantitative.

No data are available on the recovered neutral oil.

PROCESS.

The middle oil entered the top of a column 4m high, e.g. 5 Litr/h, in which liquid ammonia rose from the bottom at the rate of 4 Litr/h. The phenol was quantitatively absorbed by the liquid ammonia. The ammonium-phenolate solution also absorbed a certain portion of neutral oil. The charged ammonia, whose density could not be determined, was carried over at the head of the column, while neutral oil free of phenol accumulated at the bottom of the column and could be drawn off. The quantity of this neutral oil varied somewhat and averaged 2.8 Ltr.

The ammonium-phenolate solution carried over was washed with light gasoline in a second column 4m high, in which the ammonia entered at the top and the gasoline (15 Ltr.) at the bottom. The light gasoline, density 0.672, almost quantitatively absorbed the neutral oil, which was probably dissolved in the ammonium-phenolate solution, either molecular or colloidal, as well as a small amount of phenol (abt. 1%) and ammonia. Its density rose to 0.710 to 0.720 in this process. It was carried over at the top of the column and caught in a storage vessel. It was freed of its dissolved constituents by pressureless distillation and then returned to the process.

The ammonium-phenolate solution, which left an evaporation residue with approx. 40% phenol before the gasoline wash, produced a raw phenol with 86 to 96% pure phenol after washing with gasoline.

The density of the washed ammonium-phenolate solution could not be determined because of technical difficulties. The product accumulated at the bottom of the second column and was drawn into a storage vessel from there. The phenol was freed of ammonia by pressure distillation and the ammonia returned to the circulating system.

The equipment was in operation 4 days. Towards the end it was run with twice the thruput (10 Ltr. oil, 8 Ltr. NH_3, 30 Ltr. gasoline, per hour) without appreciable difficulties.

No balance could yet be made.

/fkb

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-343

840

KCBraun
4-25-47

Substituting Cooling Oil for Cold Gas

Dr. Pier's Files, 13 June 1942

Cooling oil (catchpot heavy oil) was substituted for cold gas in the coal stalls at Wesseling, whereby the formation of caviar was greatly reduced though not quite entirely eliminated. Dr. Peukert of Wesseling mentioned this further advantage of cold oil over cold gas, that the cold oil has a notable wash-effect and thus greatly relieves the circulating gas washing.

However, the complete elimination of cold gas and its replacement by cold oil also has one disadvantage, briefly mentioned here:

__When operating with cold gas__ the H_2-consumption of each converter is more than covered by the cold gas. The H_2-partial pressure in the following converters is somewhat lowered only by gasification (C_1H_4, etc.), because converter input gas and cold gas have the same composition.

__When operating with cold oil__, however, not only is the input gas reduced by the H_2-consumption of each converter, but gasification also sharply depresses the H_2-partial pressure, since less H_2 passes thru the converters in total.

With full thruput conditions in Wesseling are the following:

Paste thruput/stall		45.2 t/h	
of which pure coal, about		17.0 t/h	
Input gas (Converter I)	30000		50000 m^3/h
of which H_2 (80%)	24000		40000 "
" " pollutions (20%)	6000		10000 "
H_2-consumption/stall		17000	
H_2 remaining in last conv.	7000		23000 "
Pollutions in last converter	9000		13000 "
Total gas in last converter	16000		36000 "
H_2-partial press. in last conv. (@670 atm total press.)	290		430 atm

It is apparent that even with a gas input of 50000 m^3/h, the H_2-partial pressure in the last converter is only 430 atm. Since this quantity of gas would give too high velocities in the preheater, part of it would have to be added, preheated, to converter I directly, as done at Leuna.

One possibility to improve the H_2-partial pressure would be:

a) either to inject cold oil only into the endangered converters I and II, but to leave the cold gas on the other converters,

b) or to use cold oil and cold gas at the same time, in which case the cold oil takes the basic load, unregulated, while the cold gas regulates the peaks. The cold gas here must be sufficiently preheated to prevent any harmful, excessive cooling.

/fkp

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-344

841 KCBraun
4-28-47

Quality of Hydrogenation Coal

By Dr. Ost, Bergwerksgesellschaft
Hibernia, Herne,
10 Sept. 1942

In a letter of July 16, 1942, Hydro-Works Scholven reports of operating difficulties believed to be due to a deterioration of the quality of the coal, characterized by an increase in the C-content and the alkalinity of the ash.

1.) An increase in the C-content above 82% with a simultaneous decrease in volatile constituents below 38% would indeed have the effect of a more sluggish hydrogenation. Now, the figures for volatile constituents reported by Scholven are in sharp variance with the results of the mine laboratories for Scholven-Zweckel as well as for Blumenthal coal, variations such as were never found at the introduction of the coking test in the quartz glass crucible by the coal syndicate, even with high volatile coal (Gasflammkohle).

With Zweckel coal the differences are:

1942	April	May	June	July	August
Hydro-Works Scholven:	36.1	35.1	35.4	34.9	not yet known
Hibernia Main Lab:	38.27	37.97	36.68	38.46	38.27

The daily tests of the Hibernia main laboratory do not show the sharp deviations as the tests at Scholven. In order to eliminate all doubts, the Hibernia main laboratory will procure a Radmacher coking oven and clarify the differences by an umpired analysis. The C-content in the seam samples obtained in the coal wash at Scholven will also be determined by an umpired analysis. In the meantime, the ash content has been lowered to below 4% by order of the board of directors.

2). According to statements by Scholven, the alkalinity of the ash has caused operating disturbances by the formation of salt encrustations. In the acidic operations (Sauren Fahrweise) at Scholven, the Ca and Mg content of the ash is converted into chlorides which form a sticky mass of melted salt and cause encrusted walls. Such a formation of melted salt is possible at a reaction temperature of 475°C, but only if the NaCl content exceeds a certain amount. The melting points of individual components as well as of the eutectic mixtures are given below:

MELTING POINTS

Salt		Salt Combin.	Eutectic Temp.	% Content (Eutectic)
NaCl	605°C	$CaCl_2$-$MgCl_2$	621°C	57.2%/Wt. $CaCl_2$
KCl	775°C	NaCl-$CaCl_2$	500°C	52.8%/Mol. NaCl
$CaCl_2$	777°C	NaCl-$MgCl_2$	430°C	56.0%/Wt. NaCl
$MgCl_2$	711°C	KCl-$CaCl_3$	600°C	26.5%/Wt. KCl
		KCl-$MgCl_2$	490°C	33.0%/Mol. KCl

If the formation of encrusted wall is not due to still other causes, a sufficiently large NaCl content of the coal can cause a eutectic mixture and therewith a precipitation of a melting sticky mass, whose melting or sintering point is possibly lowered still more by the lead salts present; we found up to 6% lead in the water soluble in the catalyst converter residue. The chlorides of calcium and magnesium can not produce such a low melting eutectoid by themselves. Since it was never intended to be the task of a bituminous coal wash to remove the constituents of the "inner ash", the nearest to it was to remove the most important constituents of the above mentioned salt mixtures, NaCl, by more intense washing. That is why the water circulation at both washes, Blumenthal and Scholven I, was increased by adding Ruhr water; the coal was heavily drenched before going to the bunkers or loading pockets, with very good results, see below. The analysis of the drip water was not suitable for the control of the washout, because the content of these waters varies greatly and very irregularly, depending upon the manner and time of removal. Better suited for operating control is to let the load samples stand in distilled water for 12 hours, followed by titration of the chlorine content. This method of determination not only includes the chlorine content of the coal but the drip water chlorine corresponding to the water content of the coal as well, and can be done in a short time. Analyses of the drip water from Zweckel hydrogenation coal indicated that the evaporation residue consists of 91 - 92% NaCl, 1 - 2% $MgCl_2$ and 6 - 7% $CaCl_2$.

Results:

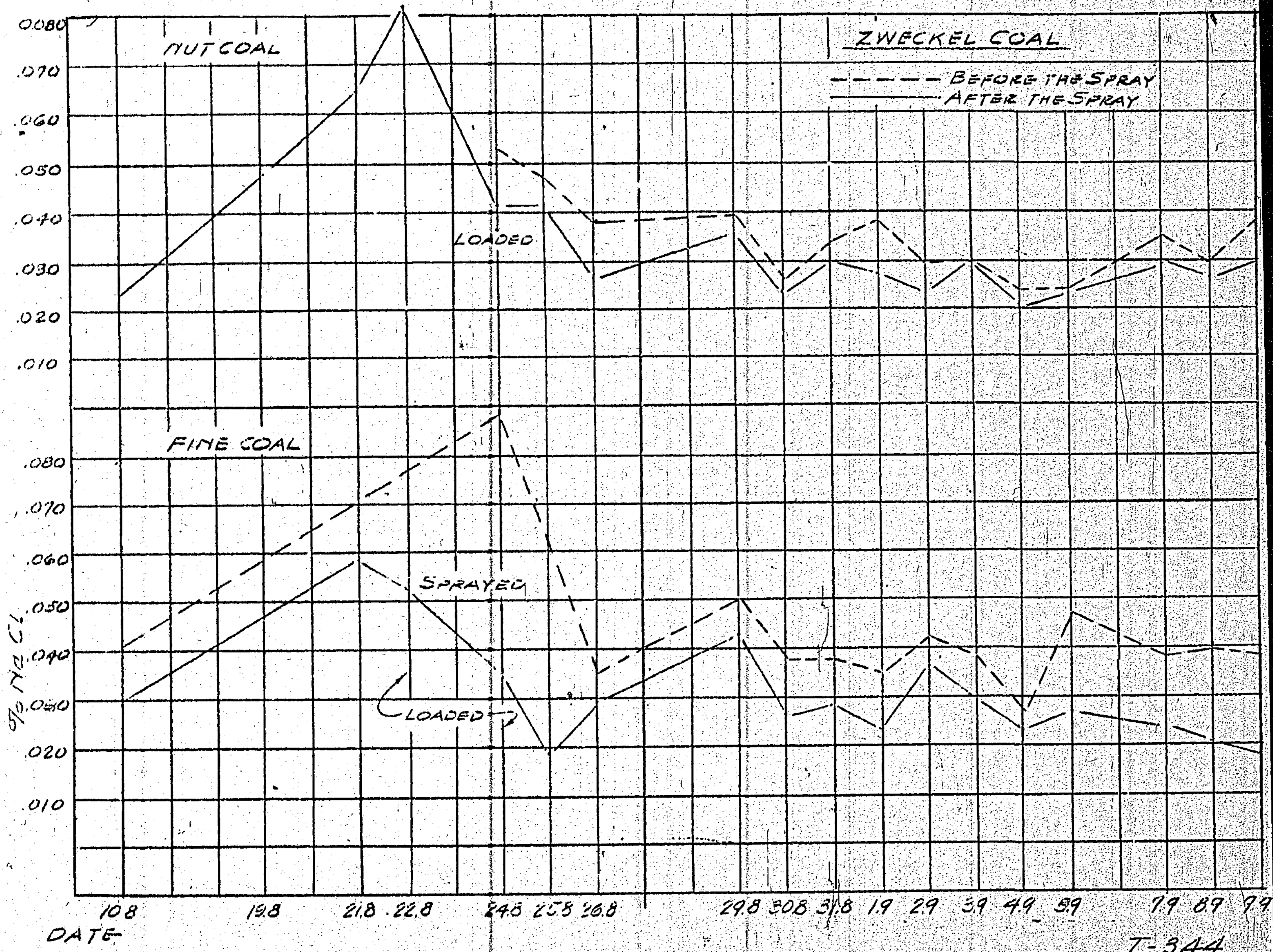
When washing 400 t/day of hydrogenation coal, Scholven I wash now uses additional 800 m^3 Ruhr water. The entire Ruhr water is used for hydrogenation coal wash, while the well water used in the past is used for washing coking coal. The hydrogenation nut coal is no longer sprayed at the loading hoppers, but by three sprays in the delivery trough to the classifying screen. In this manner the coal loses more water and taking samples at the loading hopper becomes quite satisfactory. The fine coal is also sprayed by three successive sprays on the dewatering screen in such a manner that the water is sprayed diagonally against the moving coal, thus increasing the residence time of the wash water a little. The run-off water below the sprays has only 1/10 the concentration of the circulating wash water, abt. 0.25 g NaCl/Ltr, but with this washing method it again runs into the circulating water. It would seem desirable to use the water more efficiently in future wash installations and to increase its residence time with the coal. At present there is only this advantage, that the total circulating water for both washing systems is diluted by the added water, thus also removing more of the salt from the coking coal, which is very desirable for the coke ovens and our efforts to lower the chlorine content of the coke oven tar. At Scholven I the salt content of the wash water has been reduced from abt. 2.7 g/Ltr. to 1.6 - 2.1 g/Ltr. At Blumenthal, where about 840 m^3 additional Ruhr water is used for each 800 t hydrogenation coal, the salt content of the wash water has dropped from 2.64 g/Ltr. to 1.72 g/Ltr. The NaCl content of the loaded coal is shown for Zweckel on the attached diagram and is now uniform throughout. At Blumenthal the values are the same, i.e. 0.030 - 0.035% NaCl before the spray and 0.025 - 0.030% NaCl after the spray. Consequently, the salt content has been appreciably lowered from the former 0.060 - 0.100% of the raw coal.

The salt content of the hydrogenation coal from the Nordstern mine 3/4 is 0.012% NaCl, with a water content of 6 - 8%. The circulating wash water there has a salt content of 0.7 g/Ltr. The water consumption was given as 1000 m^3/4000 t; water from the Rhein-Herne canal @ 4 pf/m^3.

However, a lower salt content of 0.018% has, at times, been obtained with Zweckel hydrogenation coal. It is to be expected that the NaCl content will be lowered further by the loss of drip water in transit.

According to a communication from Dr. Schönfelder, no further trouble has been encountered in operation. It is, therefore, desirable to find out from the hydro-works if the troubles in the catalyst converter have also been eliminated without the addition of ammonium-sulfate and if other causes of these operating difficulties have since been found, which have nothing to do with the salt content of the coal. Even though the washing and spraying of hydrogenation coal will receive more attention in the future, the mine desires to avoid too much additional water, for operating reasons, not because of the additional water cost.

/pkl


ZWECKEL COAL
Before the Spray
After the Spray
NUT COAL
FINE COAL
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SPRAYED
LOADED
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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-345

W.M.Sternberg
May 1947

845

High Pressure Experiments,
Leuna, 558.

7-9-42

A Numerical Expression of the Splitting Efficiency of Benzination Catalysts, or the Benzination Property of Oils.

From Dr. Pier's Files

Summary:

The splitting activity of catalysts have heretofore been expressed by the gasoline concentration obtained at certain temperatures. The other experimental conditions have already been standardized. A comparison of two experiments was impossible with such treatment; it was not clear, e.g., whether a catalyst giving 70% gasoline at 21 mv, is to be preferred to one giving 55% at 20 mv.

A formula has been derived on the strength of voluminous material on the relationship existing between temperature and the concentration of gasoline produced, which permits recalculating gasoline concentrations to any desired temperatures. The temperature of 19.5 mv = 382°C was selected as the standard. The gasoline concentration calculated for 19.5 mv is called the "splitting efficiency" (S), and when feeds are being tested for the readiness with which they are benzinated, it will be called their "benzination property" (B).

Another rule, as yet not based on a sufficient empirical foundation, is used in the calculation of thruputs; according to it, the gasoline concentration in tests performed under similar conditions is approximately inversely proportional to the (square?) root of the thruput.

/s/ Günther

A. Discussion of the problem and the nature of the tests.

We may briefly summarize here the problems on the small scale experimentation in benzination:

1) Testing the benzination catalyst delivered by the catalyst factory for its splitting efficiency.

2) Testing new catalysts for their splitting activity and other splitting properties (e.g. isomerization)

3) Testing the benzination properties of the a and b-middle oils, simultaneously establishing the quality of the gasoline produced.

These a-middle oils are here produced directly from the raw material by distillation (eventually to be refined), while the b-middle oils are produced either from a standard raw material with a newly developed prehydrogenation catalyst (problems of development of prehydrogenation catalysts), or of any raw material whatsoever, but using some standard prehydrogenation catalysts (problems of two-step vapor phase for any raw material for the conversion into 87 o.n. motor gasoline). The word "raw material" is used here to denote "the raw material for the vapor phase."

It would be sufficient to test a catalyst under set conditions regarding the type of converter, pressure, temperature, thruput, gas:oil ratio, etc., to pass judgement on the splitting efficiency of the catalyst or the hydrogenating property of an oil, in terms of concentration or production with a fixed final boiling point. In addition to the requirements to make gasoline with a predetermined boiling endpoint, there is in most cases also the requirements made at present of a "correct boiling behavior of the gasoline", and "the technically permissible efficiency and yield of gasoline", which can not, however, be satisfactorily answered under the fixed conditions. The experimental material collected with small converters during the last years show that all these requirements can be met by setting all the conditions <u>except the temperature</u>.

B. Fixed Experimental Conditions.

1) Type of converter: 50 ml converter, 17 mm clear width, with upward flow according to sketch RSK 3981a.

2) Pressure:
   a) for testing of batch (production of catalyst) 200 atm.
   b) for testing new catalysts, 200 or 250atm.
   c) to test the benzination property of oils - 250 atm, except in Leuna tests (200 atm).

3) Thruput.
   a) for batch testing, 2.0 kg/li/h
   b) for new catalysts 2.0 kg/li/h (occasionally 1.5 kg/li/h)
   c) for testing benzination property 1.5 kg/li/h

4) Gas:oil a) with thruput 1.5 m^3 gas:2.66 kg oil (=200 li gas/h)

b) with thruput of 2.0 m^3 gas: 2.5 kg oil (= 250 li gas/h)

5) Other specifications:

a) 0.75% CS_2 is always added to the starting material, unless otherwise specified for some definite reasons.

b) Catalysts are tested now (since about 1 1/2 years ago) with the Bruchsal Gasol (180 - 325°, a.pt. 68) in direct pass.

c) In the testing of benzination properties of oils, 6434 T pills from the catalyst laboratory are used, with a splitting activity of 0 - 70 (v.i.)

6) Temperature is set depending on results, to produce 40 - 70% gasoline from the unstabilized catchpot products, endpoint 150°, and the stabilized gasoline would contain 50 - 60% gasoline boiling below 100°. The start is made in such a way that the temperature would not have to be reduced.

C. Earlier Methods of Recording Results.

Data on the splitting activity are primarily important when testing the benzination property, also to estimate the yield of gasoline and its properties. The splitting activity is characterized by the concentration of gasoline and the temperature required for it, the yield of gasoline, the gasification; the properties of gasoline by its composition, octane rating, iodine number, as well as some possible other data on the stabilized gasoline.

Indicating the splitting activity by two numbers, (temperature and concentration of gasoline) has the disadvantage of occasionally preventing a direct comparison of results; e.g., it is not immediately clear, whether a catalyst which produced 70% gasoline at 21 mv is a better splitting catalyst than another, which produces 55% gasoline at 20 mv. For a comparative testing of feeds with respect to their benzination the following considerations may be used.

D. Derivation of the Characterization of Splitting Activity of a Catalyst or the Benzination Property of a Feed by a Single Number.

Attempts have been made to find the empirical effect of the benzination temperature upon the gasoline concentration in order to obtain a single number which would characterize splitting, and to permit then recalculating the gasoline concentration obtained at some operating temperature to a standard temperature by using some correction factor. The numerous runs made during the last years show, that when petroleum oils or coal products are benzinated with different catalysts, the concentration of gasoline increases about 1.2 times for every 0.5 mv temperature rise, when the gasoline concentration is between 10 and 75%. This relationship permits us to recalculate gasoline concentrations obtained at any temperatures to "the gasoline concentration at 19.5 mv." This value is called the splitting activity (S) when testing the catalysts, and the ease of splitting, or the "benzination property" (B) when testing oils. The formula for calculating S or B is:

$$B \text{ (or } S) = c \times 1.2^{(19.5-T)}$$

The tabulated factors of $1.2^{(19.5-T)}$ used in the recalculation are:

Operating temperature (mv)	$1.2^{(19.5-T)}$
17.5	2.07
18	1.73
18.5	1.44
19.	1.20
19.5	1.000
20	0.833
20.5	0.695
21.	0.578
21.5	0.483
22	0.403
22.5	0.336

Tests performed under other conditions than shown in section B can be recalculated to the established thruput by using a correction factor which has not as yet been sufficiently verified, on the assumption that in tests, where the other conditions were kept standard, the concentration of gasoline is inversely proportional to the square root of the thruput. E.g. when the thruput of 1.0 is to be recalculated to 1.5, the values for S or B found by using the temperature formula, is to be multiplied by 0.81, while for the recalculation of a 2.0 thruput to 1.5, it is to be multiplied by 1.15. Practically no empirical material is as yet available for the recalculation of values at different pressures.

/fkp

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV. 849 T-346

KCBraun
4-29-47

The Limits of Solids and Asphalt With Low H_2-Supply in Liquid Phase.

By Rank, Ludwigshafen, 12 October 1942

The calculation of conversion and oil balance in the liquid phase is based on the determination of solids in the products of hydrogenation. A number of solvents may be used for the determination of solids, which, in general, will give different values. The question, therefore, arises, which solvent to choose for the determination of solids.

Table I

Insoluble in Solids	Benzol	Py	Py;CS_2	Pasting Ni-Oil
H.O.L.D. Gelsenberg	21.5	18.9	19.5	--
" Scholven	30.0	21.2	18.5	--
" Extraction Lu 700 atm	9.8	--	--	6.9
" Extraction Lu 300 atm	21.3	--	--	11.8

The solvents chosen must have the following properties:

1) The behavior of the solvent with respect to its solvent properties must be similar to pasting oil in which the coal is pasted or in which the hydrogenation residues are processed, e.g. by centrifuging or filtration.

2) The solvent may not dissolve anything, or only very little, of the coal substance proper under the conditions of the analysis.

3) The solvent must well dissolve the asphalts and resins obtained in hydrogenation. It must not precipitate asphalts or resins in any case and thus simulate too high solids content.

All of these conditions are naturally met best by the circulating pasting oil. However, this oil can normally not be considered for analysis because of its high boiling curve. For this reason, solvents have been proposed for the laboratory analyses, which are easily evaporated and resemble the pasting oil most closely in their solvent properties.

The solvent used most is benzol.

As may be seen from Table I, there is very little difference between the various solvents for good hydrogenation conditions, such as running to gasoline and middle oil @ 700 atm. From this we may conclude that benzol here very closely approaches the pasting oil itself in its solvent properties and will, therefore, give true conversion values.

However, conditions change as soon as different hydrogenation conditions are employed. For example, when operating @ 300 atm to gasoline and middle oil different solvents will give appreciably different values for solids and consequently different conversions. Benzol will give a comparatively high solids value for Scholven H.O.L.D., compared to pyridine, which dissolves asphalt and resin more readily. We must, therefore, ask ourselves if benzol does not simulate lower conversion values than the related (arteigen) pasting oil would give.

With still more unfavorable hydrogenation conditions, such as extraction with H_2 addition, benzol can most certainly not be used, from our experiences. In this case, reflux middle oil from the process itself is used as pasting oil and thinning oil in let-down filtration. As shown in the table, an appreciably greater portion of the letdown obtained is soluble in middle oil than in benzol. This is particularly noticeable in 300 atm extraction, i.e. the worst hydrogenation conditions. If conversion here were calculated on the basis of the benzol insoluble, a value much lower than that obtained in the practical processing by filtration in reflux middle oil would be obtained.

From this, it must be concluded that with poor hydrogenation conditions substances are formed which are precipitated by benzol. With good hydrogenation conditions such substances are not formed, or they are formed in the initial stages and are subsequently changed by further hydrogenation so that they lose their benzol-insolubility.

For the extraction of Upper Silesian coal with H_2 addition @ 300 atm, some figures are available which permit more definite conclusions about the properties of these benzol-insoluble substances.

Table II shows the elementary analysis of benzol solids and middle oil solids.

Table II

	Benzol Solids	Mi-Oil Solids	Calculated differential substance soluble in Mi-Oil and insoluble in Benzol
% C	88.73	91.29	86.30
H	3.70	3.77	3.63
O	4.26	1.26	7.12
N	1.52	1.59	1.45
S (org)	1.79	2.09	1.50

The substance insoluble in benzol and soluble in middle oil shows a remarkably high oxygen content. An asphalt decomposition conducted by Suida and Motz with this substance gave the following results:

24.1% hard asphalt & carbene,
23.8% asphalt resin,
35.6% oil resin,
16.0% oil.

We are here concerned with a substance soluble in middle oil and precipitable in benzol, i.e. primarily resin.

The bitumina occurring in the various extraction processes contain these resins in greater or lesser quantity. By bitumen we mean the filtrate freed of middle oil obtained in the extraction. These bitumina are soluble in middle oil and must be considered converted.

Table III shows analyses of various bitumina, which, on the one hand, have been subjected to decomposition with benzol and standard gasoline (benzol-soluble and s-asphalt) and on the other, to asphalt decomposition according to Suida-Motz-Lemme (hard asphalts, asphalt resins, oil resins and oil).

Table III

Kind of Bitumen	Welheim Bitumen	Bitumen Extraction Lu. 300 atm	Bitumen Extraction Lu. 500 atm	Bitumen Extraction Lu. 700 atm
% insoluble in benzol (benzol solids)	62.0	28.5	21.2	9.2
% soluble in benzol (s-asph.) insoluble in gasoline	18.4	24.1	24.8	26.0
% soluble in benzol and gasoline (oil)	19.6	47.4	54.0	64.8
% hard asphalt & carbene	60.5	26.1	13.7	7.2
% asphalt resin	5.5	11.1	3.0	6.1
% oil resin	23.0	26.3	34.0	67.2
% oil	10.5	36.5	49.2	19.5

The products are so arranged in the table that the hydrogenation conditions are improved from left to right. Welheim operates only with middle oils giving off hydrogen @ 100-150 atm without gaseous hydrogen. In the extraction experiments in Ludwigshafen, the 300 atm experiment with the addition of hydrogen already shows considerably better hydrogenation and splitting conditions than Welheim, at the higher pressures even more so.

The table indicates a dependence of the bitumen constituents on the degree of hydrogenation (Aufhydrierungsbedingungen) with respect to decomposition with benzol and gasoline as well as according to Suida-Motz-Lemme. In the Welheim bitumen, least hydrogenated and split, 62% are benzol-insoluble substances, in 700 atm extraction only 9%. The s-asphalt is somewhat increased here, due to increased hydrogenation.

According to Suida and Motz-Lemme large quantities of hard asphalts are found in the Welheim bitumen, which constantly decrease towards the 700 atm extraction, while the asphalt resins hardly show any change.

The characterization of the bitumina as well as the hydrogenation conditions employed can, therefore, very well be done by means of the asphalt decomposition method of Suida and Motz, as well as by means of the separation with pasting oil, benzol and gasoline. The given example indicates that a comparison of the determination of solids with pasting oil, e.g. liquid phase middle oil, with the benzol solids determination could eventually be used as a criterion for well or poorly chosen hydrogenation conditions, because it is easily possible that the occurrence of benzol insoluble oil constituents in coal hydrogenation is always connected with incomplete or poor hydrogenation.

A parallel to bituminous coal hydrogenation is also offered in this connection by the coking and carbonization (L.T.C.) of coal. High temperature pitches and products of hydrogenation from them also contain benzol insoluble substances, as do L.T.C. tars from bit. coal. In the flushing gas tars, e.g. the so-called red resins are insoluble in benzol. These resins are largely destroyed by cracking in heating surface carbonization. It is known that these resins consist largely of unsaturated hydrocarbons, are unstable and very sensitive to temperature. It is thought that these substances, precipitable with benzol, are primarily products of the decomposition of coal bitumina, in hydrogenation as well as in carbonization, which become soluble in benzol only by further hydrogenation or cracking.

/fkp

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-347
W.M.Sternberg
853 June 1947

High Pressure Experiments,
Leuna, 1.

5/17/44

TUNGSTEN-FREE SPLITTING CATALYSTS OF THE TYPE OF THE SiO_2-Al_2O_3-Fe_2O_3 HYDRATED OXIDE MIXTURES, TREATED WITH HF.

From Dr. Pier's Files

Summary

1). The splitting activity of the SiO_2 - Al_2O_3 - Fe_2O_3 catalysts, mixed in different proportions, was tested after being treated with different amounts of hydrofluoric acid (benzination of Bruchsal mineral oil).

2). It has been found that with an amount of HF equal to 50 equivalent percent of Al + Fe, very active catalysts for splitting were obtained with a 20 - 90% SiO_2, when the Al_2O_3 content was greater than Fe_2O_3. The results are shown in the appended triangular diagram.

3). The most active SiO_2-Al_2O_3-Fe_2O_3 splitting catalyst obtained from these tests (80:15:5) confirmed the effect of HF treatment. The maximum splitting activity was found after treatment with less than 35%, preferably with 5 - 20 equivalent percent of HF, calculated to Al + Fe (Splitting activity 135 - 140; for comparison, splitting activity of 6434 about 100).

4). Long time tests with the a-middle oil from moneral oil and with b-middle oil from coal were run with two of the best of these catalysts, with 50% HF / Al+Fe (splitting activity 100 and 90). They produced a better splitting, with the other results about the same as with 6434. No loss of activity was observed in spite of the frequent troubles resulting from aerial warfare. The sensitivity of these catalysts towards nitrogen is somewhat greater than of 6434.

On the strength of suggestions brought by Dr. Pier from the ANIC in Italy, the HF treated SiO_2 - Al_2O_3 - Fe_2O_3 benzination catalysts were systematically studied, with Drs. v.Führer and Wittmann. First of all SiO_2-Al_2O_3-Fe_2O_3 mixtures with 90 - 10% SiO_2 were prepared, with the Al_2O_3 : Fe_2O_3 in the proportions of 3 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 3, and the hydrated oxide mixtures so obtained were treated with 50 to 100 equivalent percent HF, calculated to Al + Fe. A fairly large number of untreated catalysts, and catalysts treated with HF were tested under strictly comparable conditions for their splitting activity against Bruchsal gasoil. These tests showed:

Rather wide limits are permissible with respect to SiO_2 content in the production of actively splitting catalysts. The Fe_2O_3 content of the catalyst has to be lower than the Al_2O_3. When treated with 50 equivalent percent of HF, referred to Fe + Al, very active splitting

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Jointly with

Dr. Peters Dr. v.Führer
Dr. Hesse Dr. Wittmann
D.C.Trofimow.

catalysts are obtained. On the other hand, when treating with 100% HF, the splitting activity becomes almost completely lost, and is even appreciably lower than that of the untreated hydrated oxide mixtures.

For the reasons just mentioned, the first step in the investigation was the study of the effect of HF treatment of a mixture composed of 80 SiO_2, 15 Al_2O_3, 5 Fe_2O_3, which has been found satisfactory. The mixture of hydrated oxides was treated with 0, 5, 10, 20, 35, 50, 70 and 100 equivalent percent of HF referred to Al+Fe, and the catalysts tested with Bruchsal Gasoil for their splitting activity. The most active splitting catalysts were treated with between 5 and 30% HF/(Al+Fe), but even with 50% HF/(Al+Fe) the activity was as good as with 6434.

Another series of catalysts with 80% SiO_2, treated with 50% HF/(Al+Fe) was used to study the effect of the Al : Fe ratio. The catalysts made contained 100, 95, 85, 75, 60, 50, 25 and 0% Al_2O_3 in the Al_2O_3+Fe_2O_3 mixture. For some unknown reasons, possibly the results of aerial war activities on the experimental work, or possibly because of the preparation of the catalysts, the splitting activity in this series of catalysts did not prove to be as good as was expected. The effect of the Al_2O_3 : Fe_2O_3 ratio did however manifest itself very plainly: the activity of the catalysts was much lower with 0 - 15 and again with over 50% Al_2O_3 in the mixture, than with 15 - 50% Al_2O_3 (sic).

To complete the series of tests on the Si-Al-Fe triangular diagram, the catalysts located on the corners and along the sides of the triangle were treated with 50% HF, and tested. The pure SiO_2 and the Al_2O_3 and Fe_2O_3 treated with HF, as well as the SiO_2 - Al_2O_3 and SiO_2 - Fe_2O_3 two component systems have extraordinarily slight splitting activity. While the Al_2O_3 - Fe_2O_3 mixture is not yet a splitting catalyst, its activity is appreciably greater than of the other catalysts along the sides of the triangle and the corners.

Details of the results with the Bruchsal oil are given in tables 1 - 6.

More exhaustive tests were made with a few of the best catalysts of that time as soon as the first promising results had been obtained. A 43 day test with the Bruchsal oil was run with catalyst 9233 (splitting activity 100), with which the gasification and the quality of the gasoline were tested three times, carrying out an exact fractionation test, and testing the catalyst for its sensitivity to nitrogen. No reduction in the catalyst activity was found in 30 days without the addition of nitrogen compounds. The nitrogen sensitivity is somewhat greater than of the 6434 catalyst. The residual gasoline was also tested. A 42 day run with coal b-middle oil was made with catalysts 9242 (splitting activity 90) after an 8 day run with Bruchsal gasol. There was no loss of activity. During this run, gas analyses were also made, also large scale investigations, fractionation tests and testing of residual gasoline. Table 7 contains some of the characteristic results with the SiO_2 - Al_2O_3 - Fe_2O_3-HF catalysts and their comparison with some older results with the 6434 catalyst. With almost identical results with catalyst 6434, the tungsten-free Si-Al-Fe catalyst gave somewhat better splitting activity. No long time tests are as yet available with the best catalysts known today, 9297, 9298 and 9299 (splitting activity 135 - 140). Some of these catalysts produced better octane numbers with the Bruchsal oil than 6434.

Table 1.

Series of tests 1a and 1b.

Composition of catalyst % SiO_2	% Al_2O_3	% Fe_2O_3	Percent equivl HF: Al+Fe	I No.	Cat.No.	Exper. No.	Start	Split. activ.
90	5	5	100	1582a	9184	5439	10/22/43	4
80	10	10	100	1583a	9185	5442	10/22/43	2
60	20	20	100	1584a	9186	5443	10/22/43	6
40	30	30	100	1585a	9187	5446	10/24/43	7
20	40	40	100	1586a	9188	5447	10/24/43	7
10	45	45	100	1587a	9189	5449	10/24/43	15
100	0	0	50	2094b	9353	5766	5/ 4/44	1
90	5	5	50	1582b	9241	5562	1/18/44	59
80	10	10	50	1583b	9226	5519	12/18/43	28
60	20	20	50	1589b	9190	5450	10/24/43	37
40	30	30	50	1585b	9239	5557	1/15/44	80
20	40	40	50	1586b	9240	5569	1/19/44	58
10	45	45	50	1587b	9237	5550	1/12/44	64
0	50	50	50	2093b	9352	5765	5/ 4/44	31

Table 2.

Series of tests 2a, 2b and 2c.

				Date	Cat.No.	Splitting activity
90	7.5	2.5	100	11/13/43	9208	7
80	15	5	100	12/27/43	9231	5
60	30	10	100	12/27/43	9229	21
40	45	15	100	1/12/44	9234	7
20	60	20	100	1/22/44	9244	22
10	67.5	22.5	100	1/12/44	9235	26
90	7.5	2.5	50	1/24/44	9242	90
80	15	5	50	1/10/44	9233	100
60	30	10	50	12/27/43	9230	78
40	45	15	50	1/27/44	9243	80
20	60	20	50	2/ 4/44	9245	90
10	67.5	22.5	50	1/11/44	9236	60
90	7.5	2.5	0	-	-	-
80	15	5	0	2/11/44	9274	70
60	30	10	0	2/ 2/44	9257	47
40	45	15	0	-	-	-
20	60	20	0	2/11/44	9275	25
10	67.5	22.5	0	-	-	-

Table 3.

Series of Tests 3a and 3b.

Composition of catalyst					
%SiO_2	%Al_2O_3	%Fe_2O_3	Equivale. percent HF/ Al+Fe	Date	Splitting activity
90	2.5	7.5	100	-	-
80	5	15	100	-	-
60	10	30	100	1/27/44	7
40	15	45	100	-	-
20	20	60	100	-	-
10	22.5	67.5	100	2/ 7/44	3
90	2.5	7.5	50	2/ 2/44	40
80	5	15	50	2/10/44	18
60	10	30	50	2/ 2/44	13
40	15	45	50	2/ 7/44	7
20	20	60	50	1/28/44	5
10	22.5	67.5	50	-	-

Table 4.

Series 4.

						Cat.No.
80	15	5	0	3/10/44	35	9293
80	15	5	5	3/11/44	140	9299
80	15	5	10	3/10/44	138	9298
80	15	5	20	3/10/44	136	9297
80	15	5	35	3/11/44	67	9300
80	15	5	50	3/18/44	112	9285
80	15	5	70	3/12/44	56	9302
80	15	5	100	3/10/44	4	9292

Table 5.

Series 5.

80	20	0	50	4/29/44	18*
80	19	1	50	4/28/44	14
80	17 85%	3	50	4/28/44	32
80	15 75%	5	50	4/28/44	47
80	12 60%	8	50	4/28/44	35
80	10 50%	10	50	5/ 3/44	60
80	5	15	50	4/24/44	10
80	0	20	50	4/24/44	3

* cf text about the absolute values of these activities.

Table 6.

60	40	0	50	4/30/44	5
60	0	40	50	5/ 4/44	4
0	50	50	50	5/ 4/44	31
100	0	0	50	5/ 4/44	1
0	100	0	50	5/ 5/44	3
0	0	100	50	5/ 5/44	3

Table 7.

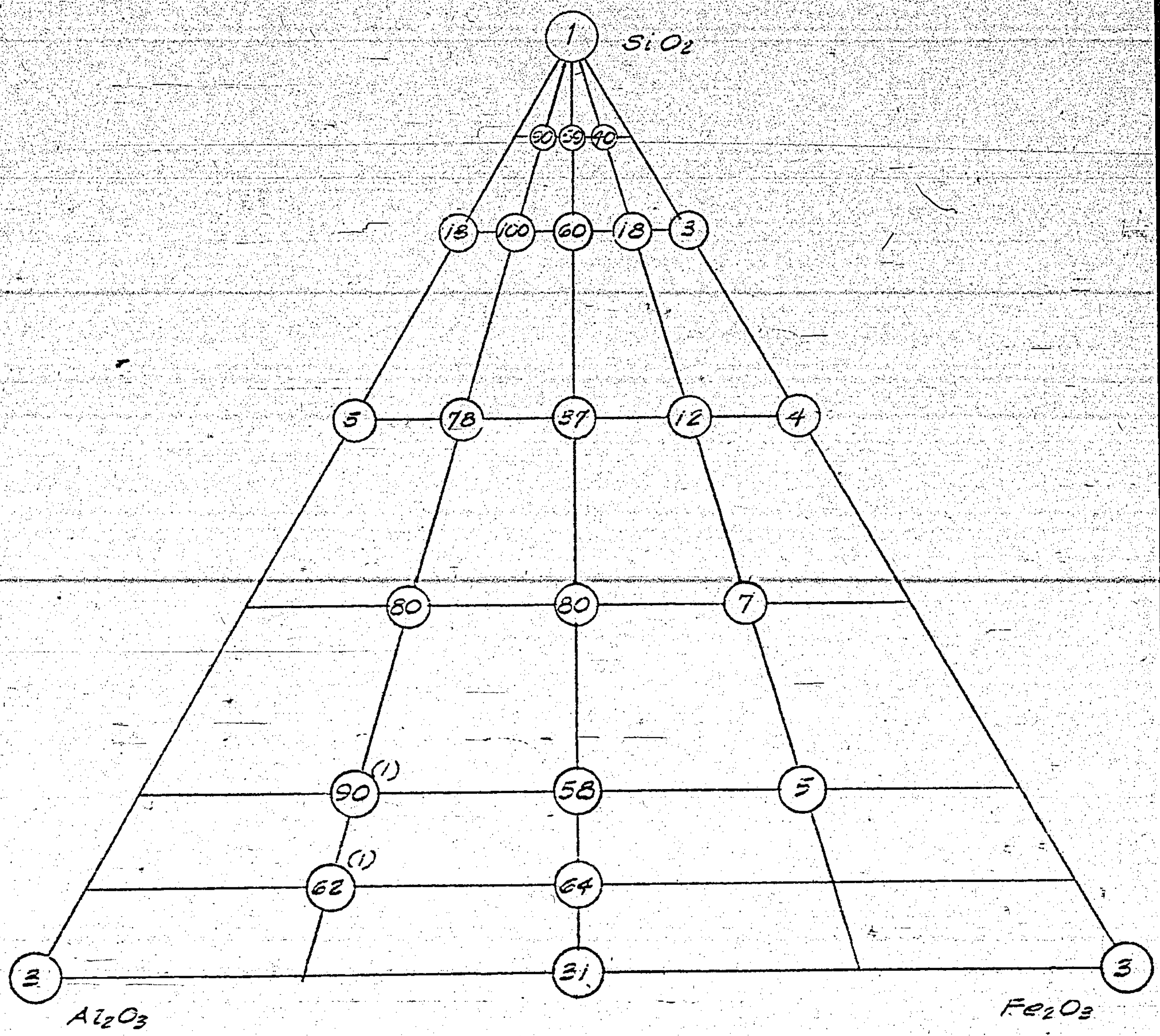
Comparison of Si - Al - Fe Catalysts and 6434.

Feed	Bruchsal Gasol		Coal B-Middle Oil	
Catalyst No.	6434	9233,	6434	9242,
Composition	Terrana + 10% WS_2	table 2.	Terrana + 10% WS_2	table 2.
Pressure, atm	200	250	250	250
Thruput, kg/li/hr	2.0	1.5	1.5	1.5
Temperature, mv.	19.5	18.7	19.5	19.0
Gasoline con, not stabilized, -150°	50	68	56	58
Splitting activity	65	90	56	70
Gasoline prod., stabilized	0.77	0.85	0.76	0.78
Gasification	22.7	18.9	19.6	22.0
% C_4 in gas:iso in the C_4	70:70	60:67	70:70	967:61
Gasoline to:	150°	150°	150°	145°
a.p. I/II	55/61	55/62	51/53	49/52
Start boiling	54/00	54/00	57/00	58/00
%-70°	9	9	5	4
%-100°	55	54	54	56
End point	152/99	151/99	153/98	145/99
% paraffines	66	65	43	38
% naphthenes	26	26	54	57
% aromatics	8	8	3	4
% unsaturated	0	1	0	1
Octane number, motor	70.0	69.0	73.5	75.0
M 0.12	91.0	88.5	93.8	89.0
Gasoline residue % -100°	55	51	56	53
o.no., motor	66	68.5	73.0	75.0
M 0.12	89.5	88.0	91.2	91.0
75 - 100° fraction				
% paraffines	62	66	34	27
naphthenes	32	30	63	69
aromatics	5	4	2	3
O.no Motor/m 0.12	71.7/93.0	70.5/90.5	76.5/93.0	77.5/91.0
Gasol. residue 75-100°, Mot/M 0.12	70.7/90.5	71.5/90.5	77.0/94.5	76.5/92.0
140-160° fract.				
% paraffines	68	67	43	43
naphthenes	17	13	51	49
aromatics	14	20	5	8
O.no Mot./M 0.12	55/80.2	54.5/76.5	63/82.5	58/77.0
Res.gas.Mot/M 0.12	44/74.5	44.0/73.5	59.2/-	54.5/-

/fkp

TRIANGULAR DIAGRAM OF THE $SiO_2 - Al_2O_3 - Fe_2O_3$ CATALYSTS WITH 50 EQUIVALENT PERCENT HF CALCULATED TO Fe + Al

SPLITTING ACTIVITY



(1) THESE TWO CATALYSTS WERE TREATED WITH 35 EQUIVALENT HF BY MISTAKE. THE RESULTS WOULD BE SOMEWHAT LOWER WITH 50 EQUIVALENT PERCENT. HF

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T-348
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5-1-47

Pretreatment of Bituminous Coal for Hydrogenation
(Older Experiments)
By Hupfer, Ludwigshafen, 29 March 1943

Coal paste becoming plastic within certain temperature limits, which may cause plugging in the preheater tubes, has been observed only with bituminous coal. It does not, as a rule, occur with brown coal. This phenomenon, called "swelling" of coal and explained as such, has, therefore, been placed in parallel to the increase in volume of the coal in coking or carbonization, which has been observed with melting bituminous coal, but not with brown coal, which latter produces a powdered coke.

It may be remarked in passing, that this parallelism does not exist in all cases. The French coal, lignite Gardanne, which is between a bituminous and a brown coal, according to its composition, shows very heavy swelling in the preheater, although it produces a sandy coke.

Otherwise, the very frequent occurrence of both phenomena at the same time caused us to entertain the possibility that those treatments of coal which reduce its baking ability, also improve its behavior in the preheater. Since such effects are difficult to measure with small apparatus, unequivocal results of experiments are not available. However, certain predictions may be made about the influence of a pretreatment of coal for hydrogenation.

The following kinds of pretreatments have been considered:

1) - Preheating.

An influence of preheating of Brassert coal on the pressure plugging of the preheater could not be detected. Saar coal Louisenthal, which was preheated in an H_2-stream @ 250 atm for 3 hours, produced a better asphalt content and lower gasification in an autoclave experiment.

2) - Anoxidation.

The change in the coal by the absorption of oxygen increases the viscosity of the coal paste, measured without pressure, while preheating in vacuum has no effect. Commercially dried Saar coal (Püttlingen), i.e. possibly anoxidized to some extent, produces increased splitting and gasification and higher asphalt content.

3) - Sulfur Treatment.

The baking ability of Saar coal could be destroyed by the addition of 2.5% pulverized sulfur and heating to 110°C for 1-1/2 hours in a stream of H_2S, without appreciably diminishing the volatile content. On heating to 200-250°C the volatile content dropped sharply.

When neutralized Saar coal Louisenthal, dried in an H_2S-stream, is used, a slight but bearable deterioration of the yield with about equal gasification would be observed. To be sure, the processing of the residue would be changed at the same time by the absorption of the centrifuge oil topping with its certainly unfavorable effect. In general, a more or less distinct improvement might be expected from an absorption of sulfur.

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T-349

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5-1-47

Regeneration of Coal Paste by Dilution with Middle Oil

By von Müffling and Hupfer
Ludwigshafen
17 February 1943

In order to heat a greater portion of the coal in the heat exchangers, it was proposed to dilute the paste at Blechhammer from the present 45.5% to 40% solids by adding middle oil and thus make it more receptive to heat exchange, and then again remove the added middle oil from the coal paste in vapor form by a separator before the converter.

The attached calculation shows that in Bleckhammer the quantity of paste gas would have to be increased from 2.6 m^3/kg pure coal to a maximum of 5.0 to 6.5 m^3, in order to remove the added middle oil as vapor at roughly 400°C, or above the swelling range. Accordingly, roughly 2 m^3 gas/kg pure coal would have to be added to the coal paste in order to produce the proposed conditions. In consequence, the quantity of circulating gas would almost have to be doubled, which would require additional circulating pumps.

By increasing the quantity of paste by roughly 13% and the gas by about 100%, the number of calories transferred to the paste mixture in the heat exchangers would be increased, to be sure, but in the opinion of Dipl. Ing. Schappert, such a severe drop in the outlet temperature of this mixture would have to be expected that the preheater in Bleckhammer would be unbearably overloaded.

Rough Calculation of the Quantity of Gas Required to Vaporize the Middle Oil

The Problem:

It is required to compute the quantity of gas necessary to remove a given quantity of middle oil from the coal paste at a given final preheater temperature, assumed to be 400° C in this case.

Basis for Calculation:

The Engler boiling curve of the middle oil looks like this:

Initial boil:	220°C
- 250°	30%
- 275°	62.5%
- 300°	84%
- 325°	96%

The middle oil content of the oil constituent in the diluted coal paste is about 50% to start. For lack of more accurate data, it is assumed that the decrease in vapor pressure of the middle oil, caused by the dilution with higher boiling constituents, and the increase in vapor pressure (press effect) due to the presence of 600 atm. H_2 partial pressure, will about equalize each other, so that we may figure the same as if pure middle oil were present.

Course of the Calculation:

It is first determined how the vapor pressure of the middle oil changes at constant temperature with increasing vaporization of the lighter constituents. If we assume the conditions of the Engler distillation, we get the following, based on the above Engler curve:

At 220° C the middle oil reaches a vapor pressure of 1 atm. After 30% has been distilled off the remaining oil reaches this vapor pressure at 250° C. At 220° C the remaining 70% of the original oil would have a lower vapor pressure, which we take from a vapor pressure-temperature diagram drawn by Wilson and Bahlke for a number of n-paraffins and benzol, and which we also assume to be applicable to our oil. From this we get a vapor pressure of 0.48 atm. for the remaining oil after evaporation of the first 30% of the oil. The application of this process to the entire boiling curve at 400° C is given in Curve I for a decrease in vapor pressure with an increase in the quantity of oil driven off.

We can now give a mean vapor pressure for approximately each 10% of the vaporizing middle oil, under the assumption that for such short pieces the sections of the curve can be replaced by straight lines with sufficient accuracy. For example, the first 10% @ 400° C would vaporize at a mean partial pressure of 16.7 atm. With a mean mol weight of 200 for the oil the first 100 g of the oil (with 1 kg to start) assume a volume under these conditions, according to the gas law, of

$$V_1 \cong 22.4 \times \frac{100}{200} \times \frac{673}{273} \times \frac{1}{16.7} \cong 1.65 \text{ Ltr.}$$

The hydrogen contained in these 1.65 Ltr. at an H_2 partial pressure of 600 atm. and a compressibility factor $C \cong 1.18$,

$$V_2 \cong 600 \times 1.18 \times 1.65 \times \frac{288}{673} \cong 500 \text{ Ltr,}$$

measured at 15° C and 1 atm.

The anologous calculation for the other middle oils is given in Curve 2, which shows, how many liter H_2/kg of middle oil are required under the given conditions to vaporize the oil constituents indicated in the abscissa in %.

Consideration of the following two cases is based on Curve 2:

1) - All of the gas, including that going thru the converter, goes thru the heat exchanger. Behind the heat exchanger as much gas is drawn off as is required to remove the added oil. Since under conditions applicable to Blechhammer, 62% of the middle oil contained in the diluted coal paste passing thru the heat exchanger must be removed before entry into the converter, at least 62%, in case all of the middle oil is in vapor form, of the gas leaving

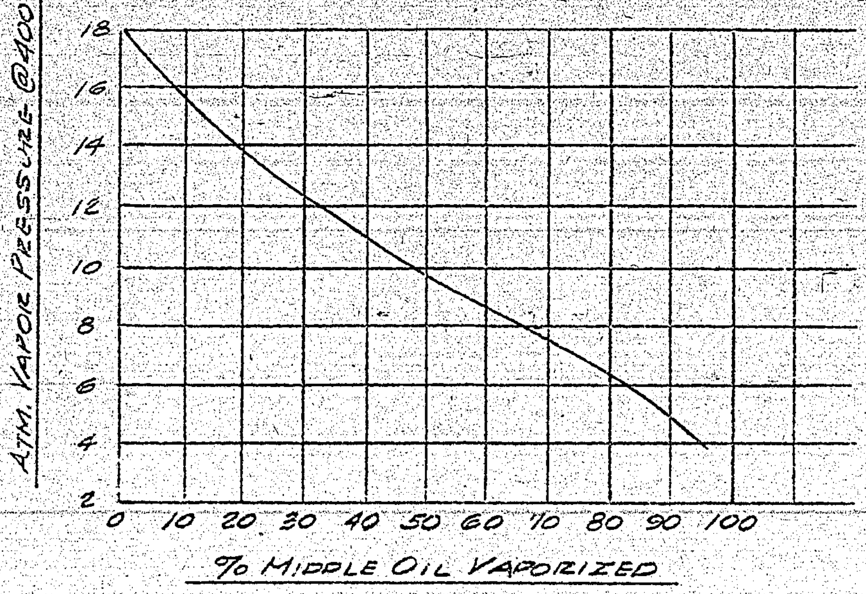
the heat exchanger must be drawn off. The quantity of paste gas to be charged into the converter is 2.6 m^3/kg pure coal. Since the diluted coal paste (40% solids) that can be regenerated contains 31% pure coal, the oil constituent 27.8% middle oil, and the entire paste, therefore, has a middle oil content of 16.7%, the quantity of gas going into the converter is equivalent to 4.8m^3/kg middle oil. With this quantity of gas the middle oil is vaporized, according to the values from Curve 2. If we assume that this calculation is too unfavorable, because, in reality, some heavy oil constituents will already be vaporized, so that the quantity of oil present in the vapor phase (Dampfphase) is really greater than the entire middle oil quantity, the result would, therefore, be a little too unfavorable and we could assume the quantity of gas to be run thru the heat exchanger as about 2 to 2.5 times that to be injected into the converter, or 5 to 6.5 m^3/kg pure coal.

2) - As a second possibility we may consider the case in which practically all of the gas going into the heat exchanger is drawn off again behind the heat exchanger and new gas is injected into the converter. According to Curve 2, 4.5 m^3/kg middle oil is required to vaporize 62% of the middle oil, or 2.4 m^3/kg pure coal. To this must be added 2.6 m^3/kg pure coal, which must be injected into the converter, so that the entire quantity of gas required will likewise be in the neighborhood of 5 m^3/kg pure coal.

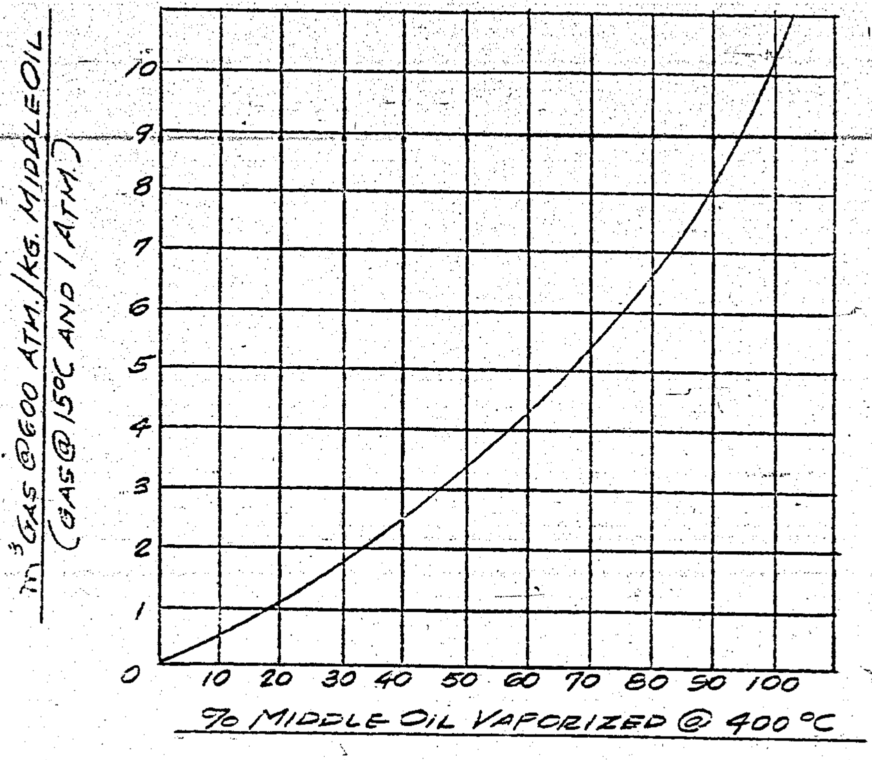
We may, therefore, assume that the minimum amount of gas to be added before the inlet to the converter is about twice as much with this operating method as with the normal operating method, regardless of how the gas streams are run.

/pkk

CURVE 1



CURVE 2



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PROCESS FOR DE-ASHING LIQUID CARBONACEOUS FUELS

German Patent 722406
Class 12_o, Group 10_5
18 Sept. 1936

Issued To

I.A. Farbenindustrie A. G.
Frankfurt A. M.

By

Dr. Mathias Pier, Heidelberg, and
Dr. Walter Kronig, Ludwigshafen, Rh.

DRP. 722406

In the processing of liquid or semi-solid products of pressure hydrogenation or extraction of substances, as coals, oil shale or peat, it has been found extraordinarily troublesome and disadvantageous, if said substances contain ash so finely distributed that it can not be removed by mechanical treatment, such as filtration, centrifuging or precipitation. This is of particular disadvantage, if the substances are to be subjected to pressure hydrogenation or splitting, possibly in the presence of catalysts.

For example, the ash may be retained on the surface of the catalyst at elevated temperatures when the liquid substances are conducted over it, thereby effecting a premature deterioration of catalytic effectiveness. It has further been found that, in using these kinds of oils for pasting coal for pressure hydrogenation or pressure extraction, the ash may at times, be separated in the reaction vessel in relatively coarse form, either by itself or combined with the ash in the coal to be processed. It may accumulate and thus reduce the available reaction space.

It has now been found that said substances may be de-ashed in a simple manner, if they are treated with CO_2 or ammonium carbonate in the presence of water at increased temperature and preferably under pressure. About 0.2 to 10% of water, based on the quantity of oil to be de-ashed, should be used for this purpose. In this treatment, the ash in solution or fine distribution assumes such a coarsely dispersed form that it may subsequently be removed without difficulty by mechanical means, such as filtration, centrifuging or precipitation.

For example, the feed oils may be directly treated with ammonium-carbonate and the water added separately if it isn't already present in sufficient quantity. But the oils may also be mixed with a watery solution of ammonium-carbonate. When using CO_2 alone or together with ammonia gas it is proper to use increased pressures varying between 5 and 100 atm. The temperatures to be maintained may vary between 100 and 400°C. It is advisable to use additional H_2 under pressure, in order to avoid undesirable decomposition of the oils. The products of pressure hydrogenation and extraction may also be treated in the described manner immediately after their production, while they are still hot, e.g. on the cooling run from the reaction converter.

Compared to the use of H_2SO_4, as is customary for de-ashing tars, the process at hand has this advantage, that no losses occur due to the formation of acid resins. In the known process a viscous mass resembling pitch is separated, which is not the case in the process under consideration. In the well known use of alkali-humate solutions, also, H_2SO_4 is added, so that here, too, losses due to the formation of acid resins must be counted on. Apart from this advantage, the process at hand uses simple and inexpensive media, which separate themselves and do not pollute the substance to be processed.

Example 1.

Central German brown coal is pasted with oil and subjected to pressure hydrogenation in a high pressure converter in the presence of an iron catalyst at a pressure of 200 atm and a temperature of 465°C. The reaction material is conveyed from the converter into a catch-pot, from which the sludge (letdown) is drawn off at the bottom and the products of reaction, consisting of gasoline, middle oil and a part of the heavy oil, is taken off the top, together with the H_2. The heavy oil constituents of these products of reaction, boiling above 325°C, are separated by distillation and added to the letdown. The resultant mixture is then centrifuged, in which process an oil is obtained containing 2.7% ash, which will pass through even the finest filters.

To this centrifuge oil containing ash is then added 5% water and the resultant mixture heated for 30 minutes to 340°C in the presence of a mixture of H_2 and CO_2 at a pressure of 75 atm, wherein the H_2 partial pressure is 40 atm and that of the CO_2 is 35 atm. In subsequent filtration an oil containing only 0.1% ash is obtained.

If the centrifuge oil containing ash is mixed with 10% ammonium-carbonate and 3% water and heated to 310°C for 1 1/2 hours in a closed vessel at 5 atm, the filtered oil will contain 0.3% ash.

Example 2.

An extract obtained from Rhenish brown coal by pressure extraction with tetra-hydronaphthalene and containing 0.7% unfiltrable ash, together with the extraction medium (80% extract and 20% tetra-hydronaphthalene), is stirred and heated to 130°C for 24 hours while CO_2, ammonia and steam are passed thru it, the evaporating tetra-hydronaphthalene being constantly replaced. The liquid is then filtered at 180°C and the filtrate freed of tetra-hydronaphthalene. The extract obtained contains only 0.1% ash.

Patent Claim.

Process for de-ashing liquid and semi-solid products of pressure hydrogenation or extraction of substances, such as coals, oil shales, or peat, characterized by treating said substances with CO_2 or ammonium-carbonate at elevated temperatures in the presence of water, preferably under pressure, and separating the ash herein converted to a coarsely dispersed form by mechanical means.

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COMPARISON BETWEEN ACID AND ALKALINE H.O.L.D. AT SCHOLVEN and THE INFLUENCE OF PASTE THRUPUT IN STALLS ON CONVERSION OF COAL.

Gelsenkirchen Buer
29 Nov. 1943

I. Comparison between Acid and Alkaline Operations.

During the months of January to June 1943 a number of letdowns (Abschlämme S sludges) from acid and alkaline operations were investigated, following a method formerly proposed by us. (Compare combined reports of 2 March 1942 on tests conducted at Scholven to provide a suitable method for the decomposition of asphalt). In most cases, such stalls were compared, in which the paste thruput and other factors of influence on the composition of the letdown were kept equal and which were operating smoothly at the time of the tests. Tests of pasting oil were made at the same time, see Table 1.

Figure 1 shows the composition of the letdown and the A-, B-, C-asphalts. Table 1 shows the average composition of the acid and alkaline letdowns.

From these figures it may be seen that the letdowns obtained in acid operations generally contain less salts soluble in water and less oil resins and neutral oils, but more ash free of salt, and particularly more ash-free pyridine insolubles (organic solids) and A-, B-, C-asphalts than the letdowns obtained in alkaline operations. The difference in the A-, B-, C-asphalts is especially great. While the alkaline letdown contains an average of only 11.5% A-, B-, C-asphalts, that in the acid letdown is 15.1%. That this difference is not alone due to the fact that in alkaline operations the letdown is diluted by the addition of soda oil can be proved, if the soda oil added before the hot catch pot is mathematically eliminated. This soda oil contains 10% soda and for the rest consists of pasting oil, the mean composition of which is given in Table 1. On the assumption that 12.5 t of alkaline letdown contain about 1.5 t of soda, the soda oil contained in the alkaline letdown can be mathematically eliminated with the mean composition of the pasting oil given in Table 1. This mathematically determined composition of the alkaline letdown free of soda oil is compared with that of the acid letdown in Table 2. It may be seen therefrom, that the alkaline letdown free of soda oil also contains less asphalt, 12.0 compared to 15.1%, and less ash-free pyridine insoluble than the acid letdown.

This result is contrary to the former opinion that alkaline additions in hydrogenation are polymerizing and that, therefore, these alkaline products must contain more organic solids and asphalts than the letdowns obtained in acid operations. To clarify this contradiction, experiments were made in a revolving autoclave in cooperation with Dr. Schmidt, in which a letdown obtained in acid operations was again hydrogenated, both with and without the addition of 1% soda (not suspended in oil). This letdown was also mixed with a quantity of thinning oil proportioned to the soda oil and then hydrogenated. The letdowns so hydrogenated were also decomposed by our method, wherein the thinning oil added to the letdown in the preceding case was mathematically eliminated. The results are summarized in Tables 3 and 4. Unfortunately, the two influences cannot be directly compared with each other because of the different H_2 partial pressures used in the experiments. In spite of the few experiments and the scattered values obtained, it nevertheless appears probable that, in the case of the addition of 1% soda to the letdown, the hydrogenated letdown contains more ash-free pyridine insoluble and more A-, B-, C-asphalts than the letdown hydrogenated without the addition of soda, and that, on the other hand, a product with less ash-free solids and less A-, B-, C-asphalts is obtained with the letdown mixed with thinning oil and then hydrogenated than with the letdown hydrogenated without the addition of thinning oil. Accordingly, soda has indeed a polymerizing effect, as had been previously assumed. If this effect cannot be recognized when soda oil is added, it is probably due to overlapping effects, i. e.;

1) - the polymerizing influence of soda,

2) - the influence of the added thinning oil in reducing the asphalt and solids, as previously determined by us. (Compare report on the influence of the addition of thinning oil to the hot catchpot of coal stalls on the composition of the letdown, the report on asphalt decomposition, of 9 May 1943, and report on improving the carbonization yield in the L.T.C. of letdown by adding thinning oil to the hot catchpot, of 16 Dec. 1943.)

Apparently, the second influence is the stronger, so that the polymerizing effect of soda is completely covered up.

We may, therefore, well assume that in alkaline operations letdowns with low asphalt and solids content are obtained only because of the favorable influence of the oil in the soda oil, and that a like favorable effect could be obtained in acid operations by adding thinning oil before or into the hot catchpot.

II. Influence of the Coal Paste Thruput and the H_2 Partial Pressure in the Coal Stalls on Coal Conversion.

In Fig. 2, the A-, B-, C-asphalt content of the letdowns investigated and the conversion, based on insolubles in pyridine benzol and carbon-tetrachloride, calculated from the salt-free ash with the aid of the content of salt-free ash in the coal paste, is compared with the coal paste thruput, H_2 partial pressure, and the C-content of the hydrogenation coal. The calculation of the conversion on pyridine-, benzol- and carbon-tetrachloride insolubles, which, of course, is dependent upon our letdown decomposition into organic solids, ash-free pyridine insoluble and A-, B-, C-asphalt, was done in order to determine how far the pyridine-, benzol- and CCl_4-insolubles put into the coal paste were actually liquefied or converted into asphaltic or A-, B-, C-asphalt-free oils. The degree of liquefaction of the coal can probably best be seen from the conversion calculated from the pyridine insoluble, because the solubility of pyridine corresponds approximately to that of A-middle oil or heavy oil, while benzol precipitates a number of substances, which are first dissolved in letdown oil. Carbon-tetrachloride, for its part, does not dissolve all of the A-, B-, C-asphalts. The conversion calculated from the CCl_4-insoluble accordingly corresponds to the coal converted to A-, B-, C-asphalt-free oils.

Because of the multitude of varying factors, to those already mentioned must be added the changes in catalysts and catalyst quantities summarized in Table 5, not too much can be determined from Fig. 2. However, the influence of high paste thruput (acid letdown tests of 22 April to 17 May 1943) on conversion is clearly recognized. The conversion calculated from the salt-free ash in these tests is strikingly low in proportion to the high paste thruputs. This sharp decrease in conversion, however, might also be due to the comparatively low H_2 partial pressures at the time.

It is of further interest that the decrease in conversion is particularly noticeable in the figures calculated from the CCl_4-insoluble. The conversion in the above mentioned changes in thruput drops from about 75% to 63%, or by 12%, while the conversion calculated from the benzol-insoluble drops only from 82% to 73%, and that calculated from the pyridine-insoluble from 86% to 79%. This observation can also be made with some of the letdowns obtained in alkaline operations. It would mean that with poor hydrogenation properties the asphalt conversion is particularly lowered, while the liquefaction of coal to asphaltic oils is not influenced so strongly. Further investigations in this field are under way.

Summary.

The investigations of acid and alkaline letdowns indicate that the alkaline letdowns have a lower content in organic solids (ash-free pyridine insoluble) and A-, B-, C-asphalts than the acid letdowns. This decrease, however, is not due to the alkaline operation as such, or the addition of soda, but to the oil addition into or before the hot catchpot, which had previously been shown to be favorable. As shown by small scale experiments, an actual increase in organic solids and A-, B-, C-asphalts is obtained, if, instead of soda suspended in oil, soda alone is added.

The experiments further indicate that, with higher paste thruputs in the coal stalls, the liquefaction of coal to asphaltic oils is not influenced as much as the conversion of the asphalts to oils.

/pkl

TABLE I

	Mean Composition of acid letdown betw. 1/13 & 6/25/43	Mean Composition of alkaline let-down betw. 1/13 & 6/15/43	Mean Composition of pasting oils betw. 1/13 & 6/25/43
% Salts	1.5	2.2	0.8
% Salt-free ash	5.2	4.1	1.7
% Ash-free pyridine insoluble	11.3	9.5	5.9
% A-asphalt	6.2)	4.5)	3.2)
% B-asphalt	0.8) 15.1	1.4) 11.5	1.0) 9.1
% C-asphalt)	8.1)	5.6)	4.9)
% Oil Resin	13.3	16.4	14.1
% Neutral Oil	53.6	56.2	68.3

TABLE 2

	Mean Composition of acid letdown betw. 1/13 & 6/25/43	Mean Composition of acid let-down betw. 1/13 & 6/15/43, from which the soda paste added before the hot catchpot has been mathematically eliminated.
% Salts	1.5	1.05
% Salt-free ash	5.2	4.5
% Ash free pyridine insoluble	11.3	10.0
% A-asphalt	6.2)	4.7)
% B-asphalt	0.8) 15.1	1.5) 12.0
% C-asphalt	8.1)	5.8)
% Oil Resin	13.3	16.9
% Neutral Oil	53.6	55.5

TABLE 3

Influence of 1% Soda Addition on Hydrogenation of Letdowns in Revolving Autoclaves

Composition of hydrogenated letdown	Letdown in hydrog. @ 95 atm H_2 Filling press, without soda. Temp. 23 mV		Letdown hydrg. @ 95 atm H_2 filling press, with 1% Soda. Temp. 23 mV	
	Exper. 1	Exper. 2	Exper. 1	Exper. 2
% Salts soluble in H_2O	2.3	2.2	2.9	3.0
% Salt-free ash	6.6	6.6	6.8	6.8
% Ash-free pyridine insoluble	23.4	20.5	23.0	30.5
% A-asphalt	5.1)	5.2)	4.9)	4.6)
% B-asphalt	2.3) 11.6	2.6) 10.9	1.1) 12.2	1.6) 12.5
% C-asphalt	4.2)	3.1)	6.2)	6.3)
% Oil Resin	11.5) 56.1	13.1) 59.8	11.2) 55.1	7.7) 47.2
% Neutral Oil	44.6)	46.7)	43.9)	39.5)

TABLE 4

Influence of Thinn. Oil Addit. on Hydrogenation of Letdown

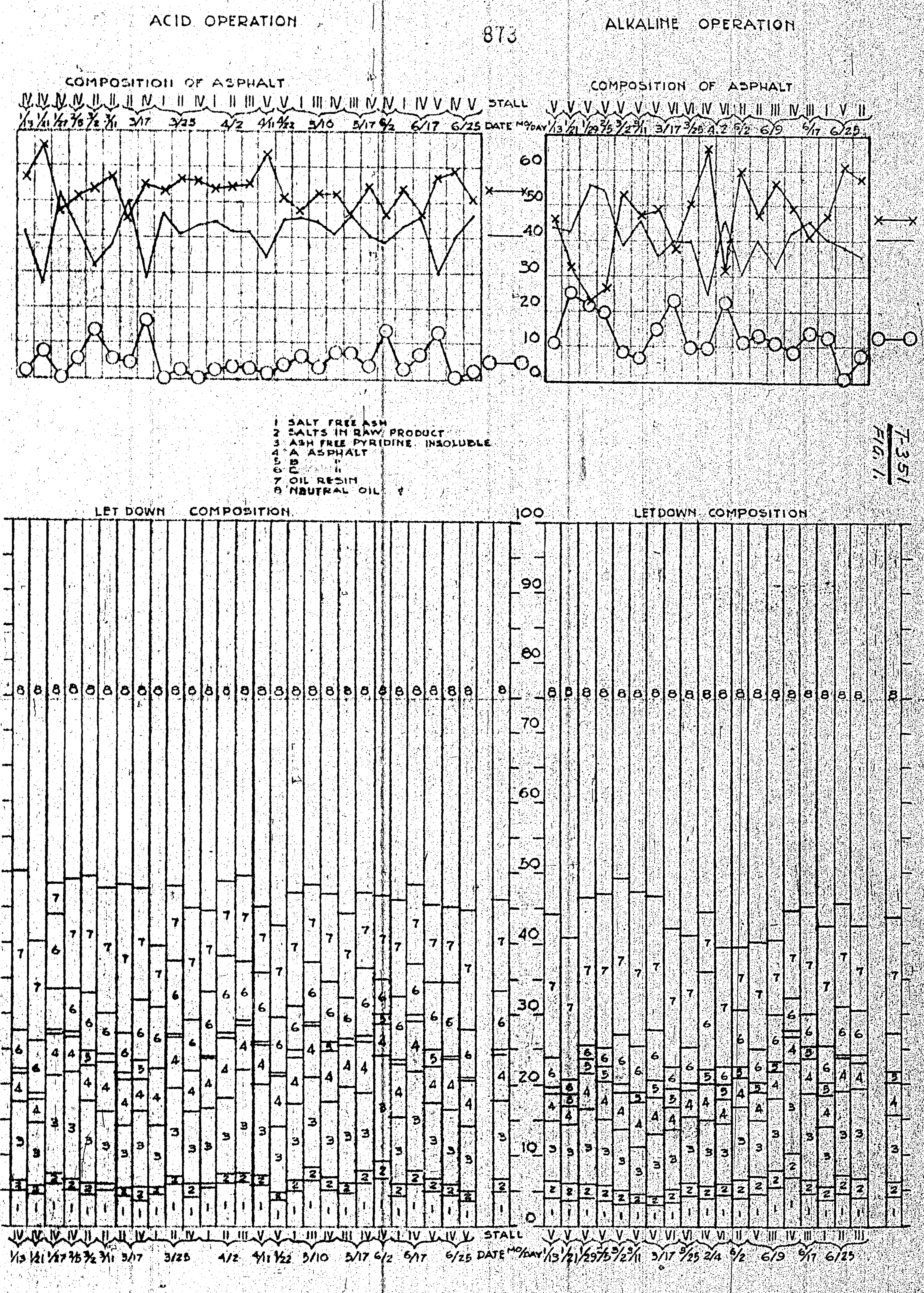
Composition of hydrogenated letdown	Letdown hydrog. @ 140 atm H_2 filling pressure Temp. 23 mV		Letdown + 14% Thinn. Oil hydrog. @ 140 atm H_2 fill. press. wherein the Th. Oil was later math. elim. Temp 23 mV	
	Exper. 1	Exper. 2	Exper. 1	Exper. 2
% Salts soluble in H_2O	2.2	2.6	2.2	2.3
% Salt-free ash	6.4	7.3	6.7	6.4
% ash-free pyridine insoluble	15.3	21.4	13.9	13.9
% A-asphalt	4.6)	5.3)	4.1)	4.1)
% B-asphalt	1.7) 11.6	1.0) 11.2	1.4) 9.3	2.2) 10.2
% C-asphalt	5.3)	4.9)	3.8)	3.9)
% Oil Resin	11.0) 54.5	9.3) 57.5	67.9	67.2
% Neutral Oil	53.5)	48.2)		

OPERATIONAL CHANGES IN THE STALLS

	Stalls	Date Day/Mo.	Proportion		Catalyst				H_2 Partial Press.	Thruput, t past'g. oil/h	Thruput, t coal paste/h
			Light oils & gas	Letdown	FeSO$_4$	IIa Pb. Acetate	II Snox	I NH$_4$Cl			
Acid Stalls	IV	13/1	57.9	42.1	-	0.12	0.03	0.6	232	0.5	24.0
	IV	21/1	56.7	43.3	-	"	"	"	236	1.5	23.0
	IV	29/1	58.6	41.4	2.0	-	"	"	239	1.0	23.0
	IV	5/2	55.9	44.1	-	-	0.06	0.9	246	1.0	24.0
	II	2/3	45.0	55.0	0.5	0.12	0.03	0.6	225	"	23.0
	II	11/3	45.8	54.2	"	"	"	"	237	"	23.0
	II	17/3	32.5	67.5	"	"	"	"	236	"	21.0
	IV		39.1	60.9	"	"	"	"	236	"	22.0
	I	25/3	54.8	45.2	"	"	"	0.9	243	"	25.0
	II		59.6	40.4	"	"	"	"	243	"	23.0
	IV		46.3	53.7	"	"	"	"	243	"	24.0
	I	2/4	56.3	43.7	"	"	"	"	231	"	24.0
	II		54.8	45.2	"	"	"	"	231	"	23.0
	III		47.3	52.7	"	"	"	"	231	"	25.0
	V	11/4	(1)52.6	47.4	-	"	"	"	218	"	23.0
	V	22/4	(2)38.8	61.2	-	"	"	0.7	221	"	28.0
	I	10/5	(1)40.5	59.4	-	"	"	"	224	"	27.0
	III		(3)54.8	45.2	-	"	"	"	229	1.5	26.0
	IV		(2)50.2	49.8	-	"	"	"	215	1.5	28.0
	III	17/5	(3)57.1	42.9	-	"	"	"	217	"	26.0
	IV		(2)46.4	53.6	-	"	"	"	210	"	28.0
	IV	2/6	58.1	41.9	-	"	"	1.0	238	0.5	22.0
	I	17/6	48.6	51.4	-	"	"	0.7	230	1.0	23.0
	IV		52.8	47.2	-	"	"	"	231	0.5	22.0
	V		49.3	50.7	-	"	"	"	232	1.0	25.0
	IV	25/6	47.8	52.2	-	"	"	"	204	0.5	21.0
	V		49.6	50.4	-	"	"	"	209	1.0	26.0
Alkaline Stalls	V	13/1	39.5	60.5	-	0.12	0.03	0.6	234	1.0	25.0
	V	21/1	48.7	51.3	-	"	"	"	232	"	24.0
	V	29/1	43.9	56.1	2.0	-	"	"	229	"	25.0
	V	5/2	(4)37.1	62.9	-	-	0.06	0.9	221	"	25.0
	V	2/3	40.1	59.9	0.5	0.12	0.03	0.6	235	2.5	25.0
	V	11/3	39.7	60.3	"	"	"	"	244	1.0	25.0
	V	17/3	44.1	55.9	"	"	"	"	236	3.0	23.0
	IV		44.7	55.3	"	"	"	"	236	1.0	21.0
	IV	25/3	42.7	57.3	"	"	"	0.9	243	"	23.0
	IV	2/4	43.5	56.5	"	"	"	"	242	"	22.0
	VI		40.3	59.7	"	"	"	"	233	"	23.0
	II	2/6	55.2	44.8	-	"	"	1.0	228	0.5	20.0
	II	9/6	59.2	40.8	-	"	"	"	240	"	21.0
	III		45.4	54.6	-	"	"	"	240	2.0	23.0
	IV		47.6	42.4	-	"	"	"	240	0.5	22.0
	III	17/6	45.1	54.9	-	"	"	"	232	2.0	23.0
	I	25/6	39.1	60.9	-	"	"	"	214	1.0	22.0
	II		53.0	47.0	-	"	"	"	213	0.5	20.0
	III		59.0	41.0	-	"	"	"	220	1.0	24.0

(1) without cold paste
(2) with cold paste
(3) Low temp.

(4) Neut. 3rd Conv.


ACID OPERATION
ALKALINE OPERATION
COMPOSITION OF ASPHALT
COMPOSITION OF ASPHALT
STALL
DATE MO/DAY
1/13 1/21 1/27 2/5 2/12 3/11 3/17 3/25 4/2 4/11 4/22 5/10 5/17 6/2 6/17 6/25
1/13 1/21 1/29 2/5 2/23 3/11 3/17 3/25 4/2 6/2 6/9 6/17 6/25
0
10
20
30
40
50
60
1 SALT FREE ASH
2 SALTS IN RAW PRODUCT
3 ASH FREE PYRIDINE INSOLUBLE
4 A ASPHALT
5 B "
6 C "
7 OIL RESIN
8 NEUTRAL OIL
LET DOWN COMPOSITION
LETDOWN COMPOSITION
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
STALL
DATE MO/DAY
1/13 1/21 1/27 2/5 2/12 3/11 3/17 3/25 4/2 4/11 4/22 5/10 5/17 6/2 6/17 6/25
1/13 1/21 1/29 2/5 2/23 3/11 3/17 3/25 2/4 6/2 6/9 6/17 6/25

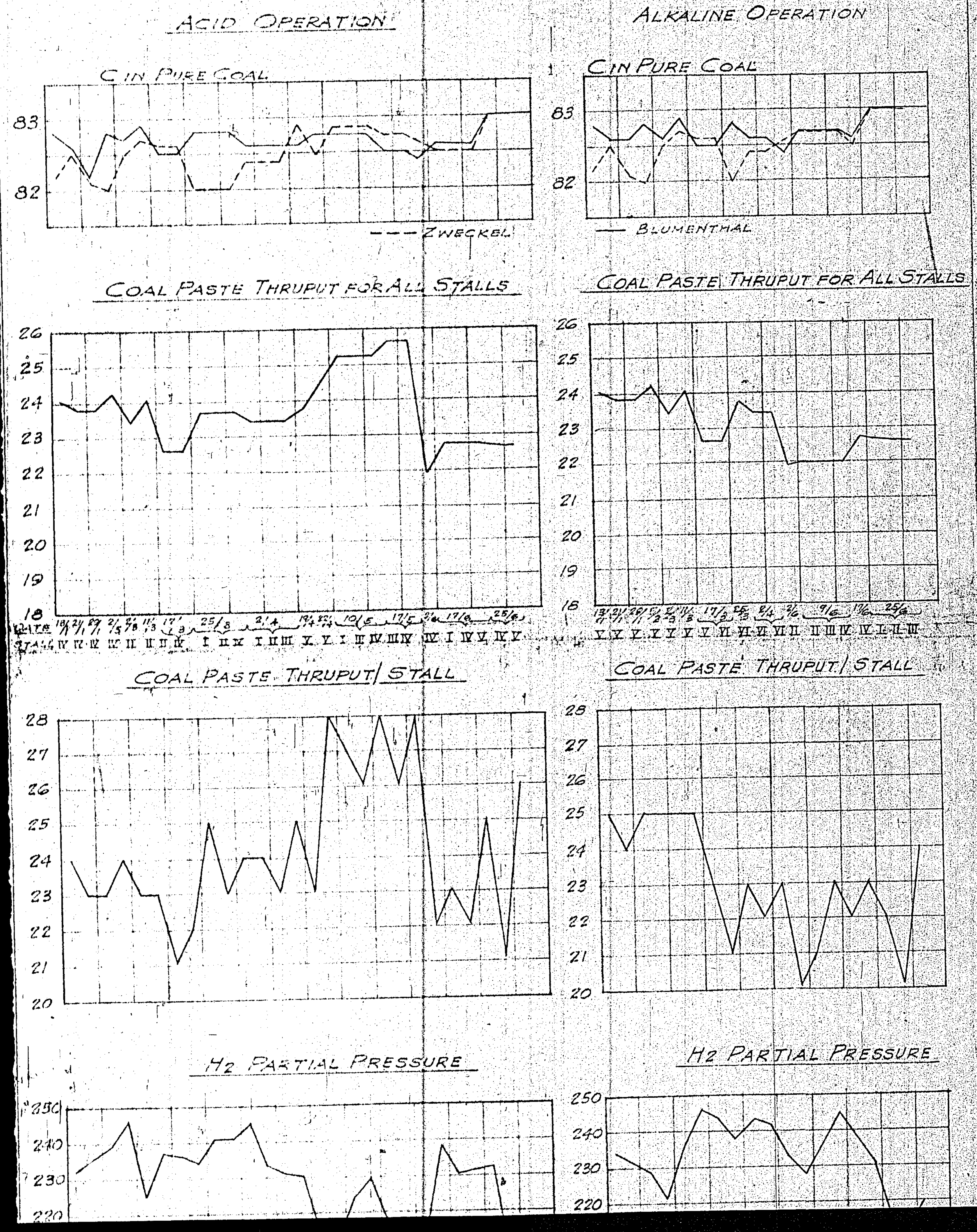
T-351
FIG. 1.

FIG. 2

874

COMPARISION OF LETDOWNS FROM ACID AND ALKALINE OPERATIONS

BETWEEN 13.1 - 25.6.43



ACID OPERATION

ALKALINE OPERATION

C IN PURE COAL

C IN PURE COAL

COAL PASTE THRUPUT FOR ALL STALLS

COAL PASTE THRUPUT FOR ALL STALLS

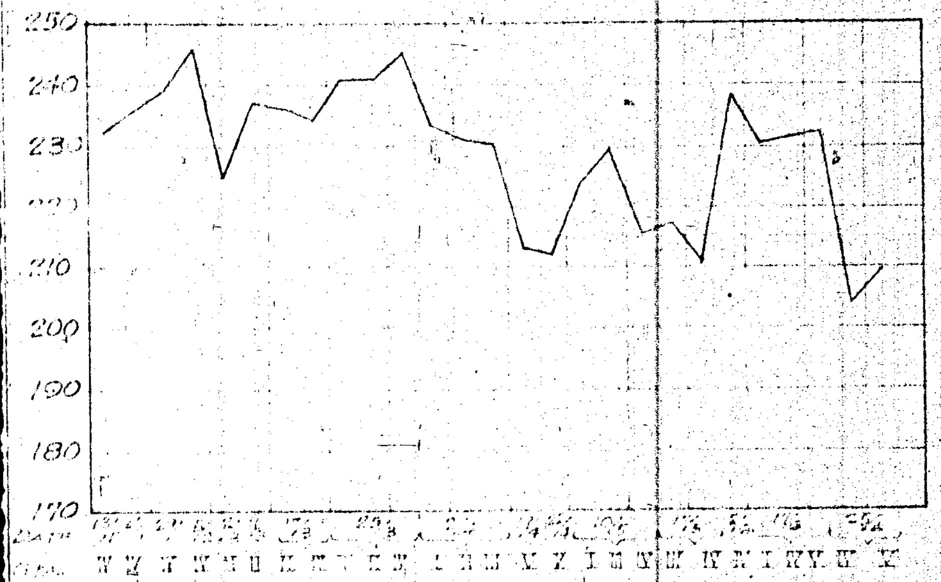
COAL PASTE THRUPUT / STALL

COAL PASTE THRUPUT / STALL

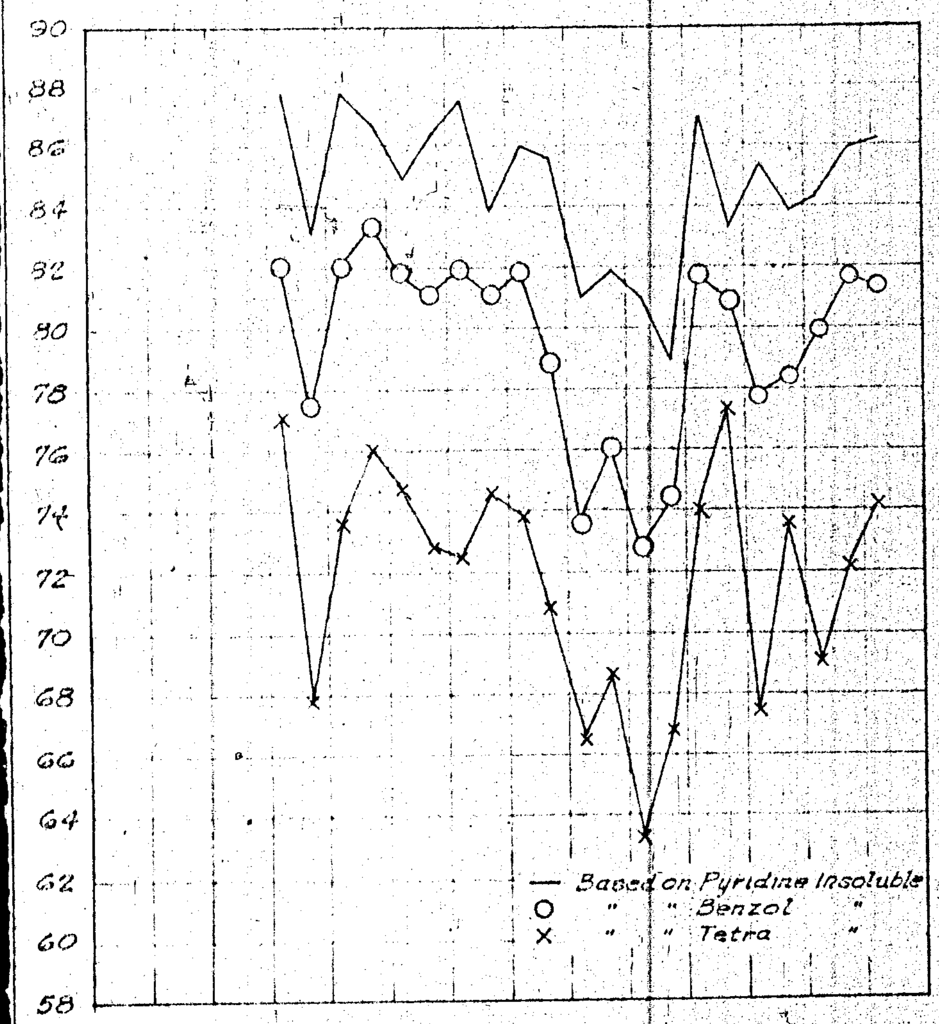
H2 PARTIAL PRESSURE

H2 PARTIAL PRESSURE

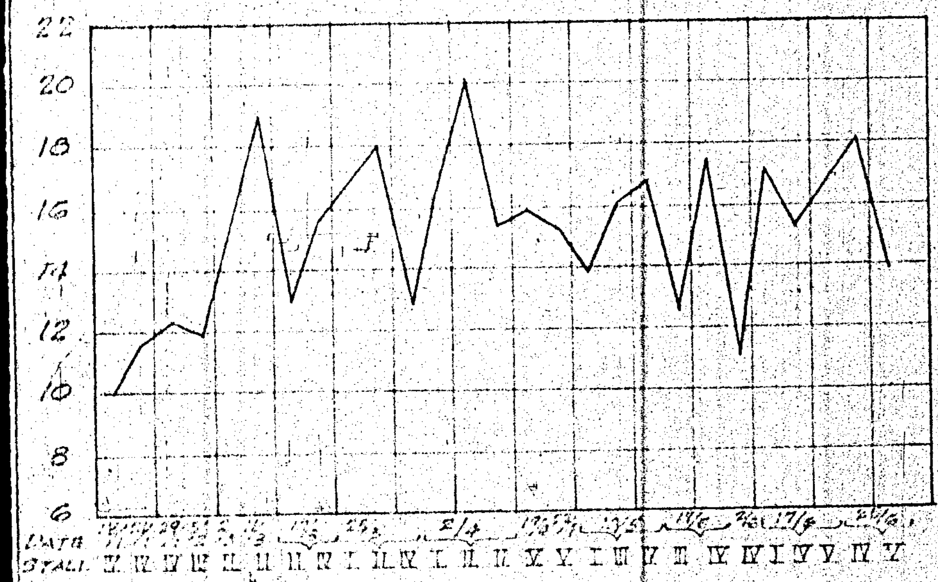
H2 PARTIAL PRESSURE



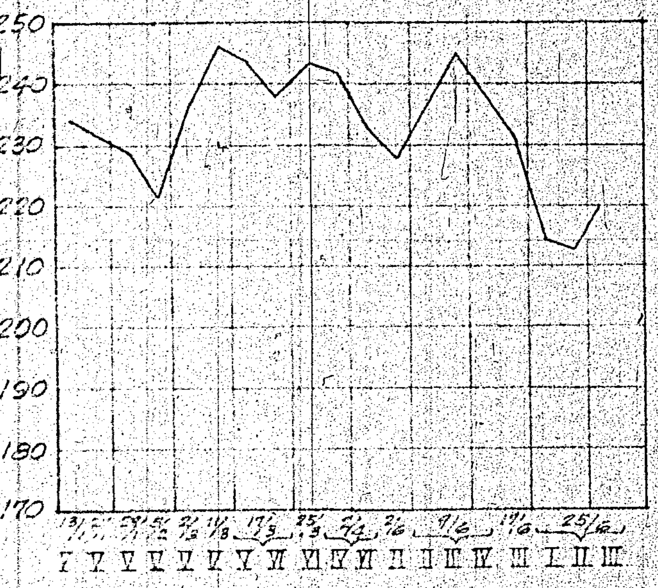
COAL CONVERSION



A+B+C ASPHALT IN LETDOWN



H2 PARTIAL PRESSURE



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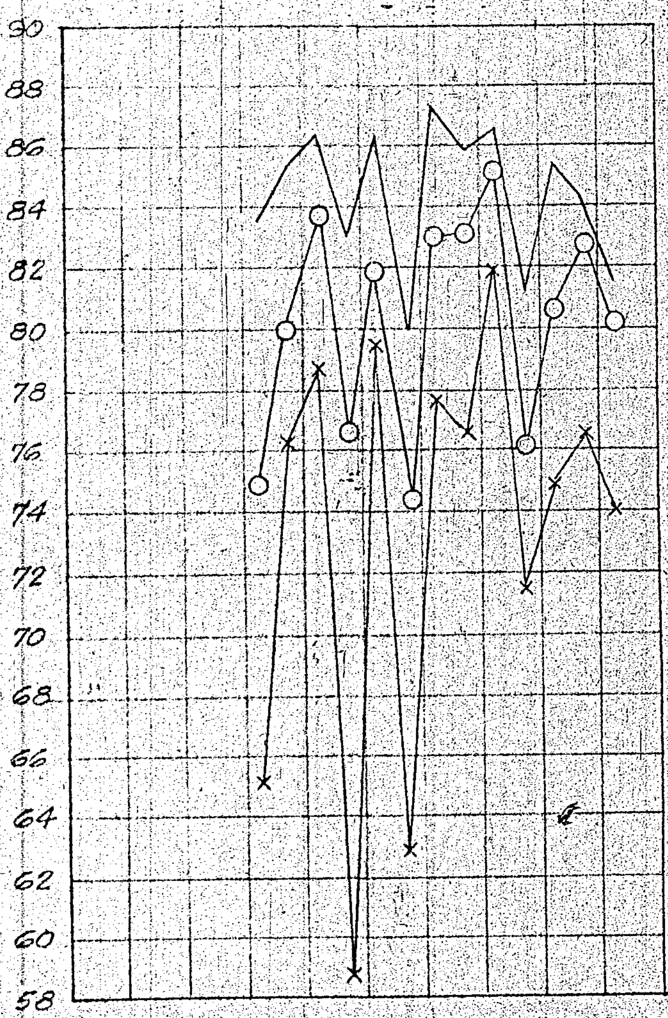
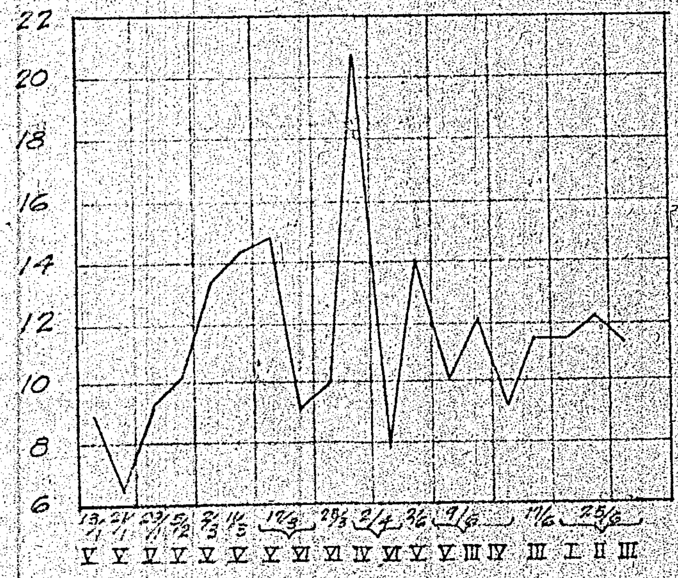


A+B+C ASPHALT IN LETDOWN



U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-352

KCBraun
5-5-47

Comparison of Liquid Phase Operations, Pölitz and Gelsenberg.

By Dr's. Gromann & Berger, Pölitz
Dr. Jakob & O. I. Egli, Gelsenberg
Dr. Becker & D. I. Schappert, I. G.

Gelsenkirchen-Horst
18 June 1942

1) - Coal:

	Pölitz			Gelsenberg		
	% H_2O Raw Coal	% H_2O Dry Coal	% Ash Dry Coal	% H_2O Raw Coal	% H_2O Dry Coal	% Ash Dry Coal
Jan.	5.4	2.6	6.6	7.6		4.3
Feb.	5.4	2.4	7.2	8.1	2.0	4.5
March	4.5	2.7	1.1	8.4		4.3
April	4.5	3.0	6.8	8.0		4.6

	% C in pure coal	% H in pure coal	% O in pure coal	% C in pure coal	% H in pure coal	% O in pure coal
Jan.	81.5		11.6	83.0	5.5	8.7
Feb.	82.2		11.4	83.3	5.6	8.4
March	82.2		11.4	83.0	5.5	8.7
April	83.1		10.4	82.9	5.6	8.8

To determine the quantity of coal charged into the stalls in Gelsenberg, the coal is weighed before crushing. Belt conveyor scales and Hilburg scales (proportioning scales?) are available. The pure coal is then determined by deducting the water and ash in the coal.

In Politz the coal is weighed dry and, because of difficulties in weighing, the quantities are checked by the number of paste press strokes. The volumetric efficiency of the paste presses was established at 0.95, based on calibrated containers. In order to compute the pure coal, the solids in the paste and pasting oil must be taken into consideration.

2) - Catalysts based on Dry Coal:	Politz	Gelsenberg
Bayermass	2.5	2.0
Iron sulfate	1.7	1.3
Sulfigran	0.15	0.33
3) - Coal Paste:		
Total Solids	51.8	52.9
4) - Letdown		
% Solids	20.0	20 - 24
% Asphalt	18.0	16 - 18

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1) - **Coal:**

	Pölitz			Gelsenberg		
	% H_2O Raw Coal	% H_2O Dry Coal	% Ash Dry Coal	% H_2O Raw Coal	% H_2O Dry Coal	% Ash Dry Coal
Jan.	5.4	2.6	6.6	7.6		4.3
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3) - **Coal Paste:**		
Total Solids	51.8	52.9
4) - **Letdown**		
% Solids	20.0	20 - 24
% Asphalt	18.0	16 - 18

Reaction Water in the Coal Phase:

Referring to a report from HP-Research, Lu, Stettin states that in the liquid phase 75% of the oxygen contained in the coal is obtained in the reaction water. Another 10% is obtained as CO_2 and 4% as CO, the rest in phenols.

At first, Gelsenberg figured on 10% new water formation based on pure coal, including salts. Recent checks of analyses of pure coal and the cold catchpot liquor (Abstreiferwasser) indicated that 6.6% new water formation plus 1.7% for salts and phenols should be figured. This corresponds to the values used in Pölitz, so that it was agreed to use the Stettin formula for computing the reaction water in the future.

5) - **High pressure oil yield**, based on the available oil yield, plus the losses occuring in low pressure operations:

	Pölitz		Gelsenberg	
	HP-Oil Yield Kg/t Pure Coal	% Gasol. ≠ Mi-Oil	HP-Oil Yield kg/t pure coal	% Gasol. ≠ Mi-Oil
Jan.	544		637	96.9
Feb.	533		640	94.6
March	569		646	80.0
April	576		649	81.7
	Available Oil Yield	% Gasol. ≠ Mi-Oil	Available Oil Yield	% Gasol. ≠ Mi-Oil
Jan.	472	98.8	588	104.5
Feb.	459	100.0	585	103.2
March	497	105.9	601	85.5
April	484	111.0	603	87.7

6) - Difference between HP-oil yield and available oil yield ≅ loss in residue processing:

	Pölitz		Gelsenberg	
		Diff. in % of HP-Oil Yield		Diff. in % of HP-Oil Yield
Jan.	72	13.2	49	7.7
Feb.	74	13.9	53	8.6
March	72	12.7	48	7.4
April	92	16	46	7.1

7) - **HP-Oil Yield**, including indeterminable losses in gas and oil:

	Pölitz		Gelsenberg	
		Loss		Loss
Jan.	567	23	685	48
Feb.	559	26	705	63
March	596	27	688	42
April	611	35	693	44

8) - **Conversion**, based on analyses:

	Pölitz kg solids in Centrifuge Residue	Gelsenberg kg solids in Centrifuge Residue
Jan.	91.5	96.4
Feb.	90.5	96.5
March	92.2	96.0
April	91.7	96.0

9) - **L.T.C. (Schwelerei)**

	Pölitz			Gelsenberg		
	Kg solids in Centrif. Residue	% Solids in Centrif. Residue	L.T.C. Yield	Kg solids in Centrif. Residue	% Solids in Centrif. Residue	L.T.C. Yield
Jan.	19.4	39.0	78.4	10.0	36.3	80.8
Feb.	21.0	38.5	79.2	11.0	35.4	79.4
March	19.2	38.2	79.7	11.3	35.5	80.6
April	19.4	39.0	79.0	11.0	35.8	78.2

10) - **Theoretical Liquefaction: kg C x Conversion/0.86 =**

	Politz	Gelsenberg
Jan.	867	931
Feb.	866	935
March	882	926
April	886	932

11) - **Gasification:** C as oil in hydrocarbons (C_1 to C_4) + CO_2 + CO including 1% circulating gas loss:

	Pölitz	Gelsenberg
Jan.	Monthly figures are.	237
Feb.	not available and	219
March	individual daily	220
April	figures vary too much.	207

The calculation of gasification does not rest on a very sound basis. It seems, therefore, more accurate to compute gasification from the difference between the theoretical liquefaction and the HP-oil yield. In this the indeterminable gas and oil losses are added to gasification. These values can be determined very accurately:

12) - Gasification calculated from the difference between the theoretical liquefaction and the HP-yield:

	Politz	Gelsenberg
Jan.	300	246
Feb.	307	232
March	286	238
April	275	239

13) - Summarizing the Balance:

Attached Table 1, shows a comparison between the monthly balances of both plants.

14) - Differences in Operating Results:

The differences for the month of April are taken as an example, from which we get a difference in the available oil yield of

603 kg for Gelsenberg
min. 484 " " Politz
= 119 kg/t pure coal

This difference of 119 kg may be explained as follows:

a) varying c-content of coal: 82 - 83	10 kg
b) variable conversion: 91.5 - 96.5	50 "
c) variable losses in residue processing (lower conversion, higher ash)	25 "
d) variable gasification and indeterminable gas and oil losses	18 "
e) variable gasoline concentration in oil yield	7 "
" lub. oil " " " "	5 "
	Abt. 115 kg.

/pkl

TABLE 1

Comparison of Balances between Pölitz and Gelsenberg

	PÖLITZ				GELSENBERG			
Month, 1942	Jan.	Feb.	Mar.	April	Jan.	Feb.	Mar.	April
Pure coal/kg	1000	1000	1000	1000	1000	1000	1000	1000
Conversion/%	91.5	90.5	92.2	91.7	96.4	96.5	96.0	96.6
Theoret. Liquef/kg	867	866	882	886	931	935	926	932
Gasific. based on C converted/%	34.6	35.4	32.4	31.0	26.4	24.7	25.7	25.6
Gas + Oil loss indeterminable/% based on C-converted	2.6	3.0	3.1	4.0	5.2	6.7	4.5	4.7
HP-Oil Yield/kg	544	533	569	576	637	641	646	649
Loss in residue processing, based on HP-Oil yield/%	13.2	13.9	12.7	15.9	7.7	8.72	7.0	7.1
Available oil yield	472	459	497	484	588	585	601	603
Aviat. gasoline yield						87%		

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

W. M. Sternberg
June 1947

Two Papers on the Effect of Nitrogen Contents on the Splitting Properties.

From Dr. Pier's Files

1. EFFECT OF ADDED NITROGEN COMPOUNDS ON THE SPLITTING OF MINERAL OIL AND GASOL OVER 6434 CATALYST.

High Pressure Experiments
Leuna, 558

April 19, 1943

Summary

It has been found in the study of the effects of nitrogen of the oils upon their splitting properties, that the prehydrogenated brown coal and bituminous coal middle oils from low temperature carbonization were still readily hydrogenated with a considerably higher nitrogen contents, than the prehydrogenated middle oils from bituminous coal tar or from bituminous coal or brown coal liquefaction products. The assumption was here made, that the nature of the nitrogen products exerted some influence.

In order to get an insight into this question, a number of splitting tests were run under strictly comparable conditions, but with the addition of certain amounts of nitrogen in the form of different compounds (dibutylamine, aniline, n-dimethyl aniline, methyl naphthyl amine, pyrrol, pyridine and quinoline). No naphthenic nitrogen compounds or saturated heterocyclic compounds have so far been tried.

The differences in the specific splitting interfering action was so slight, that the effects mentioned above could not be attributed to the individual nitrogen-compounds.

/s/ Günther.

.... The conditions under which the effects of nitrogen were studied were as follows:

Type of converter:	50 ml converter with upward flow
Catalyst:	6434 T pills, 50 mls = 40 g.
Pressure:	250 atm gas (= abt 245 atm H_2)
Temperature:	19 mv = 373° C
Thruput:	1.5 kg oil/li catalyst/hour = 75 g/hr.
Gas : oil:	2.67 m^3/kg = 200 li/hr.
Oil:	Redistilled P 1203 gasol, -325° C (Bruchsal) produced 8/25/42
Additions:	0.75% CS_2 + 0.015 % N in the form of the compound studied.

The following organic nitrogen compounds have been studied: dibutyl amine; aniline; methyl naphthaline; pyrrol; pyridine; quinoline; i.e. aliphatic nitrogen compounds, aromatic nitrogen compounds with the N atom in the ring, and unsaturated heterocyclic nitrogen compounds; but not naphthenic and saturated heterocyclic compounds.

The tests were always first run for 2 - 3 days without the addition of the nitrogen compounds. In the individual tests 64; 62; 63; 66; 67, 69 and 67% -150° gasoline were obtained in the catchpot. These results were in good agreement among themselves.

As a continuation of the above tests, the compounds of nitrogen were added to the starting product, and the catchpot was tested daily for the next 5 days for its content in the -150° fraction. After these five days, the addition of nitrogen was again suspended, and the gasoline determinations made in the production for the next three or four days. The results are entered in table I and evaluated on Table II. The N compounds are arranged in the table in the sequence: aliphatic N compounds, aromatic amines of increasing molecular weight, unsaturated heterocyclic compounds of increasing molecular weight. Towards the end a test was run with the 8797 catalyst (terrana-FeF_3) with the addition of aniline. The addition of nitrogen compounds caused a reduction of the amounts of gasoline produced to 30 - 55% of the original value (Column K II/K I, table II). The concentrations rapidly increased after suspending the addition of nitrogen, and again reached the values between 78 and 102% (K III/K I, table II) of the original concentration; i. e. while the bases present with the splitting catalyst did result in a reduced amoung of splitting, no harm was done to the catalyst. In addition, the values K II/K III are also given in the table. The average of K II/K I and K II/K III (i.e. the ratio between the gasoline concentration during the periods before and after the addition) is a measure of the interference with splitting of the nitrogen compounds used.

Attempts to systematize the information were unsuccessful. When examining molecular weights, we do notice, that substances with the lowest molecular weight have the least splitting-inhibiting action, those with the highest molecular weights the greatest. Other values, however, in particular dibutyl amine and aniline do not occupy their proper places. Neither can any system be obtained by arranging the compounds by their chemical characteristics. It is however worthy of notice, that the heterocyclic compounds do not have the same splitting-inhibiting action as the compounds with nitrogen in the side chains.

The catalyst 8797 seem to be somewhat more sensitive to nitrogen, than 6434.

In view of the relatively low splitting-inhibiting action of nitrogen on the B products from the bituminous and brown coal low temperature carbonization tars, it might be desirable to run some tests with naphthenic nitrogen products (of the hexahydroaniline type), also with saturated heterocyclic compounds (pyrollidine, piperidine, etc.). Dr. Bueren and Dr. Wittmann supplied us with the nitrogen compounds.

/pkl

Table 1

Splitting of Bruchsal Gasol. over the catalyst 6434 with the addition of different nitrogen compounds.

Feed during the period of addition of compounds of nitrogen	P 1203 gasol. alone Concentration K I				P 1203 Gasol - added bases Concentr. K II on 5th day							Again P 1203 gasol. alone Concentr. K III on last day				
Day	1.	2.	3.	4.	1a	1b	2.	3.	4.	5.	6.	1.	2.	3.	4.	5.
P 1203+0.140% Dibutylamine	59	64	-		49	46	38	27	32	38		-	66	65	-	
P 1203+0.100% Aniline	59	62	62		56	43	38	23	22	19		28	45	43	54	
P 1203+0.130% N-Dimethylaniline	58	66	63		56	37	36	28	27	23		46	53	53	55	
P 1203+0.157% Methylnaphtylamine	66	66	-		67	71	66	44	28	19		42	56	58	-	
P 1203+0.072% Pyrrole	67	68	-		64	69	47	34	36	38		43	46	53	50	52
P 1203+0.085% Pyridine	58	69	69		57	36	30	26	30	26		39	60	60	64	
P 1203+0.140% Quinoline	58	71	-		66	55	31	29	24	24		38	61	62	-	
P 1203+0.100% Aniline w. catalyst 8797	50	57			47	28	18	19	17	17		28	50	50	-	

Table II

Evaluation of Results Tabulated in Table I

Nitrogen compound added	Mol. Weight	Gasoline concentration in catchpot at start of test P 1203 alone	at end of test period with addition of nitrogen compound	at end of test P 1203 alone	KII K I	KII KIII	Average	KIII K I
0.140% Dibutylamine	129	64	35	65	55	54	55	102
0.100% Aniline	93	62	20	54	32	37	35	87
0.130% N-Dimethylaniline	121	63	24	55	38	44	41	87
0.157% Methylnaphtylamine	157	66	20	58	30	35	33	88
0.072% Pyrrole	67	67	36	52	54	69	62	78
0.085% Pyridine	79	69	28	64	41	44	43	93
0.140% Quinoline	129	67	24	62	36	39	38	93
0.100% Aniline (catalyst 8797)	93	57	17	50	30	34	32	88

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-353-2
W.M.Sternberg
May 1947

EFFECT OF THE NITROGEN CONTENTS ON THE SPLITTING PROPERTIES AND THE DETERMINATION OF THE NITROGEN CONTENT

High Pressure Experiments
Leuna, 558

April 19, 1943.

The nitrogen content is one of the factors affecting the splitting properties of the middle oils. We have selected the concentration of the fraction boiling -150° as a measure of the splitting properties of an oil, benzinated under some specific experimental conditions. These experimental conditions were as follows:

Type of converter	50 ml. converter with upward flow.
Catalyst:	6434 T pills, new catalyst.
Pressure:	250 atm = abt 245 atm partial pressure of H_2
Thruput:	1.5 kg/li catalyst/hr = 75 g/h.
Gas : oil	2.67 m^3/kg = 200 li/hr
Sulfur addition to oil:	0.75% CS_2
Temperature:	set to obtain about 5% gasoline -150° in the catchpot.

The splitting property is then obtained from the concentration found and the temperature by dividing the concentration by 1.2 for every 1/2 mv above 19.5 mv (or multiplying by 1.2 for every 1/2 mv below 19.5 mv).

$$\text{Splitting property} = \frac{\underline{\text{gasoline concentration}}}{1.2^{2x(\text{temp.} - 19.5)}}$$

We consider splitting property above 50 as good.

Fig. 1 and 2 show the splitting property of a number of oils in relation with the analytically obtained Kjeldahl nitrogen values, or the so-called "basicity". No regularities could be observed in the Kjeldahl nitrogen, but the basicity values do nevertheless permit us to recognize some relation to the splitting property. The following figures were obtained:

Basicity (methyl orange)	Splitting property.
0.0 to 1.0	65 - 80
1.0 - 2.0	50 - 80
2.0 - 3.0	35 - 65
3.0 - 5.0	30 - 60
5.0 - 8.0	20 - 55
8.0 - 15.0	5 - 40
over 15	0 - 20

The scattering of the results (width of the band in the diagram) follows from:

1) The oils included in the diagram are of the most diverse origin (high temperature coking tar, bituminous coal liquefaction oil, brown coal liquefaction oil, petroleum A middle oil, liquid phase middle oil from petroleum distillation, cracking residues and DHD residues, but not low temperature carbonization oils of bituminous or brown coals, because somewhat different relationships exist for the prehydrogenation of the latter).

2) The oils differ occasionally greatly in their boiling point curves, especially the boiling end point, aniline point, phenol content, and proportion of unsaturated.

3) Limits of reproducibility of a splitting property test.

4) Limits of errors of the analytical determination of basicity.

On the strength of the experimental material obtained in small scale runs at Ludwigshafen we consider basicity a suitable factor to evaluate the splitting properties of an oil, in line with other analytical data, such as the aniline point, phenols, etc. It may also be used for the control of efficiency of prehydrogenation.

Different methods have been proposed for the determination of the nitrogen content of oils, none of which have proved acceptable, except a modification of a method developed in Leuna.

Kjeldahl and Dumas methods for the determination of nitrogen in middle oils give no concordant results. The scattering of the nitrogen values with them is way outside the permissible limits. Thus, in pure cogasine (Fischer-Tropsch diesel oil) the following values have been obtained, all the samples being taken from the same flask:

Kjeldahl method:	0.006% N 0.011% N
Dumas method:	0.071% N 0.140% N.

It must be borne in mind in this connection that pure cogasine is a nitrogen-free synthetic product.

The values obtained by both methods fluctuate by 50%, and moreover, the values obtained by Dumas' method are some 10 times higher than obtained by the Kjeldahl. The scatterings in the Dumas method are occasioned by a higher blanc value, necessitated by a larger weight of the sample, while in the Kjeldahl method the catalyst fails with the necessarily large samples used, which results in a variation in the losses of nitrogen.

The ter Meulen method is inapplicable to the determination of nitrogen in middle oils, because the middle oils are partially cracked during the determination, and some of the nitrogen fails to become hydrogenated. It can not be used for readily and completely volatile substances.

Neither does the diazo method give usable results, because different dyes are formed after diazotization and developing because of the different constitution of the bases to be determined; moreover, no diazotizable nitrogen is probably present in many of the middle oils.

Leuna has informed us in January 1941 of a method for the determination of "basicity". Values obtained by this method are in a substantially better agreement with the splitting property. The directions for the determination of "basicity" by the Leuna method is as follows:

500, 1000 or 2000 mls of the substance to be tested are shaken 6 times for 10 minutes in a separatory funnel with 10% sulfuric acid, using 5% of the acid, referred to the product tested. After the separation of the layers, the acid layer is drawn off. The six extracts are collected in a distilling flask, which is connected to an ammonia distillation outfit. Ammonia and organic bases are then steam-distilled from a solution made strongly alkaline with sodium hydroxide, and the distillate received in N/10 acid.

When the distillation is complete, the acid in the receiver is titrated with N/10 NaOH, using methyl orange as an indicator. The acid consumed represents the total organic bases and ammonia present in the substance.

Calculations: Used: 500 mls substance
5.5 mls N/10 acid.

$$\frac{5.5 \times 1.7}{0.5} = 18.7 \text{ mg } (NH_3 + \text{organic bases}), \text{ calculated as mg } NH_3/\text{liter}$$

This method therefore includes only the basic nitrogen of the middle oils.

Since the receipt of the directions, the method has been used for the determination of nitrogen in the middle oils, but the results obtained by this method were also scattered.

We may show the reproducibility of the results obtained on two series of mixtures of middle oils, the basicity of which was determined. The starting oils were:

1. Coal liquefaction middle oil prehydrogenated over 7846 W (designated A. Nitrogen-poor).
2. Bruchsal gasol 180 - 330° C (marked M; intermediate N content).
3. Teitbrook gasol (marked R; high in nitrogen).

The two tables below give the values found in the determination of a series of mixtures:

I. Series of Mixtures.

Oil Used	"Basicity" found, mg NH_3/ 1i	Theor. aver.	Pract. aver.	Average Deviations from the average
1000 mls R	48.6; 46.6; 43.9; 42.2; 42.0	44.7	44.7	2.4
800 mls R + 200 mls A	32.7; 37.1; 42.8	36.2	37.5	3.3
600 mls R + 400 mls A	28.9; 28.9; 28.1	27.6	28.6	1.0
400 mls R + 600 mls A	19.6; 20.3; 19.6	19.1	19.8	0.7
200 mls R + 800 mls A	10.9; 11.9; 10.7	10.5	11.2	0.7
150 mls R + 850 mls A	10.2; 7.7	8.4	8.9	2.3
100 mls R + 900 mls A	6.8;	6.3	6.8	0.5
50 mls R + 950 mls A	13.4; 7.7	4.2	10.7	6.3
1000 mls A	2.4; 2.1; 1.6	2.0	2.0	0.3
II. Series of Mixtures.				
1000 mls M	16.2; 16.9	16.6	16.6	0.3
750 mls M + 250 mls A	17.3; 17.7	13.0	17.5	4.5
500 mls M + 500 mls A	11.1	9.3	11.1	1.8
250 mls M + 750 mls A	7.5	5.7	7.5	1.8
1000 mls A	2.1; 2.4; 1.6	2.0	2.0	0.3

The "basicity" of the two series of mixtures should theoretically be located on a straight line. The two curves (sheets I and II) give the deviations from the theoretical values.

The potentiometric titration of the bases in the distillate gives information on the principal causes of the scattering of results mentioned above. Fig. 3 presents the course of titration of 1000 R, as well as the titration curve of the coal liquefaction middle oil of Scholven. The two curves have the same in common:

1. A strong change in the slope is found at pH 2.5, which is certain to have been caused by an equivalence of the acid and base. The point of equivalence is therefore considerably different from the point of inversion of methyl orange, and when titrating with methyl orange as indicator, only part of the bases are indicated. The arrows drawn in Fig. 3 represent the titration values obtained in titration with methyl orange.

2. The curve does not represent the titration of a single weak base with a strong acid, but of a mixture of bases present.

The law of mass action gives the following relationship for the equivalent point of a weak base and a strong acid:

$$pH_{equivalent} = 7 - 1/2\ pB - 1/2 \log c$$

where pB is the negative log. of the dissociation constant of the base K_B, and c the total salt concentration.

Potentiometric titration permits therefore the calculation of the dissociation constant of the base, or, conversely, when the dissociation constant is known, the concentration of the hydrogen ion at the equivalent point can be calculated.

For the titration shown in Fig. 3,

$c = 10^{-2}$; $\log c = -2$

$pH = 2.5$

and K_B is therefore 10^{-11}.

Bases with a dissociation constant of $K_B = 10^{-10}$ can be titrated with indicators like dimethyl yellow, thymol blue or Tropeolin 00 using a N/1 acid solution, with an accuracy of about 1%, while with a N/10 acid solution the errors made will amount to 10%. Bases with still smaller dissociation constants can therefore no longer be titrated with indicators.

The middle oil bases must therefore be titrated potentiometrically with N/1 acid, because with N/10 acids the equivalent point is located almost in the pH range of the dilute acid, and the change in the potential becomes very slight. The two series of mixtures were therefore titrated potentiometrically with N/1 acid. Fig. 4 shows the titration curves with the mixture series A-R.

The table below averages the values found in the two series of mixtures:

Series of mixtures A-R

Oil used	"Basicity" found, mg NH_3/li	Theoretical Value	Deviation from theoretical value.
1000 mls R	67.1; 66.3	-	-
750 mls R + 250 mls A	52.7	52.1	0.6
500 mls R + 500 mls A	37.4	37.6	0.2
250 mls R + 750 mls A	22.1	23.1	1.0
1000 mls A	8.5	-	-

Series of Mixtures A-M:

Oil used	"Basicity" found, mg NH_3/li	Theoretical Value	Deviation from theoretical value.
1000 mls M	23.8	-	-
750 mls M + 250 mls A	20.4	19.9	0.5
500 mls M + 500 mls A	16.1	16.2	0.1
250 mls M + 750 mls A	11.9	12.4	0.5
1000 mls A	8.5	-	-

The results agree well among themselves, but it must be remembered that the evaluation of such curves has so far not been done either theoretically or experimentally. Fig. 5 shows the characteristic differences between the titration curve of a single base and the titration curve of a mixture of bases from the gasol Reitbrook. A distinct change in potential (inversion point) is observed in the titration curve of aniline (dissociation constant $K = 3.5 \times 10^{-10}$) which permits a definite determination of the endpoint. 50 mls aniline were taken (N/10) and correspondingly 85 mg NH_3 were found. In the titration of the mixture of bases from P 1338 there is only a change of slope, which permits a comparison between different middle oils.

Three variables enter the titration curve of a mixture of bases, namely the dissociation constants of the individual bases, their relative proportions and their absolute concentrations. A theoretical-mathematical treatment of such titration curves has not so far been done. The experimental investigation of this problem will be continued at the proper time.

We may mention in addition that the endpoint value obtained with a potentiometer are always appreciably higher than obtained by titration with methyl orange. The results obtained potentiometrically and with methyl orange are presented in Figs. 1a and 1b at the end of the article.

DIRECTIONS FOR THE DETERMINATION OF "BASICITY".

The material to be tested is washed three times in a separatory funnel with water (oil : water = 1 : 3). The layers are separated and the material is distilled, collecting the cut from 150 or 180°, to an end point of 325 - 350°, depending on the origin of the oil.

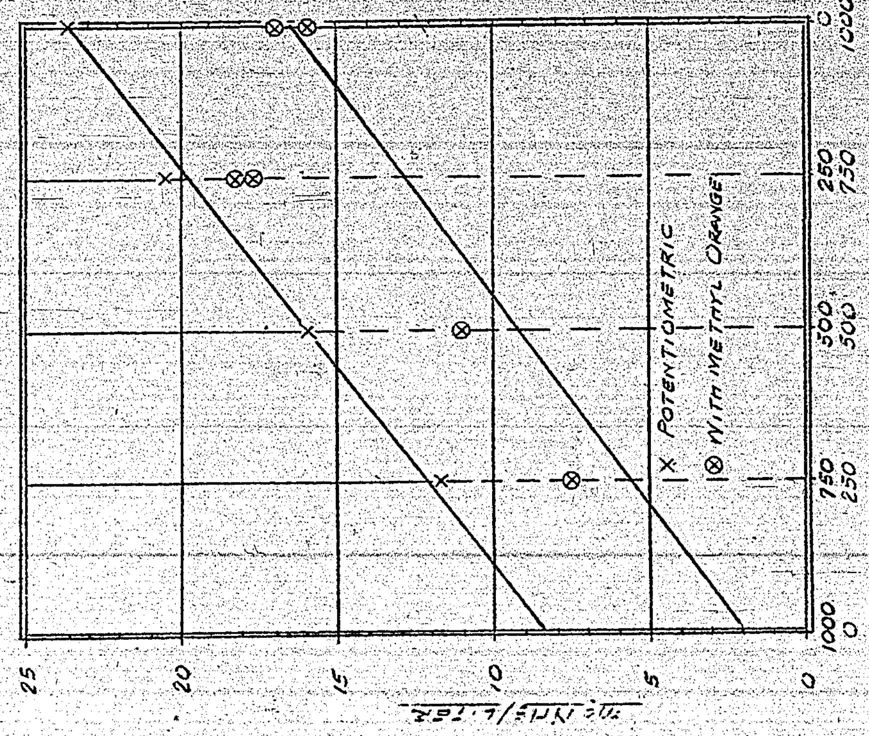
1000 mls of the middle oil are vigorously shaken in a shaking machine 6 times with 50 mls of 10% sulfuric acid for 10 minutes. The acid solution is drawn off after the layers have separated. The six extracts are combined in a distillation flask, which is a part of an ammonia distillation outfit. The solution is made alkaline with sodium hydroxide and the organic bases are distilled over with steam into a receiver containing 50 mls N/1 sulfuric acid. After 30 minutes uniform boiling the distillation is interrupted. The acid in the receiver is back titrated potentiometrically with N/1 sodium hydroxide. It has been found advisable to finish the titration of the last 10 mls of NaOH using a microburette and adding 0.1 ml at a time to the endpoint if the basicity is up to 100 mg NH_3/li. The electrodes of the potentiometer are antimony and a N/1 calomel electrode. A very sensitive galvanometer with compensation connections is to be used as a zero point indicator (sensitivity about 10^{-7} A; i.e. Pehavi). The titration curves are evaluated graphically, by plotting on a system of coordinates the mls NaOH added against the pH readings. The 50 mls N/1 sulfuric acid need not be accurately measured because the endpoint of the titration is characterized by pH = 7. (The basicity is the difference between the volumes of NaOH used at the inversion point and at pH = 7. Translator)

Calculations: mls NaOH used x 17.0 = basicity of solution (in mg NH_3/li).

With high-nitrogen oils an emulsion is frequently formed during shaking with 10% sulfuric acid, which can not be broken. Premixing the oil with n-heptane in proportion of 1 : 3 has been found in every one of the cases encountered to be effective.

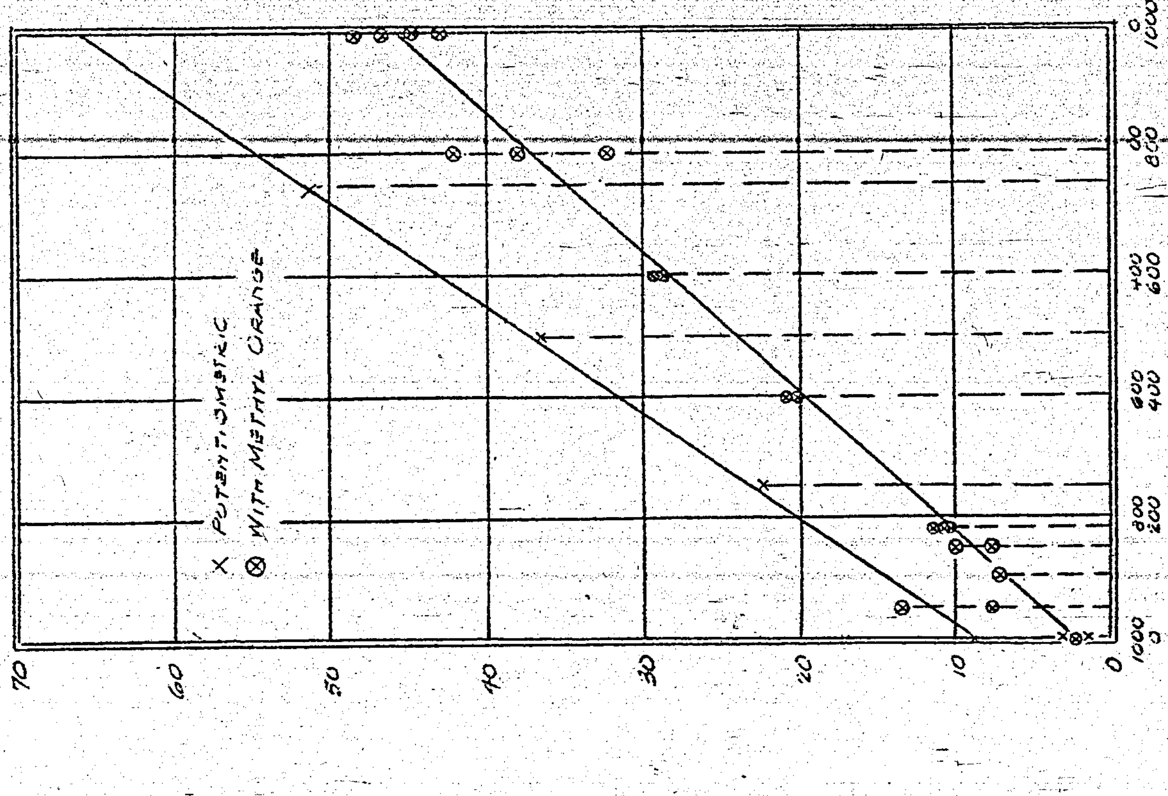
__Results:__ It has been found that potentiometric titration gives comparable results in nitrogen determination ("basicity") in middle oils, with scattering limited to ± 1 mg NH_3.

/fkp



SERIES OF MIXTURES A-M

FIG. 1-B



SERIES OF MIXTURES A-R

FIG 1-A

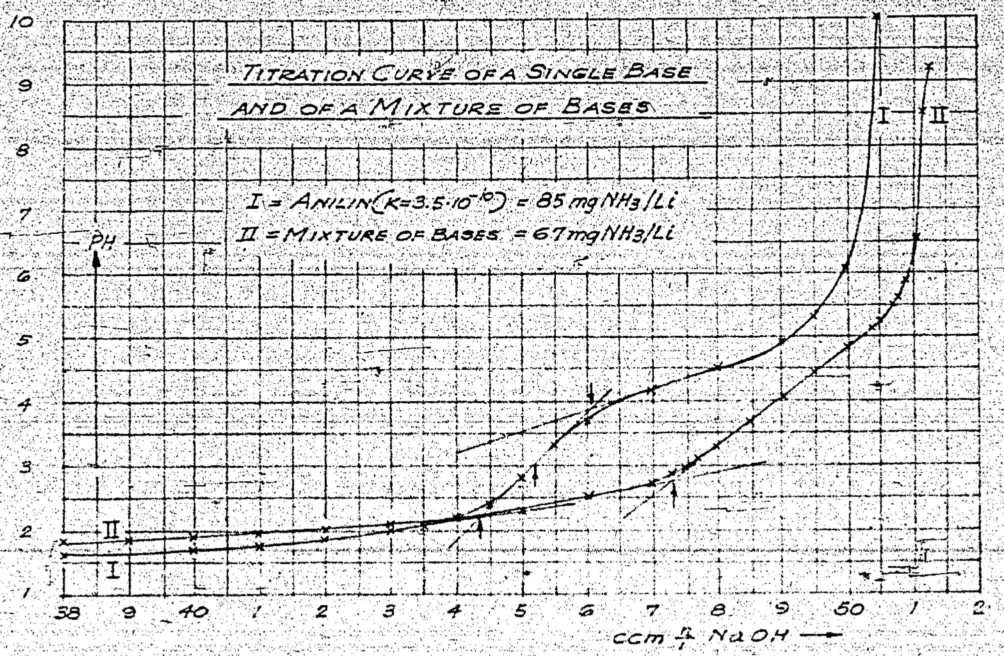

TITRATION CURVE OF A SINGLE BASE
AND OF A MIXTURE OF BASES
I = ANILIN ($K = 3.5 \cdot 10^{-10}$) = 85 mg NH_3/Li
II = MIXTURE OF BASES = 67 mg NH_3/Li
PH
10
9
8
7
6
5
4
3
2
1
38
9
40
1
2
3
4
5
6
7
8
9
50
1
2
ccm $\frac{n}{1}$ NaOH →
I
II
I
II

FIG. 5

Relation Between Splitting Property of Oils and Their Kjeldahl Nitrogen Content

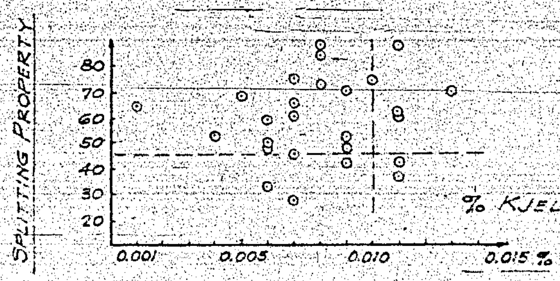


Fig. 1

Relation Between Splitting Property of Oils and Their Basicity

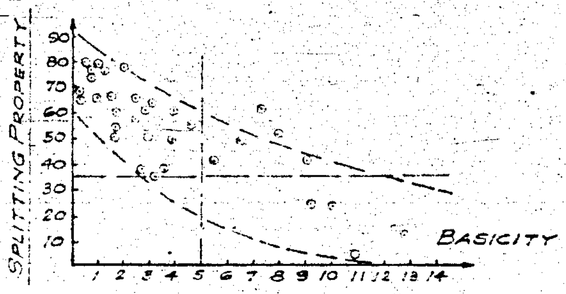


Fig. 2

U. S. BUREAU OF MINES 893 T-354
HYDRO. DEMON. PLANT DIV.

KCBraum
5-6-47

Saving Molybdenum in the Liquid Phase
High Pressure Research, Ludwigshafen, 3 February 1941

At the present time, the raw materials available in Pölitz, bituminous coal tar pitch, gas producer tar, and bituminous coal tar oil are processed in a mixture of 1:1:1 to heavy oil in a 10 Ltr. converter above 325° C with 2% iron-titanium-Grude (coke). According to results obtained to date, it appears possible to process this mixture with a space-time thruput of 0.5, a reflux of 1:0.4 heavy oil (light oil bottoms) and 1:0.3 letdown. The heavy oil reflux is necessary to be able to control the converter at a temperature of about 484° C required for the conversion of solids and asphalt. The new letdown obtained in quantities of 15 - 20% of the fresh oil could be carbonized without any trouble in a small ball kiln. The attached Table 1 shows a comparison of the raw material and the operating method with those formerly used and Mo-catalyst.

Former experiments with bituminous coal tar pitch (17% solids) in a 1 Ltr. converter at 600 atm yielded 0.36 middle oil with Mo-Grude catalyst + Cl, and 0.21 - 0.26 with FeS-catalyst (sulfured Luxmass), or a yield lower by about 30 - 40%.

An experiment with bituminous coal gas producer tar residue, spec. gravity 1.085/100°C, 7% solids, 33% asphalt and 7 available H/100 C, ran for 2 weeks without any difficulty, after the letdown reflux had been increased to 1 part for each part fresh oil feed. The catalyst used was 1% Grude with $FeSO_4$ and 0.2% Na_2S. It should, however, be noted that this tar residue is easier to work than coke oven tar pitch.

In summary, it may be said on the basis of small experiments in 1 and 10 Ltr. converters that the Pölitz bituminous coal tar mixture, which contains only 1/3 bit. coal tar pitch, can be processed with iron catalyst without molybdenum. It is probable that with the present iron catalyst the yield will be decreased at least 20%.

On the basis of other experiments in a 10 Ltr. converter it appears that this tar mixture could be added to the coal, about 15% of the coal, without decreasing the yield.

/fkp

Table 1

Processing Bituminous Coal Tar Pitch

Catalyst	Mo-Grude	Fe-Tit-Grude	Fe-Tit-Grude
Raw Material	Ruhr Tar Mixture		Pölitz
Properties:			
Sp. Grav/100°C	1.062	1.062	1.104
% Solids	8	8.1	12.9
% Ash in Solids	4.5	4.5	4.8
% Asph. in Oil	26.7	26.7	16.9
% -325°C in Oil	2.4	2.4	9.8
Thruput	0.64	0.62	0.5
Letdown Reflux, % of Fresh Oil Feed	0	0	40
Heavy Oil Reflux, % of Fresh Oil Feed	50	50	30
Converter Temp. °C	478	476	484
Catalyst Quantity, %	1.0	1.5	2.0
Yield (gasol. + mi-oil + Heavy Oil)	0.51	0.48	0.4
L.T.C. of Letdown in ball kiln	not possible	not possible	possible
Converter	411	411	411
Date	Sept. 1940	Sept. 1940	Feb. 1941

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T-355

KCBraun
5-6-47

Using 700 Atm. in the Vapor Phase
at Blechhammer Extension II
(Discussion at Welheim, 29 January 1941)

By Dr. Walter Krönig, Schlesien-Benzin, 29 January 1941

Dr. Krönig pointed out that benzination in Blechhammer I had been definitely set @ 300 atm, and that this could not be changed, but that the question of 300 or 700 atm in the vapor phase was still open for Blechhammer II. This question should be settled not later than April 1, 1941.

For extension II were available 120000 t liquid phase gasoline to 325° C, of which an estimated 48000 t to 200° C.

Dr. Winkler of Ruhröl declared that this quantity was about right for 2 double aromatization converters, though the high proportion of liquid phase gasoline in the injection was a disadvantage.

To this Dr. Krönig remarked that it appeared fundamentally possible to make an exchange between extensions I and II in such a way that extension II would supply liquid phase gasoline to extension I and extension I supply extension II with a corresponding quantity of middle oil. The limits for such an exchange are given by the following considerations:

1) In extension I the quantity of liquid phase gasoline must not increase so much and the quantity of middle oil drop so much that the two double 6434-stalls will be underloaded.

2) The shifting between gasoline and middle oil in extension I must not go so far as to reduce the anti-knock value of the gasoline from extension I to any extent.

3) The exchange must not go so far as to reduce the fraction of heavy gasoline available in extension I for DHD too much.

It may be assumed, without making detailed investigations, that the liquid phase gasoline fraction to 125° C from extension II, which amounts to about 60% of the liquid phase gasoline to 200° C, 29000 t/ann. more or less, can be exchanged for middle oil from extension I. From the standpoint of distillation also, cutting out the fraction to 125°C could be done. Dr. Krönig promised Dr. Winkler to notify him, if an exchange to such a degree were possible in I.G.'s opinion. Dr. Winkler would then discontinue his small experiments along this line. Dr. Winkler will also investigate one 10 Kg sample each of liquid phase gasoline and liquid phase middle oil obtained from running Upper Silesian coal to fuel oil at Ludwigshafen, particularaly for their phenol content, since phenols in higher concentration, especially carbolic acid, damage the catalyst, in order to establish a basis for his opinions. On the basis of Dr. Krönig's data and the results of the then discontinued experiments, Dr. Winkler will prepare a flow sheet for extension II at Schlesien-Benzin, which will include all important details for such a decision.

Dr. Winkler submits the following data on VT-706-b, end point 165° C, from pitch liquid phase middle oil @ 700 atm and stabilized in Scholven. (The gasoline is refined with 0.5% of 96% H_2SO_4 and then washed with a 10% solution of caustic soda. It is then redistilled to 3% residue, which is returned to the vapor phase):

Sp. Grav./15° C	0.800
Turbidity point	-4°C
Beginning of crystallization	-60°C
Vapor pressure	0.40 atm
Initial boil	42°C
10%	75.5°
20%	83.5°
30%	91.0°
40%	97.0°
50%	103°
60%	113°
70%	125°
80%	137°
90%	153.5°
95%	164.5°
Boiling end 98% @	170°
Residue	0.9%
Reaction of residue is neutral.	
100° point	45%/vol.
Kennziffer (Mean boiling point-?)	114.1
Aniline point	-4.5°
" " (dearomatized)	+47.5°
Corrosion test	negative
Doctor test	"
Glass dish test	0.02 mg
Bomb test	0.12%
Resin not absorbed (permissible	18.4 g/100 cc
" directly " (limit is 10 mg)	8.6 mg/100 cc
Lead sludge	12 mg/200 cc
Iodine number	2.4
Aromatics - Olefins	51%/vol.
Naphthene	37%/vol.
Paraffins	12%/vol.
Elementary Analysis:	
C	88.38%
H	11.61%
S	0.0072%
Octane number, M.M. without lead	81
with 0.05% "	87.5
" 0.12% "	91.0

Dr. Winkler recommends that Schlesien-Benzin get in touch with Dr. Dehmlow of the ministry of aviation in Berlin regarding the evaluation of the Welheim gasoline, as well as CV_2b or DHD gasoline. As far as Dr. Winkler knows, the CV_2b from Scholven could not meet the specifications of the air force with respect to iodine number, resin test and light stability. DHD gasoline could not meet the lead sludge test. This group of high test fuels must basically have a minimum aromatics content of 50%. Welheim gasoline is added to the 87 octane gasoline to the extent of 70%, so that the aromatics content of the mixture is 40%.

Welheim gasoline is produced in a stall containing 10.5 m³ catalyst. The stall consists of:

2 heat exchangers
1 gas fired preheater, with 23 hairpin coils (fuel gas consumption = 4000 m³/h @ 5500 kcal).
2 converters
  1 @ 900 mm Ø x 12 m long, and
  1 @1000 mm Ø x 15 m " .
  Both converters have standard insulation.

The converters have no trays or baffles. Nevertheless, the temperature distribution in the converter is excellent. With an injection x) of

9 t/h fresh oil : B-middle oil = 1:1 xx)
28000 m³/h inlet gas (72-74% H_2 = 450 atm H_2 partial pressure)
5000 m³/h cold gas

the converter temperatures were:

<u>Converter I</u>

Elements	1,	2,	3,	4,	5,	6.
Millivolt	25.1,	25.5,	25.7,	26.2,	26.2,	26.2.

<u>Converter II</u>

Elements	112,	111,	110,	109,	108,	107,	106,	105,	104,	103,	102,	101.
Millivolt	25.0,	25.1,	25.5,	25.8,	26.0,	26.2,	26.0,	26.2,	26.2,	26.0,	26.2,	26.0.

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x) Triplex beam pumps were formerly used. These were entirely unsatisfactory because they could not be satisfactorily regulated. At present, 5 m³ paste presses are used, which, though more expensive, can be accurately regulated.

xx) The reflux is held around 1:1, if possible, because the converter operates most uniformly with a strong reflux, even when starting a new catalyst. This is also important because of the phenol content, which should not exceed 10% in the injection, since a higher content deteriorates the catalyst appreciably.

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Controlling the temperature with a thruput (space time) of 0.4 offers no greater difficulties than a 5058 stall in operation for some time. Within 2 years of operation the stall temperature has risen beyond control only 3 times, in each case for mechanical reasons not connected with the process. With an injection of 10.5 t/h the inlet gas is 28000 m³/h. the cold gas 6000 m³/h. The cold catch pot product concentration is 50-55%/vol. (Abstreiferkonzentration). In the benzination of liquid phase gasoline + liquid phase middle oil from the pitch stall the high pressure losses are 12.4%, the losses in stabilization and transportation to Scholven 3.1-5.1%. Dr. Winkler will make up a C-balance, from which the accurate composition of gasification, including stable gas, can also be determined. In previous experiments the composition of the gasified C, without stable gas, was as follows:

C_1	C_2	C_3	n-C_4	i-C_5
16.2	22.1	31.8	21.1	8.8

The H_2 consumption is 700 IG-m^3/t (@ 735 mm & 15° C) of unstabilized gasoline. There is no circulating gas wash. On the contrary, the aromatization stall acts as a gas wash for the liquid phase stall, since it is on the same gas circuit.

Dr. Winkler figures on a catalyst life of at least 1/2 year, possibly over 1 year. The longest catalyst life so far obtained in large scale production has been 180 days. A check of this catalyst in a small converter showed that it was still quite active. In any case, the deterioration of the catalyst is much less than with 7019 in Scholven. The catalyst is used in pills of 10 mm. It is practically free of government controlled metals. It would be supplied by Welheim. The cost of the catalyst was roughly estimated at about RM. 1500/m^3. Its bulk weight (Schüttgewicht) is 0.65. Its strength is outstanding. The latest catalyst differs from that formerly used in that it produces gasolines rich in aromatics from the very start, while the former catalyst had to be run in for some time before it would produce highly aromatic gasoline.

To the question of using 700 atm vapor phase in peace time, Dr. Winkler declared that in peace time the gasoline would be cut off at 185°C. He was convinced that a premium would also be paid for its use in automobiles, compared to 70 octane gasoline, that Welheim gasoline to 185°C possesses benzene-gasoline blend quality (Aralqualität)and is a desirable blend gasoline for Fischer gasoline as well. If gasoline rich in aromatics should really find no sale in peace time, there was always the possibility of producing H_2-rich gasoline with a different catalyst at a temperature of 22 mV.

Summary.

The discussion brought out that the use of 700 atm in the vapor phase would appear to be very advantageous for Blechhammer II, assuming that:

1) an exchange of liquid phase gasoline and liquid phase middle oil between extensions I and II is possible without harming the requirements of extension I.

2) a high test gasoline able to meet air force specifications can also be obtained from Scholven middle oil @ 700 atm.

3) the government (Reichsamt) is satisfied with the reduced quantity of isobutane.

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5-7-47

Sulfur Balance in Hydrogenation Works

High Pressure Research, Ludwigshafen, 1 Dec. 1943

Attached Table 1 shows the sulfur processed in combined or elementary form in the various German Hydrogenation Works. Combined sulfur is found in the raw material and the liquid phase catalysts, elementary sulfur is added to the coal in some works and to the a and b middle oils, to the latter generally as H_2S, in all works except Lützkendorf and Zeitz.

The total production of all hydro-works, expressed in auto gasoline, is 3,550,000 t/ann.

For each 100,000 t/ann auto gasoline, 5110 t sulfur is obtained, or a surplus of 4240 t, divided as follows:

1090 t in water gas for H_2 prod.	2900 t in hygas, water & product, less 870 t for own use = 2030 t	1120 t in residues

The sulfur from the water gas for H_2 production (Nullwassergas = OWG), the hygases and make-up water can be recovered = 3120 t. The yield is approximately 80% = 2500 t.

Table 2 contains detailed figures for the sulfur input in the raw material and catalyst and that combined with the residues.

pkl

TABLE 1
SULFUR BALANCES OF HYDROGENATION WORKS
Estimated for 1944

	Scholven	Gelsenberg	Pölitz	OHW Blechhammer	Leuna	Rheinbraun	Brüx	Böhlen	Magdeburg	Zeitz	Welheim	Lützkendorf
Production in t/ann auto gasoline	210,000	300,000	640,000	430,000	530,000	215,000	395,000	200,000	190,000	265,000	125,000	51,000
Hydrogenation raw material	Bit. Coal	Bit. Coal	Bit. Coal, Pitch Tar & Petrol	Bit. & Br. Coal	Br. Coal	Br. Coal	Br. Coal Tar	Br. Coal Tar	Br. Coal Tar	Br. Coal Tar	H. T. Pitch	Mi-Oils fr. Bit & Br. Coal
Quantity, t/ann	460,000	595,000	868,000	946,000	1,470,000	465,000	500,000	250,000	240,000	320,000	180,000	57,000
Sulfur content, %	0.73	0.65	0.56	0.63	5.4	0.45	0.39	1.5	1.5	1.5	0.8	0.15
Sulfur in raw mat'l, t/ann	3,360	3,840	4,865	5,945	75,000	2,100	1,950	3,750	3,600	4,800	1,440	85
Liq. Ph. Cat. & quantities, t/ann	Snox	4400 $FeSO_4$ 5800 Bayerm. 1600 Sulfigr.	5300 $FeSO_4$ 13000 Bayerm. 1330 Sulfigr. 3650 Cleaning Mass	6750 $FeSO_4$ 8900 B. M. 2500 Sulfigr.	125,000 Bayerm.	23,700 Bayerm.	1,500 Grude-Iron	500 Grude-Iron	500 Grude-Iron	--	900 Grude-Iron	--
Sulfur content, %	--	--				--	6.5	6.5	6.5	6.5	6.5	--
Sulfur in cat, t/ann	--	1,590	1,700	2,440	--	--	100	33	33	--	60	--
Sulfur added as elementary S (S ≠ H_2S) t/ann	1,320	1,900	1,670	1,425	13,500	5,550	4,060	1,200	1,200	--	--	--
Quantity OWG	$390x10^6m^3$	$800x10^6m^3$	$260x10^6m^3$	$1160x10^6m^3$	$1460x10^6m^3$	$600x10^6m^3$	$690x10^6m^3$	$215x10^6m^3$	$215x10^6m^3$	$175x10^6m^3$	$100x10^6m^3$	$43x10^6$
Sulfur in OWG, %	0.3	0.3	0.3	0.3	0.6	0.8	0.8	0.8	0.8	0.8	0.3	0.3
Sulfur in OWG, t/ann	1,550	3,200	1,100	3,420	11,700	6,400	5,500	2,300	2,300	1,850	400	170
Sulfur input without OWG, t/ann (Catr. Res. [illegible] 20% Sol.)	4,680	7,330	8,235	9,810	88,500	7,650	6,110	4,983	4,833	4,800	1,500	85
Sulfur input with OWG, t/ann	6,230	10,530	9,335	13,290	100,200	14,050	11,610	7,283	7,133	6,650	1,900	255
Hydro. Residue, t/ann	73,000	67,500	124,000	127,000	440,000[8)]	76,000	12,000	1,000	1,000	--	5,000	--
Sulfur in resid, %	3.15	5.0	4.2	4.9	5.6	6.5	2.28	6.0	6.0	--	3.55	--
Sulfur cont. in resid, t/ann (+ bit. coal tar)	2,300	3,400	5,210	6,200	19,700	4,950	274	60	60	--	177	--
Recoverable S in t/ann (without OWG)	2,380	3,930	3,025	3,610	68,800	2,700	5,836	4,928	4,773	4,800	1,323	85
Recoverable S in t/ann (with OWG)	3,930	7,130	4,125	7,090	80,500	9,100	11,336	7,228	7,073	6,650	1,723	255
Cat. consumption, t/ann	1,320	1,900	1,670	1,425	13,500	5,550	4,060	1,200	1,200	--	--	--
Recoverable S pr. 100000 t/ann (without OWG)	1,130	1,310	475	840	13,000	1,250	1,460	2,440	2,500	1,850	1,020	167
Recoverable S pr. 100000 t/ann (with OWG)	1,870	2,380	645	1,650	15,200	4,220	2,850	3,600	3,700	2,560	1,340	500

T-357
(Table 2)

TABLE 2

[illegible]	Scholven	Gelsenberg	Pölitz	OHW	Leuna	Rheinbraun	Brüx	Böhlen	Magdeburg	Zeitz	Welheim	Lutzkendorf	Total
in raw mat'l. %	0.73	0.65	0.56	0.63	5.4	0.45	0.39	1.5	1.5	1.5	0.8	0.15	
t/ann	3,360	3,840	4,865	5,945	75,000	2,100	1,950	3,750	3,600	4,800	1,440	85	110,735
per 100000 t gasoline	1,600	1,280	760	1,385	14,150	975	495	1,875	1,890	1,850	1,150	167	
in catalyst t/ann	--	1,530	1,700	2,440	--	--	100	33	33	--	60	--	5,812
%	3.15	5.0	4.2	4.9	5.6	6.5	2.3	6.0	6.0	--	3.55	--	
in residue t/ann	2,300	3,400	5,210	6,200	19,700	4,950	274	60	60	--	173	--	31,731
100	1,100	1,130	815	1,440	3,720	2,020	70	30	32	--	141	--	

The Sulfur Situation in German Hydrogenation Works
(condensed)

Leuna Werke
13 Dec. 1943

An attempt has been made to report as exhaustively as possible on the input of sulfur in the raw materials, the production of sulfur or products containing sulfur, as well as the sulfur consumed by themselves, of German hydrogenation works. The report can make no claim for completeness , because it is very difficult to grasp and compare the different conditions in each plant to any extent. The purpose of this report was to determine as quickly as possible, whether the production of sulfur could be increased within a short time or whether requirements could be reduced. In addition, it was determined, whether additional sulfur could be utilized by the construction of new plants. The investigation was limited to hydrogenation works, though for Leuna the proportions applicable to other divisions were taken into consideration. Lützgendorf, which is mainly a Fischer plant, was also taken into consideration. It is proposed to make a separate report on the Fischer plants, though it is doubtful if appreciable additional quantities of sulfur can be obtained from them.

Works included in this report are:

1. Leuna
2. Brabag Böhlen
3. Brabag Magdeburg
4. Brabag Zeitz
5. Scholven, Gelsenkirchen-Buer
6. Gelsenberg, Gelsenkirchen
7. Welheim (Ruhröl-Stinnes)
8. Union Rheinische Braunkohle, Wesseling
9. Brüx (Sudetenländische Treibkraftstoff-W)
10. Pölitz
11. Wintershall, Lützgendorf, Krumap/Merseburg
12. Blechhammer (Oberschlesische Hydr-Werke)

In all works only raw material was considered, the sulfur content of which could be recovered. For that reason, the coal for power production was not included, because it would not be practical to recover the SO_2 in the flue gases.

In summary, it can be said for all hydrogenation works, that large quantities of sulfur, recoverable in a normal way, have not been withheld from production anywhere to date. On the contrary, production within the period 1943/44 will run to about 72,000 t elementary sulfur, 12,000 t S in SO_3, and 6,000 t S in gas cleaning media, or a total of about 90,000 t/ann S, of which about 9000t/ann will be consumed again in the plants. The additional production or reduced consumption in this period of time is about 17,000 t/ann S + SO_3 — S. By comparatively little additional equipment, an additional 2,000 - 3,000 t/ann elementary sulfur could be recovered, by larger plants 7000-10,000 t/ann el. S, and between 6,000 and 7,000 t/ann SO_3 — S by building wet catalysis plants.

The detailed figures are shown in the following tables:

1). Estimated sulfur production for 1943 to end of 1944.

	Elem. S t/ann	SO_3-S t/ann	S in gas clean. media without coke oven gas. t/ann	Conc. liquor to Leuna t/ann	Addit. S consumption t/ann
Leuna	48000	8000	-	-	
Böhlen	4600	1450	2185	-	
Magdeburg	3800		2400	-	
Zeitz	5900		1150	-	
Scholven	2300		?	830	
Gelsenberg	2100	2100	-	-	
Welheim	-	420	150	-	
Wesseling	-	-	-	-	6000
Brüx	-	-	-	-	2000 → 1700
Pölitz	-	660	-	-	1700 → 240
Lützgendorf	5200	-	-	-	
Blechhammer	?	?	?	-	
	71900	12630	5885	830	abt. 9000

2). Additional production or reduced requirement in period 1943/44:

Leuna	+ 3000 S	+ 1000 SO_3 — S
Böhlen		+ 1450 SO_3 — S
Magdeburg		+ 2800 SO_3 — S (in Wolfen)
Scholven	+ 2000 S	
Wesseling	— 4000 S (Saving)	
Brüx	— 300 S (")	
Pölitz	— 1700 S (" 1943)	+ 660 SO_3 — S —220 el. S. (Saving. 1944)
	11000 S	5910 SO_3 — S = 17000

3). Quickly obtainable by comparatively little additional equipment, which should be done in any case:

Leuna	1000	t/ann S
Böhlen	320	" "
Zeitz	700	" " (present condition + 1200 S begin. mid-1944.)
abt.	2020 - 3000	

4). To be recovered by building new gas desulfuring plants:

Leuna	2800	t/ann S (perhaps not worth while)
Gelsenberg	1000	" "
Lutzgendorf	6000	" "
	9000	t/ann S

5). Recoverable by building wet catalysis plants behind Claus furnaces:

Böhlen	1270	t/ann SO_3 — S
Magdeburg	700	" "
Zeitz	1100	" "
Scholven	1080	" "
Wesseling	1200 ?	" "
Lützgendorf	1200	" "
	6550	t/ann SO_3 — S

Special consideration is given the question; how can the sulfur in hydrogenation residues be recovered? Experiments to roast the residues for H_2SO_4 production or to liberate H_2S by acid failed.

Experiments to dispose of Leuna L.T.C.-residue in the gypsum sulfuric acid process at Niedersachswerfen or Wolfen have not been made. The sulfur hereby recoverable would at most be 20000 t/ann S, if all the sulfur could be recovered, and 11000 t/ann S by using the sulfide-sulfur. The experiments are to be extended to the residue from Wesseling and the bituminous coal residues from the Ruhr hydrogenation works.

The reduction of elementary sulfur consumption in Wesseling, Brüx and Pölitz, is receiving primary consideration in Ludwigshafen, where other catalysts and operating conditions are being tried out.

Furthermore, experiments are to be made to see if the recovery of H_2SO_4 could not be increased by using brown coal multiclone dust in the $CaSO_4$ — H_2SO_4 at Wolfen from other works also.

I. Leuna

In the Leuna sulfur balance, other production divisions, such as nitrogen and methanol, which are closely connected with hydrogenation, were naturally also taken into consideration, since they participate in the production of sulfur to a considerable extent. In order to avoid possible fluctuations, the sulfur balance was adjusted to 1942. It will vary little for 1943, except for unavoidable losses due to repairs in the sulfur recovery plants.

Sulfur in raw materials (total S)	t/ann
1. Hydrogenation	56811
2. Gas Production	32886
3. Concentrated liquor processing (Starkwasserverarbeitung)	2743
Total	92440

The synthesis gases required for the three operating divisions mentioned above are desulfured partly in an active coal plant and partly in an alkazid plant. The recycle gases originating in hydrogenation are also largely desulfured in alkazid plants before further processing. The H_2S from the alkazid plants are conveyed to a Claus furnace plant, together with the H_2S driven off in concentrated liquor processing and reduced to elementary sulfur, and the waste gas from the Claus furnace is processed in a Petersen tower to 75% concentrated H_2SO_4, with a yield of 99%.

Brought in S			92440 t/ann
Recovered:	Elem. S over active coal	9395 t/ann	
	" S in Claus furnace	35473 "	
	S as 75% H_2SO_4	7811 "	
	S in catalyst	269 "	
	S in ammon-bisulfite	56 "	
		53004 "	53004 t/ann
Losses			
a) - unavoidable			
	1. - in processing coke: water gas 210, ash, sludge circ. cool water 1500, in pure gasses 960, errors 94.	4864 t/ann	
	2. - in raw brown coal & Grude processing: unusable treating gas, stage II 3830, ash, dust & to dump 2890.	6720 t/ann	
	3. - in hydrogenation: hy-residue 19344, oil losses & pure gasoline 381.	19725 t/ann	
	4. - rest of thin gases: concentration 1085, repairs in H_2S circuit 72, in ammon-sulfate 390, missing 1483	3030 t/ann	
	Unavoidable losses	34339 t/ann	34339 t/ann
b) Conditionally recoverable	Waste Claus gas for lack of cooling capacity in H_2SO_4 plant	1199 t/ann	
	Sulfur in phenol treating gas Stage II.	1058 t/ann	
	In mixed fuel gas	2843 "	
		5100 t/ann	5100 t/ann
			92440 t/ann

The following may be said about the conditionally recoverable sulfur in Leuna, now going to waste:

The Claus waste gas discharged into the atmosphere (über Dach) at the rate of about 1200 t/ann sulfur, which will probably be increased to 2000 t/ann during the course of 1943, can be recovered by means of the increased gas cooling capacity added recently. On the other hand, this is offset, to some extent, by increased interruptions due to repairs of waste heat boilers and converters because no reserves are available. A remedial program is being prepared and the Reichsamt has been advised of the present condition, thru which a loss of 2000 t/ann S must be expected in the Claus furnace and 1000 t/ann of acid by repairs on boilers.

The 1000 t/ann S as low percentage H_2S in the II stage of the phenol treating gas (Phenolbegasungsgas), now being burnt in a boiler house, could be recovered, if a suitable line were laid. The iron for the line has been approved, but it has been impossible so far to get the material to build it.

The 2800 t/ann S in the mixed fuel gas, which is also burnt at present, could be removed from the gas and recovered, if a suitable plant were built. Since this quantity of sulfur is contained in a total of more than 900 million m^3 of gas, or only $3g/m^3$, only an active coal or dry cleaning plant can be considered, which will probably require considerable steel per t/ann S.

Proposals and Experiments for Utilizing the Sulfide-Sulfur Going to Waste in Hydrogenation Carbonization Residues

The problem to recover the approximately 11000 t/ann sulfide-sulfur contained in the approximately 20000 t/ann sulfur in the hydrogenation residue is of particular interest. The former suggestion to make this sulfur available for H_2SO_4 production by roasting has been investigated in Ludwigshafen. These experiments, however, have not been successful, due to the low sulfur concentration.

The second suggestion, to recover the sulfide-sulfur as H_2S by the use of waste acid and convey it to a Claus furnace, has been thoroughly investigated at Leuna by extensive experiments. It was found that of the approximately 11000 t/ann.sulfide-sulfur contained in 440000 t/ann sulfur residue, about 6000 t/ann H_2S could be recovered as 25%/Vol. H_2S by using 18000 t/ann concentrated aqueous hydrochloric acid. This could be increased by 800 t/ann H_2S by processing another filter cake containing H_2S with an expenditure of 12000 t/ann concentrated aqueous hydrochloric acid. The hydrochloric acid could be partly replaced by H_2SO_4. However, there are nowhere near the quantities of waste acid available to make this scheme workable, apart from the equipment difficulties, which would have to be overcome by extensive experiments. For the cost of transportation media for waste acid and equipment for processing, an equivalent amount of sulfur could surely be made available elsewhere in a shorter time, e.g. from L.T. carbonization gases.

At the last meeting of the technical committee in Nordhausen a third suggestion was made to utilize the residue in the gypsum reduction to gas containing SO_2 on the sintering machine in the new sulfur plant at Niedersachswerfen, whereby the carbonization residue could possibly be transported in the empty gypsum cars returning from Leuna. Since the L.T.C. residue contains a lot of iron, the additional iron, which, in any case, is required for the production of cement on the sintering machine, could, at the same time, replace a part of the reaction coke by the combustible constituent contained in the L.T.C. residue (?) and the SO_2 content of the reaction gas could be increased by the sulfur content of the residue. Suitable samples of the L.T.C. residue have been sent to Lurgi. A sample of the residue has also been sent to Dr. Reissmann, I. G. Wolfen, for the same purpose.

II. Brabag Böhlen.

Tars and oils are hydrogenated. The hydrogenation H_2 is produced by gasifying Böhlen ASW-Grude.

The present rate of operations, after reopening the H_2SO_4 plant, has been used as a basis for a one year sulfur balance.

Incoming Sulfur in Raw Materials.

	t/ann S
Grude	6870
Tar, light oil	6390
Cleaning mass from Leuna (catalyst)	125
	13385 t/ann

The sulfur constituent from the Grude, appearing in the Winkler water gas as H_2S, is removed about 1/3 by an alkazid rough wash and the rest in a dry cleaning plant.

The sulfur going into hydrogenation, which reappears in the rich and poor gas, is removed in alkazid plants.

The H_2S recovered in the alkazid plants is processed to elementary S in a Claus plant, and the residual Claus gas is processed to 78% H_2SO_4 in a Lurgi wet catalysis.

The gas cleaning mass accrues in such a form that it can be delivered completely for roasting to the Heyden chemical plant in Dresden, where the sulfur is also processed to H_2SO_4.

Considering the described operating conditions, we get the following balance:

Brought in S			13385 t/ann
Recovered:	as El-S in Claus furnace,	4580 t/ann	
	as 78% H_2SO_4	1450 "	
	in gas cleaning mass	2185 "	
		8215 t/ann	8215

Losses.

a) unavoidable

in multiclone dust and power plant ash,	2590 t/ann		
in " " " dump	323 "		
	2913 "		
pure gasoline 36, hy-residues gummed 225, sulfide and phenolate liquors 149, rest in hy-poor gas (fuel gas) 59, with pure water gas 33, H_2SO_4 plant stack 92, Winkler waste water treating II 120		714 t/ann	
		3627 t/ann	3627

b) conditionally recoverable

1. In the hy-poor-gas delivered to ASW (power plant) as fuel gas, not desulfured, which cannot be desulfured because of overload or present location of the line, 323 t/ann

2. Part of the H_2S obtained in the gas treatment (Begasung) of waste water is processed in a Claus furnace, another part, or 690 t/ann, is unfit for the Claus furnace and later goes up the stack after burning, but could be processed to H_2SO_4, if sufficient capacity were available,	690 t/ann
3. The wet catalysis plant, originally intended for Magdeburg, is too small for Böhlen. For this reason 580 t/ann S cannot be processed to acid,	580 t/ann
Total b)	1593 t/ann

To item b) above may be remarked, that the 323 t/ann in hy-recycle gas delivered to ASW may possibly be recovered with the rest of the recycle gas. Whether, and by what means, it will be possible to run the necessary line, is being investigated at present by Brabag. Similarly, Brabag is also working on rebuilding the overloaded Claus furnace, with yield of only about 80%, to increase the yield to 85 - 90%, whereby about 300 - 500 t/ann of the 1593 t/ann conditionally recoverable S would be obtained as elementary sulfur. In any case, only about 1000 t/ann could be recovered as H_2SO_4, if it were possible to push the wet catalysis plant or to enlarge it.

V. Hydrierwerk Scholven A. G.

Bituminous coal and gas tar are hydrogenated. The hydrogenation H_2 is produced by coke gasification. Current daily averages were taken as a basis for the sulfur balance for the year.

Sulfur Input in Raw Materials	t/ann
Hydrogenation	4980
Coke-O-Watergas (only H_2S-S)	970
	5950 t/ann

The coke watergas and the hydrogenation gases are desulfured in alkazid plants, the H_2S produced, together with the hydrogenation water treatment H_2S (Begasuns-H_2S) is conveyed to the Claus furnace.

Considering the processing conditions described above, we get the following balance:

Brought in (total S)		5950 t/ann
Recovered: in Claus furnace	2270 t/ann	
(sent to Leuna in concentrated liquor (Starkwasser)	830 "	
	3100 t/ann	
Losses.		
a) unavoidable		
rest in treated waste water	130 t/ann	
L.T.C. residue	740 "	
rest in hy-poor gas	240 "	
not identified	660 "	
	1770 "	

b) conditionally recoverable
Claus waste gas, possibly
after installing a wet catalysis, 1080 t/ann
or 5950 t/ann

It may be said hereto, that, until recently, Scholven had to buy sulfur for desulfuring, but that they will now produce about 2000 t/ann S by improvements in their sulfur recovery plant. The Claus furnace waste gas, as elsewhere, could be processed to H_2SO_4 by the installation of a wet catalysis. The distribution of about 2900 t/ann S in the gas cleaning media to synthesis and coke oven gas is yet to be determined, though it is recovered by the Ruhrgas Co.

VIII. Union Rheinische Braunkohlen - Kraftstoff A. G. Wesseling

Rhenish brown coal, poor in sulfur, and some tar, is hydrogenated. The hydrogenation H_2 is also produced from rhenish brown coal in Pintsch producers and by hy-gas splitting. Since the water gas does not need to be desulfured at all, because of its extraordinarily low sulfur content, we need not consider the coal for gas production in the sulfur input in raw materials. Sulfur is added in the coal phase of hydrogenation for the purpose of breaking up, or decomposing, the coal. The greater S consumption at the start of operations could be reduced to 400 - 500 t/mo. or 5000 - 6000 t/ann. For the replacement of this sulfur or its partial recovery from the residue, see below.

Sulfur Input in Raw Materials.	t/ann
Hydrogenation	4970
Elementary Sulfur	5800
	10770

With the sulfur-poor coal the sulfur going into hydrogenation is naturally absorbed as iron sulfide by the high-iron residue. Whatever is found as H_2S in the hy-gases is removed in the alkazid plant, in order to use the cleaned gases for splitting. The losses in the water and the waste gases are very large. There may be a possibility to reduce these losses and to recover part of the sulfur in a Claus furnace or a wet catalysis plant.

Brought in (total S) 10770 t/ann

Losses.

a) unavoidable
in hydrogenation residue, 6700 t/ann
losses in dephenolizing, decompression in residual gases, in waste water containing NH_3, dirty water, phenolate liquor, etc. 2870 "
9570 "

b) conditionally recoverable
going into atmosphere in combustion of a waste gas 1200 t/ann
10770 t/ann

It might be possible to increase the quantity of H_2S still further by treating all available waste water with gas, in which their NH_3 content would, of course, offer certain difficulties. It might also pay to recover the sulfur as H_2SO_4 in a wet catalysis plant.

The situation with respect to the sulfur contained in the residue is similar to that at Leuna. 6700 t/ann S are lost in the residue, or somewhat more than the bulk sulfur added. Roasting it to a gas containing SO_2 or utilizing it in the form of waste acids can hardly be considered. Since there are no gypsum H_2SO_4 plants in Western Germany, utilizing it in a manner similar to that being investigated for Leuna would also be out of the question. One possibility to save at least the major sulfur consumption of about 5000 - 6000 t/ann is perhaps the introduction of sulfur in gas cleaning media containing iron, which are not used for extraction or roasting. Such experiments are now under way with gas cleaning media supplied by the Ruhrgas Co. for high pressure research at Ludwigshafen.

It should be noted that Wesseling has had particular difficulties with coal, which make it doubtful that gas cleaning mass can be substituted for sulfur without jeopardizing gasoline production.

XI. Wintershall A. G., Werk Lützgendorf, Krumap/Merseburg.

Although Lützgendorf is principally a Fischer gasoline plant, besides a small hydrogenation unit, it was taken into consideration in this report because it uses brown coal rich in sulfur for gas production. The Fischer synthesis gas is produced in Schmalfeldt generators from brown coal, the same as the producer gas used for fuel purposes. The month of October 1943 was taken as a basis for a sulfur balance.

<u>Sulfur Input in Raw Materials (only H_2S-S)</u>	<u>t/ann</u>
Coal for gas production	18700

Only the synthesis gas is desulfured in a rough stage with alkazid liquor and in a fine dry cleaning stage. The H_2S of the alkazid plant is converted to elementary sulfur in a Claus furnace. The sulfur in the dry cleaning mass cannot be recovered because of its low charge and the spent mass goes to the dump. If the plant were expanded to max. capacity, which, however, cannot be foreseen at present, the sulfur input for both producer (generator) gases would be increased by about 30%.

Considering the above described processing conditions, we get the following balance:

<u>Brought in (total S)</u>		<u>18700 t/ann</u>
Recovered: elementary sulfur,	5200 t/ann	
<u>Losses</u>.		
a) <u>unavoidable</u>		
in gas cleaning mass	880 t/ann	
in ash, water, etc.	<u>4100</u> "	
	4980 t/ann	
b) <u>conditionally recoverable</u>		
producer gas desulfuring,	7400 t/ann	
Claus furnace waste gas for H_2SO_4 production	<u>1200</u> "	
	8600 t/ann	

Concerning the conditionally recoverable quantities of sulfur it should be noted that:

For desulfuring the producer gas a recoverable quantity of 9500 t/ann sulfur was at first figured on. Closer investigation, however, revealed that only 7400 t/ann are present, of which 6000 t/ann could be recovered if an alkazid plant were built. The company itself is inclined towards an alkazid plant, because such a plant is already on hand and servicing would thereby be simplified. The Claus furnace waste gas could be processed to H_2SO_4 by a wet catalysis.

<u>Note</u>:

Conditions at only a few of the plants included in the original report have been described herein, since much of the information is repetitive. The plants selected for translation are representative in character and give us all essential information.

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U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-358

KCBraun
5-13-47

Velocities and Residence Times in Liquid Phase Converters.

By D. I. Schappert, Ludwigshafen, 13 July 1942

Velocities in High Pressure Converters.

Table I shows the most important data required for calculating the velocities in high pressure liquid phase converters. Three operating methods were considered for Wesseling:

a) - projected full thruput when using cold gas as cooling medium,

b) - projected full thruput when using cold gas and cold oil as cooling medium,

c) - present low thruput when using cold oil as cooling medium.

Velocities and Residence Times When Running Bituminous Coal in Liquid Phase.

Ludwigshafen, 8 July 1941

Table II shows velocities and residence times when running bituminous coal for the converters and catchpots at Nordstern, Scholven, 10 Ltr. Converter 411 and Stall 804. The report of 15 May 1939 was used as a basis for the first 3 plants, the experimental data of 29 June 1941 for Stall 804.

Contrary to the former method of calculation, in which a spec. grav. of 1.1 was used for the letdown at converter temperature, these calculations were made with a corrected value of 0.5, which is approximately correct at the high temperatures.

The residence times were calculated:

1) - as formerly, with the assumption that the gas and the liquid form a homogeneous mixture in the converter, and

2) - with the assumption that a degree of filling of only 40% is obtained, which corresponds to operating conditions in large plants. For this second case, the mean converter velocity was calculated by dividing the total converter length by the residence time.

/fkp

TABLE I

Plant		Leuna	Scholven	Nordstern	Wesseling			Pölitz	Welheim	Blechhammer
Pressure	atm	200	300	700	700			700	700	700
Number of Converters		4	4	4	4			4	4	4
Jacket Ø of Converters (I.D.)	mm	1200 800	1200	1000	1000			1000	1000	1000
Clear I.D.	mm	1044 690	1044	860	860			860	860	860
Cross-Section	m^2	0.86 0.375	0.86	0.58	0.58			0.58	0.58	0.58
Thruput	t/h	28	24	35	45.2		26	42	36	68
Inlet gas	m^3/h	28 000	28 000	35 000	38 000		30 000	32 000	20 000	49 000
Cold gas to Conv. I	m^3/h	4 500	4 500	7 000	12 000	12 000	7.0 x)	7 000	7 000	10 500
Cold gas to Conv. II	"	5 000	5 000	8 000	13 000	8 000 + 2.3 x)		8 000	8 000	12 000
Cold gas to Conv. III	"	3 700	3 700	6 000	10 000	4.8 x)		6 000	6 000	9 000
Cold gas to Conv. IV	"	5 000	5 000	8 000	13 000	6.7 x)		8 000	8 000	12 000
					a)	b)	c)			
Volumes										
Operating Condition	m^3/h									
Converter I	"	406 / 466	283 / 325	189 / 219	213 / 264	213 / 264	157	184 / 214	126 / 156	286 / 331
Converter II	"	466 / 533	325 / 371	219 / 253	264 / 320	264 / 301	159	214 / 249	156 / 191	331 / 382
Converter III	"	533 / 583	371 / 405	253 / 279	320 / 363	301 / 307	162	249 / 274	191 / 216	382 / 421
Converter IV	"	589 / 649	405 / 451	279 / 314	363 / 419	307 / 419	165	274 / 309	216 / 251	421 / 472
Velocity in the Converters										
Converter I	m/sec.	0.132 /0.151	0.091/0.105	0.091/0.105	0.102/0.127	0.102/0.127	0.073	0.085/0.103	0.061/0.075	0.132/0.158
Converter II	"	0.151 /0.172	0.105/0.120	0.105/0.122	0.127/0.153	0.127/0.145	0.074	0.103/0.120	0.075/0.092	0.158/0.183
Converter III	"	0.395 /0.431	0.120/0.131	0.122/0.134	0.153/0.174	0.145/0.147	0.076	0.120/0.132	0.092/0.104	0.183/0.202
Converter IV	"	0.431 /0.480	0.131/0.146	0.134/0.151	0.174/0.201	0.147/0.150	0.077	0.132/0.148	0.104/0.121	0.202/0.226

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x) Cooling Oil

914

TABLE II

T-358

	[illegible]	Scholven	Converter 411 (with Upper Silesian Bituminous Coal)	Stall 804
Basis of Calculation [illegible]				
Operating Press. atm	700	700	600	700
Thruput: a) Coal (Maf)	11000 kg/h	9400 kg/h	7 kg/h	577 kg/h
b) Coal Paste	23500 kg/h	23500 kg/h	27.5 kg/h	1940 kg/h Paste plus 367 kg Pasting Oil
Gas Thruput: a) Paste Gas	25000 m³/h	50000 m³/h	21 m³/h	2500 m³/h
b) Cold Gas	25000 "	12000 "	..	2020 "
Converter Gas (Outlet)	41250 "	45000 "	26 "	4150 "
Letdown Gas	440 "	190 "	0.11 "	75 "
Product Gas	400 "	330 "	0.4 "	41 "
Product	14000 kg/h	14000 kg/h	7.8 kg/h	852 kg
Letdown	9000 "	7000 "	8.1 "	1340 "
Mean Converter Temp.	480° C	475° C	493° C	468° C (max.)
Prod. as Vapor at 1 ata, 15°C (Mol. Wt. = 250)	1340 m³/h	1340 m³/h	0.75 m³/h	82 m³/h
Total Gas Vol/h, 15°C	43420 "	46860 "	27.26 "	4350 "
Total Gas Vol/h @ Operat. Conditions	191.5 "	410 "	0.14 "	15.7 "
Volume of Liquid (Spec. Grav. = 0.9)	16 "	14 "	0.0162 m³/h	2.63 "
Total Thruput/h	207.5 "	424.4 "	0.1562	18.38 "
Sizes:				
Conv.: No. per Stall	3	3	1	2
I.D.	840 mm	1040 mm	(70 mm)	330 mm
Length betw. Inlet & Outlet	47.7 m	48 m	2250 mm	18.4 m 1)
Free Cross-Section	5550 cm²	8500 cm²	35 cm²	850 cm²
Total Conv. Vol.	26.46 m³	40.95 m³	7.85 l	1.6 m³
Catchpot: I.D.	850 mm	944 mm	(70 mm)	350 mm
Length	12 m (10 m)	9 m	1.7 m (free space from bottom to catchpot outlet)	7 m 1)
Free Cross-Section	5680 cm² (5681 cm²)	7000 cm²	35 cm²	960 cm²
Total Volume	[illegible] m³ ([illegible] m³)	4.34 m³	5.95 l	0.54 m³
of which for letdown	1.6 " (1.00 ")	1.54 "	1.75 l	0.176 "
Mean Velocities in:				
I) Converter				
1) Gas plus Liquid Calculated Homogeneous Mixture	10.4 cm/sec	13.9 cm/sec	1.24 cm/sec	6 cm/sec
2) @ 40% Full				
a) for Product Gas	16.1 cm/sec	22.3 cm/sec	1.86 cm/sec	8.35 cm/sec
b) for Liquid	2.0 "	1.14 "	0.29 "	2.14 "
II) Catchpot				
a) in Prod.-Gas Section	9.4 "	16.3 "	1.18 "	4.53 "
b) in Liquid Section (calculated for width of catchpot)	0.78 "	5.56 "	0.13 "	0.77 "
Residence Times in:				
I Converter				
1) Gas plus Liquid Calculated as Homogeneous Mixture	458 sec.	348 sec.	161 sec.	314 sec.
2) @ 40% Full				
a) for Product-Gas	296 "	216 "	121 "	220 "
b) for Liquid	2380 "	4220 "	776 "	861 "
II Catchpot				
a) in Prod.-Gas Section	52.7 " (40.8")	24.6 "	108 "	83.5 "
b) Liquid Section	360 " (245 ")	396 "	390 "	238 "

1) Cylindrical Space.

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV. 915

T-359
KCBraun
5-13-47

Application of Mo- and W-Sulfides as Catalysts in Pressure Hydrogenation.

By Göhre, Ludwigshafen, 13 May 1943

Patents Issued

Day-Mo-Yr	Patent	
14- 2-25,	DRP-608466, I.G.	Coal & Molybdenum
16- 2-25,	DRP-609538, I.G.	Tar & Molybdenum
19- 3-25,	DRP-643141, I.G.	Mineral Oil & Molybdenum
14- 2-25,	DRP-633185, I.G.	Coal & Sulfide as Catalyst
16- 2-25,	DRP-619739, I.G.	Tar & Sulfide as Catalyst
19- 3-25,	DRP-664563, I.G.	Mineral Oil & Sulfide as Catalyst
26- 4-25,	DRP-657703, I.G.	Wolfram or Wolfram Compounds (WS_2) as catalyst.
	French Patent-616237, I.G. (Foreign Sulfur Combination)	Compounds of sulfur, ammonium sulfide, sulfide mixtures of several sulfides, alone or with metals, metalloids or oxides, hydroxides, carbonates or analogous compounds, sulfides of heavy metals, e.g. the iron group, alone or with other substances. Sulfites, sulfates, S + metals, metal oxide, $Fe + H_2S$ treated at high temperature.
14- 8-25,	F.P.-620735, I.G.	Fine distribution.
31- 3-26,	I.G.	$H_2 + H_2S$ addition. First publication of the foreign sulfur combination by Belg. Pat. 332018. F.P.-616237 published 29-1-27.
1- 6-26,	F.P.-634820, I.G.	First liquid then vapor phase.
14- 6-26,	F.P.-620735, I.G.	High H_2 partial pressure.
26- 6-26,	DRP-614916, I.G.	Middle oil pressure hydrogenation.
30- 6-26,	DRP-626171, I.G.	First splitting, then hydrogenating catalysts, (wolfram and compounds, e.g. WS_2)
1- 4-27,	DRP-563626, I.G.	Slightly corroded (angeätzte) metals or metallic alloys as catalyst carriers.
28- 5-27,	DRP-618315, I.G.	Hot gas circulation.
24- 7-26,	F.P.-638109, I.G.	Moving (Tanzende) catalysts.
31- 7-27,	DRP-489279, I.G.	Pretreating catalysts with non-reducible gas.
12-11-27,	F.P.-666683, I.G.	Hot liquid circulation.
19-11-27,	DRP-727921, I.G.	Refining hydrogenation in vapor phase.
24-11-27,	F.P.-663539, I.G.	Rising temperatures.
24-11-27,	F.P.-664375, I.G.	Several converters.
15-12-27,	E.P.-302354, F.P.-659462, Eling & Florentin,	Pressure hydrogenation of coal and tars in the presence of: 1) - dehydrogenating catalysts (Al_2O_3, SiO_2) 2) - non-hydrogenating catalysts (metallic substances, halogenides) 3) - hydrogenating catalysts (MoS_2, WS_2)
7- 1-28,	DRP-595234, I.G.	Strengthening catalysts with metals of the 2. & 3. groups.

Day-Mo-Yr	Patent	
1- 3-28,	U.S.-1935188, Silica-gel	Porous gel charged with H_2S, then soak with catalyst.
8- 5-28,	DRP-720002, I.G.	Refining hydrogenation in liquid phase.
15- 6-28,	DRP-669804, I.G.	Prehydrogenation.
13- 6-28,	DRP-639762, Degussa, (Austrian Pat-133142), (Varga)	Pressure hydrogenation with Mo- and W-catalysts and 1 to 6% addition of H_2S until max. increase in effectiveness is reached.
22- 6-28,	DRP-729769, I.G.	Lubricating oil refining in vapor phase.
24- 8-28,	DRP-678622, I.G. F.P.-685564	Triple combination: three different catalysts, two of which originate from a higher than the 4. group.
15-10-28,	F.P.-37394, I.G. (together with F.P.-666683)	Finely distributed catalysts, held suspended.
14-10-28,	DRP-633245, Degussa, (Varga)	Naphthalene hydrogenation with Mo and W catalysts and more than 1% H_2S, e.g. 1 to 10%, particularly 2 to 5%.
13-10-28,	E.P.-333453, Degussa, F.P.-683069	Benzol by splitting hydrogenation of naphthalene with Mo and W catalysts plus H_2S.
7-11-28,	F.P.-684718, Shell,	Luxmass and Mo.
20-12-28,	DRP-671884, Degussa,	Press. hydrog. with Mo & W catalysts and 6-15% H_2S addit.
20- 1-29,	DRP-578567, I.G.	Co, Fe metals of 5. to 7. groups or their compounds, possibly with addit. of Pb, Sn, Zn, Cd or their compounds, after pretreating above 200°C with gaseous or vaporous compounds of solid metalloids of the 5. & 6. groups (H_2S) as dehydrogenation catalyst.
8- 2-29,	F.P.-690911, Shell,	Phenol reduction with Mo to A-coal.
27- 4-29,	DRP-620746, Shell,	MoS_2 on adsorption coal.
21-11-29,	F.P.-745468	
27- 8-29,	F.P.-700891, I.G.	High product partial pressure.
31- 8-29,	DRP-670717, I.G.	Heavy metals or their compounds with volatile sulfur compounds in presence of H_2 at elevated temperatures, with or without pressure.
14- 9-29,	F.P.-694192, Shell,	Hydrocarbons finely distributed on coal.
6-12-29,	E.P.-336689, Shell,	Compounds of Cr, W, U, Mn, Co, Ni, Fe on A-coal or finely dispersed coal.
6-12-29,	F.P.-707210, Shell,	Colloidal catalysts adsorbed on coal.
23- 1-30,	DRP-616427, I.G.	Finely dispersed catalysts held in suspension.
20- 2-30,	F.P.-348243, Shell,	Metallic oxides treated with H_2S.
20- 2-30,	DRP-646916, Degussa,	Circulating gas partially decompressed, so that the H_2S required to maintain the increase in catalytic effectiveness is adjusted within the limits of 1 to 15% and recycled without removing hydrocarbons.
26- 2-30,	F.P.-711250, Shell,	Colloidal Mo on coal.
5- 4-30,	Austrian Pat, Degussa, -134989	Press. hydrog. with Fe-Co-Ni-catalysts with H_2S addition to 15%. Max. increase in effectiveness.

Day-Mo-Yr	Patent	
31- 5-30,	U.S.-2042306,Stand.,	Low H_2 partial pressure made possible by sulfides.
23- 6-30,	U.S.-1904218,Stand.,	Catalyst surface treated (ätzen) with NH_3 or steam.
19- 9-30,	DRP-607363, Stand.,	Roast used Mo and W catalysts, dissolve MoO_3 in acid, separate WO_3 undissolved, precipitate Mo from solution.
7-10-30,	F.P.-40849, Degussa, addit. to F.P.-683069	Benzol by splitting hydrogenation of naphthalene with Fe-, Ni- and Co-oxides, plus H_2S.
8-10-30,	DRP-674444, Degussa, (Varga)	Naphthalene hydrogenation with Fe-, Co-, Ni-catalyst and more than 1%, e.g. 1 to 15%, H_2S.
8-10-30,	DRP-732112, Degussa,	Benzol by splitt. hydrog. of naphthalene with Fe-, Co-, Ni-catalyst, plus H_2S.
30-10-30,	Austrian Pat, Degussa, -136670	Adjust required H_2S concentration in the hydrogenation gas in circul. system.
15-11-30,	Brenstoffchemie, Tropsch, 11S.449	MoS_3 from sulfo-salt decomposed with acid as catalyst for phenol reduction.
18-12-30,	E.P.-379587, Shell, F.P.-728287	Soak carrier in solution of metallic compounds of the 6. group.
1931,	Ukrain. Chem.7, (5/6.244) Prokopetz, & Jeru.	MoS_3 plus S.
12- 1-31,	E.P.-370909,Gas Light, & Coke Co.	Mo + Si, B, Li, P or Ca + H_2S.
30- 1-31,	DRP-686456, I.G.	Metallic sulfides treated with S.
31- 1-31,	DRP-685371, I.G.	Sulfides from thermally decomposed sulfo-salt
26- 3-31,	F.P.-729913, I.G.	Metals of the 4. to 7. groups treated at elevated temperatures with volatile sulfur compounds under pressure, e.g. 5 to 15 atm.
11- 4-31,	DRP-617236, Stand.,	Processing used sulfides with HCl until the soluble constituents, except sulfides of Cr, Mo and W, are dissolved.
17- 4-31,	DRP-589968, I.G. F.P.-735295	Pseudomorphous W & Mo catalysts
12- 5-31,	DRP-659233, Bit.Coal Liquefact.	Elementary S without other catalyst.
25- 7-31,	Reports 1931, Pg. 2631 Orlow,	Hydrogenation (according to Bergius) of hetero-cyclical compounds with MoS_3 or sulfured ammonium-molybdate.
29- 7-31,	DRP-648130, I.G.	Catalyst added after preheating.
4- 9-31,	DRP-577628, I.G.	Thermally decomposable or volatile compounds of Mo and/or W heated to sintering or melting, possibly followed by H_2S treatment.
5-10-31,	U.S.-2029100, U.O.P.	Pressure refining with thio-molybdate or wolframate, e.g. of Cu, Ag, Au, Sr, Ba, Mg, Zn, Cd, Hg, Sn, Pb, Mn, Fe, Co, Ni, Pt, Ce for Mo, also Ca, Be, Cr, but not Ce, for W. Also oxythiomolybdate, e.g. dioxydisulfomolybdic acid.

Day-Mo-Yr	Patent		
16-10-31,	U.S.-1948408,	Stand.,	Precipitate sulfides of the 6. group from an acidic solution (H_3PO_4; HF) with 1 to 4% excess acid, with H_2S.
6-11-31,	DRP-626462,	I.G.	Catalyst added in stages.
14-11-31,	DRP-695432,	Shell,	6. group on de-ashed carrier.
16-11-31,	3. Coal Conference, Pittsburgh	Tropsch,	With acid or thermally decomposable sulfo-salts as catalysts for press. hydr. and phenol reduction.
21-11-31,	F.P.-745468,	Shell,	MoS_2 from thermally decomposable sulfo-salts.
22-12-31,	DRP-681518,	I.G.	Mo+Si+S or H_2S, atomic relation of Si:Mo = 1-3.5 or 5-8:100.
22-12-31,	DRP-678485,	I.G.	Mo+B+S or H_2S, atomic relation of B:Mo = 7-10:100.
13-12-31,	DRP-681519,	I.G.	Mo+P+S or H_2S, atomic relation of P:Mo = 4-4.5:100.
29-12-31,	DRP-722405,	I.G.	Solid metalloids containing halogen compounds together with compounds of metals of the 5. and 6. groups, or sulfides, oxides, etc. of other metals.
29-12-31,	DRP-678808,	I.G.	Halogen compounds of sulfur.
1932,	J. Int.Fuel,	King & Mathews,	Press. hydrog. of tars with MoS_2+ S.
2- 1-32,	DRP-646405,	I.G.	Sulfides & metallic halogenides.
7- 1-32,	DRP-647741,		
30- 1-32,		I.G.	First publication of our sulfo-salt patent thru Belgian Pat. 385293, F.P.-728913
9- 3-32,	DRP-699656, F.P.-750296	I.G.	Sulfides plus acid.
18- 5-32,	E.P.-401724,	I.C.I.	Aromatic hydrogenation with WS_2 @ 1-10 atm & 170-300° C.
21- 5-32,	DRP-660074,	I.G.	Add catalyst before preheating, activating subatance (sulfur or sulfur compounds), after preheating.
2- 6-32,	DRP-611922,	Deutsche Hydrier-Werke.	Dissolving sulfides of the 6. group in primary or secondary organic bases.
14-10-32,	DRP-651473,	I.G.	Pretreat catalyst carriers with H_2.
18-10-32,	DRP-603763,	I.G.	Acidify carriers.
14- 3-33,	U.S.-2037781,	U.O.P.	Co-thiomolybdate + Na-aluminate for press. refining.
24- 4-33,	F.P.-754664,	Shell,	Sulfides from halogenides by sulfuring.
15- 6-33,	Brennstoffchemie, 14.221	Szeszich, & Hupe	Sulfurs part in press. hydrog.
30- 6-33,	U.S.-2037791,	U.O.P.	Metallic oxide (e.g. Fe, Ni, Co, Al, Zn, Co, Th) plus thiomolybdate and alkali or zink-aluminate for press. refining.
Sept. 1933,	Ind.Eng.Chem, 25.1012	Pease & Keighton,	MoS_2 treated with H_2 and ammonium-sulfo-molybdate decomposed by acid.
10- 1-34,	DRP-709940,	I.G.	Pretreat carrier with halogen or halogen-hydrogen.
12- 1-34,	DRP-693985,	I.G.	Double sulfides dissolved by conversion of sulfo-salts with metallic compounds or suspended in the presence of water or organic solvents.

Day-Mo-Yr	Patent	
13-3-34,	E.P.-435192, Yorkshire Tar Dist.	Phenol reduction with metallic thiomolybdate, e.g. of Co, Cr, Sn, Bi.
14- 6-34,	DRP-703736, Stand.,	Sulfide from sulfo-salt decomposed by acid and heat in presence of non-oxidizing gas, especially H_2.
11- 7-34,	F.P.-793436, I.G.	Sulfur W and Mo catalysts in presence of NH_3.
2- 8-34,	DRP-695210, I.G.	Sulfides plus small quantity of basically acting substance (NH_3).
4- 8-34,	F.P.-794397, Shell,	Hydrogenation of selectively polymerized olefins with WS_2.
10-11-34,	DRP-695271/2, I.G.	Pretreat coal with sulfur.
29-12-34,	DRP-659925, I.G.	Pretreat substances containing SiO_2, metals or metallic compounds with HF as catalyst or as carrier for catalysts, e.g. 6436 - 34.?
1935,	Z. Chem. fest. Brennstoffe, 6 (1935) 67. Prokopetz & Jeru,	Better action in naphthalene hydrogenation after autoclave wall was coated with iron sulfide.
20- 5-35,	Petroleum, (1935) #8 Galle	Behavior of MoO_3 and $Mo S_2$ compared with H_2 and H_2S.
1935,	U.S.-2105665, Dupont	Sulfomolybdate of the hydr. metals of the 1, 2, 7 & 8. groups. Preparation of ammon-molybdate + metallic salt solutions + H_2S + HNO_3. Filter off precipitate.
31- 5-34,	E.P.-479428, Mareceaux,	Stage-wise hydrogenation in presence of the 6. group. Reduce H_2S content between stages to 0.1 - 1%.
23- 7-35,	DRP-695211, I.G.	Soak coal with solutions of sulfidic Mo-ore or MoS_2 in H_2SO_4.
17- 8-35,	F.P.-810101, I.G.	Processing catalysts containing sulfides by roasting and treating with aqueous NH_3 + $(NH_4)_2S$ solution.
25-10-35,	Chem.Abstr. Pg. 933/4	Ni-Mo-S) Fe-Mo-S) on carrier $(NH_4)_2MoS_4$
5-12-35,	Austrian Pat. -157112 I.G.	Weakly acting hydrogenation catalysts with small quantities of strongly acting hydrog. catalysts FeS + WS_2.
13-12-35,	U.S.-2112292, Stand.,	Roast Mo catalyst, dissolve in H_2SO_4, dilute, precipitate MoS_2 with H_2S.
	For.Petr.Techn. 534, 529, 540 (1936) #11/12.	MoS_2 on silica-gel or Cr_2O_3. Desulfur heavy gasoline.
9- 1-35,	Reports, 1935, #1. Petrow,	Isomerization of heptane, octane and hexane with MoS_3 under pressure.
15- 3-36,	DRP-696083, I.G.	T-T-H process.
14- 5-36,	F.P.-821792, I.G.	Sulfides on double quantity of carrier substance for press. hydrog. above 300 atm.
16- 6-36,	E.P.-475911, Shell,	Hydrog. of diisobutylene with sulfides of the 6. group.
20- 7-36,	F.P.-824579, Shell,	Pretreating metals with S or H_2S to prevent separation of C in endo-thermal reactions.

Day-Mo-Yr	Patent	
21- 7-36,	DRP-725740, I.G.	Sulfide on carrier as catalyst for press. hydrog. to at least 20% gaseous hydrocarbons.
19- 9-36,	J.Soc.Chem. Ind.Japan. (1936) #12	Ammon-molybdate + acidic fuller's earth + S for hydr. shale oil.
10-10-36,	DRP-724667, I.G.	Refining and splitting press. hydrog. Diluted catalyst in both stages.
30-12-36,	U.S.-2145657, U.O.P.	Alkali-aluminate + metallic sulfides for refining hydrogenation.
Begin.-37,	J.Inst.Petr. Techn. 23. #1, Pg. 209.	$(NH_4)_2MoS_4$ for desulfuring converters.
1937,	C.1938.1. 4739, Putschkow,	MoS_2 for low temp. hydrogenation of Masut. (Russian).
11- 6-37,	(I.G.#10035)I.G.	Mo and/or W-sulfide + Ni and/or Co-sulfide for hydrog. diisobutylene.
8- 8-37,	F.P.-841898, I.G.	Sulfide on synthetic Al/Mg-silicate carrier.
11-12-37,	DRP-711470, I.G.	Add sulfur from time to time.
15- 2-38,	Brennstoff-chemie, 1908, Pg. 61 Zerbe, Grass-kopf	Lubricating oil from distillation products of coal by press. hydrog. with MoS_2
1- 4-38,	DRP-711348, I.G.	Neutralize highly active catalysts with H_2-poor hydrocarbons.
28-12-38,	E.P.-525813/4, Yorkshire Tar Dist.	Thiomolybdate or wolframate for refining hydrogenation.
14- 1-39,	Z.f.angew. Ch, 1939, Pg. 49 Fuchs & Brendlein	Agitate MoO_3 with H_2O, dry @ 110° C, crush and sulfur with H_2S + steam in the proportion of 1:1 @ 450° C.
6- 5-39,	F.P.-859311, Comp. francaise de Raffinage	Catalytic cracking in the presence of organic sulfur compounds, e.g. sulfured oil, with sulfides of Mo or W as catalysts.
6- 4-40,	DRP-725604, I.G.	Sulfides by heating dry prepared mixtures of ammon-sulfo-salts containing metals of the 6. group in the residual acid, and finely dispersed metals of the iron group recovered from the carbonyls.
5- 4-40,	(I.G.#12088), I.G.	Make iron-chloride + $(NH_4)_2S$.FeS harmless by thorough washing or addition of MgO-ammonia salt, add sulfo-salts and heat.

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921

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-360

KCBraun
5-16-47

The Topping of Hydrogenation Letdown and Centrifuge Residue

I. - Experience in Topping Centrifuge Residue and Letdown
Scholven, 30 January 1941
(See also T-330)

Beginning 1940 we started experimenting with concentrating the centrifuge residue in a topping column before L.T. carbonization in the ball kiln. This topping column had a height of 10 m and a diameter of 1.2 m. On the inside of the column were 4 perforated baffles at an angle of inclination of 45° for the purpose of dispersing the centrifuge residue falling from the top, so that the super-heated steam or heated hy-gas in counter current could more effectively distill the oil in the residue. The residue was heated to about 18 mV, or 350° C, in the product preheater of the L.T.C. kiln before injection into the column, while the steam or hy-gas was heated to about 25 mV, or 465° C, in the superheater of the L.T.C. kiln. The steam or gas with the vaporized oil constituents passed off the top of the column. The latter were condensed in a cooler and recovered as topping oil. It was possible to concentrate the residue from a solids content of about 40% to one of about 55% in this manner. This corresponds to an oil recovery of about 150 kg oil per ton of centrifuge residue. The concentrated centrifuge residue was pumped from the bottom of the column and injected into the kiln at a temperature of about 15 mV. However, no special advantages could be detected in the carbonization of this topped centrifuge residue.

If the concentrated product is not carbonized at all, but permitted to cool, it gradually hardens. It has the following approximate composition:

55% solids,
45% ash in solids,
25% asphalt in oil,
90° C softening point.

It may be used as a briquetting medium or for similar purposes. For further processing (grinding, etc.) and to recover as much oil as possible, it would be desirable to concentrate the centrifuge residue still further. However, all attempts in this direction, e.g. increasing the temperature of product and steam, varying the thruputs, etc. brought only slight results. Due to the short residence time in the column, it was possible to obtain a topping residue of at most 60%. Experiments in topping the letdown brought the same results.

These experiments showed that the topping column is ill suited to the intensive concentration of hydrogenation residues, because of the short residence time and the low supply of heat energy.

In addition, it has been clearly demonstrated that, when operating with steam in counter current, new solids are formed, thru which valuable substances, oils and asphalts, are destroyed.

At the suggestion of Dr. Urban, therefore, another method of concentrating hydrogenation residues, particularly letdown, was tried out. Letdown, which had been heated to 15 mV in the preheater, was injected into a carbonization kiln at a temperature of 23 mV = 435° C. At these temperatures no appreciable cracking takes place yet, while the oil constituents boiling to 435° C distill off. The residence time of the product in the kiln is about 1/2 hour. A second discharge device is attached to the kiln proper, as compared to the normal carbonization kiln, in the form of an overflow trap, so that the hot liquid topping residues can run off. We succeeded, on the one hand, to obtain a greater thruput. On the other hand, more oil could be topped off. The thruput we obtained, of about 4t letdown per hour, can very likely be further increased, if the temperature is correspondingly changed. If, for example, a letdown with 25% solids is concentrated to 50% solids, 1/2 ton of topping oil is obtained from one ton of letdown. This corresponds to an oil yield of 66-2/3%, based on the original amount of oil and asphalt.

The kiln runs quite satisfactorily and trouble-free with this operating method. Since there is a demand for the topping residue obtained, and this operating method also relieves the residue processing to a certain extent, this process appears entirely profitable. Furthermore, by taking out a certain amount of solids and asphalt from the hydrogenation circuit, the greater recycle of these substances, such as would occur in subsequent centrifuging, for example, can be partly nullified. The entire residue processing would thereby be put on a more profitable basis.

The combination of centrifuging and topping is of particular importance, if letdowns with specially high asphalt contents must be processed, as is the case in the production of fuel oils, for example.

An attempt is also to be made on an operating basis to find out how much the centrifuge residues can be topped and what oil yields can be expected. Since with the present carbonization method an oil yield of only about 75% is obtained, this new method also promises success, if, for example, the topped centrifuge residue can be suitably utilized.

II. - Report on the Investigation of Two Samples of Topped Residue and Topped Letdown from Scholven

Main Laboratory Mathias Stinnes
By Hoffman, Essen, 17 July 1941

The present necessity to save bituminous coal tar pitch in briquetting in order to use it for other purposes, led us to seek substitutes for tar pitch. Hydro-Works Scholven put 2 samples of hydrogenation residues at our disposal for the solution of this problem. We were to investigate the composition of these materials and their properties as briquette binders.

Analytical Data
Table I

		Topped Residue	Topped Letdown
Softening Point,	°C	96	104
Ash	%	11.37	10.32
Volatile Constituents,	%	47.99	47.22
Solids	%	39.80	36.40
CS_2 - Solubles	%	54.70	59.50

As seen from the above table, both materials are very similar in composition. The softening points are in the neighborhood of 100° C, which is a drawback for briquetting. The ash content of 10 to 11% is still bearable, since with small additions the ash content of the briquettes is only slightly increased. The solids, i.e. the constituents insoluble in tetralin-cresol (80:20), have no binding properties. With a constituent of nearly 40% solids, it is to be expected that the binding power of the products is much less than for bituminous coal tar pitch. The same conclusions may be drawn from the CS_2-insoluble constituents of 55 to 60%.

Determination of Binding Power

Even though these analytical data do not give us a particularly favorable picture, these characteristics are not enough to pass a safe judgement on the suitability of the products as binders for briquetting. For this purpose we use the determination of the binding power, a briquetting method developed by Broche and Nedelmann from practical operations. A kneading machine, in which the mixing and heating is done, is used for making the briquette mixture of coal and pitch. The finished mixture is poured into molds and formed into briquettes by a hydraulic press.

The conditions of the experiments are based on coal particles below 3 mm and pitch particles below 0.5 mm, a mixing time of 10 minutes @ 115° C, and a pressure of 225 kg/cm² at a press forming temperature of 135° C. These standard conditions, determined for tar pitch, were used in a similar manner in the testing of the hydrogenation residues.

The test briquettes so produced are tested for bending strength and the value thus obtained expressed in kg/cm², is the criterion for the binding power of the pitch.

Strength of Briquettes made from Hydrogenation Residues in the Experimental Apparatus

Table 2

% Binder	6.5 %	7.0 %	8.0 %	9.0 %	10.0 %
Topped Residue, kg/cm²	6.7	7.2	8.4	11.2	14.0
Topped Letdown, kg/cm²	6.0	6.5	8.0	10.1	12.3

In order to judge the figures in the above table, it is necessary to know the strengths obtainable with tar pitch.

Strength of Briquettes made from Mathias Stinnes Tar Pitch in Experimental Apparatus

Table 3

Tar Pitch Addition, %	3.5	4.0	5.0	6.0	6.50	7.0
Strength (Bending), kg/cm²	7.0	8.7	13.3	17.0	19.0	21.4

In comparing these 2 tables, it may be seen that the hydrogenation residues are only half as strong as tar pitch in the range between 6.5 and 10% content, based on the briquette mixture. Consequently, these residues can hardly be used in their original form as briquette binder, for economic reasons.

Properties of Mixtures of Hydrogenation Residues and Tar Pitch

The samples in question have this defect, that their softening point is too high for the briquetting process. The clearly observable advantage of the topped residue over the topped letdown is partly based on the fact that the former has a softening point of 96° C, while the latter reaches the same degree of viscosity only at 104° C. At the experimental conditions of the laboratory apparatus, which, with reference to the softening point, are very favorable, the difference of 8° C is clearly expressed in the melting property.

Tar pitch, as normally used for briquetting, has a softening point of about 70° C. It was, therefore, to be expected that molten mixtures of tar pitch and hydrogenation residues would behave better than the original samples without tar pitch, for this reason alone. The mixture proportion was always taken as equal parts of tar pitch and hydrogenation residue. The results obtained with the same apparatus and under the same test conditions are shown in Table 4.

Strength of Briquettes made from Molten Mixtures of Tar Pitch and Hydrogenation Residue in the Proportion of 1:1. (kg/cm^2)

Table 4

% Addition	6.5	7.0	8.0	9.0	10.0
Topped Residue & Tar Pitch, (1:1) Softening Point: 79° C	13.6	14.3	16.4	19.4	21.9
Topped Letdown & Tar Pitch, (1:1) Softening Point: 81.5° C	12.1	12.4	14.6		

The figures in Table 4 show the following:

With an 8% binder mixture, consisting of 4% tar pitch and 4% topped residue, we get an index of 16.4. As seen from Table 3, 4% tar pitch alone gives a strength of only 8.7. The residual 4% topped residue, therefore, gives a strength of 7.7 kg/cm^2, i.e. the hydrogenation constituent enters the mixture at roughly 90% of the binding power of the tar pitch.

If, on the other hand, we ask ourselves what quantity of tar pitch must we use to obtain a strength of 16.4 obtained in the 8% mixture, we can see from Table 3 that less than 6% is required. In this calculation, therefore, 2% tar pitch corresponds to 4% topped residue, or, in other words, the topped residue has only half the binding power of pure tar pitch.

The different conclusions, depending upon the method of reasoning, can be explained by the fact that the relations between the amount of tar pitch and strength of briquettes can not be represented by a straight line passing thru the point of intersection of the coordinate axes in a graphical representation. This is clearly seen in Table 3. While 7% tar pitch gives a strength of 21.4 kg/cm^2, only 1/3 the strength, or 7.0 kg/cm^2 is obtained with 1/2 or 3.5%, the amount of pitch.

With the necessity to save tar pitch and the assumption that only 4% tar pitch may be used, the briquette quality can be advantageously improved by adding an equal amount of hydrogenation residue. The determining factor is this, that 8% of a mixture of equal parts of tar pitch and hydrogenation product can be better distributed in the coal than 4% tar pitch alone. With this interpretation the binding power of the tar pitch will be more efficiently utilized by the addition of topped residue and the topped product will serve only as a diluting agent. Whether internal transformations to compounds of greater binding power also take place in the molten mixtures of tar pitch and hydrogenation product remains to be seen, since it can not be directly proved.

In summary it may be said that hydrogenation residues can be satisfactorily used as briquette binder only where mixed with tar pitch. Tar pitch can be saved in this way. Nothing can be said about the economy of the process at the moment, because no data is available on the cost development of the topped residues.

Conclusion

To utilize the conclusions of the report at hand, I should like to suggest that in the large scale experiment proposed at the briquetting plant of the Alstaden-Oberhausen mine we use a binder of 8% of a homogeneous mixture of equal parts of tar pitch and topped residue produced by melting. It must be ground to a grain size below 1 mm, in accordance with the general rule.

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END

T.O.M. REEL 2

B.M. 46