The first test has been run at 200°C., and the following ones each at temperature intervals of 25°C. up to 450°C.

The initial hydrogen pressure at this series of tests was about 50 atm. The heating up of the autoclave containing the shales in question was continued for a period of two hours at each of the test temperatures. The experiments were made in a rotating autoclave, system Bergius, capacity 2.6 litres, heated by means of an electrical furnace. A thermocouple was used for measuring the temperature; it was inserted in a pocket of the autoclave head.

The physical and elemental analysis of the shale in an absolutely dry state gave (in percents):

Moisture	3.76
Mineral CO_2	10.69
Ashes	41.49
Total sulfur	2.59
C	86.27 (sic)
H	9.60

In the 200 - 225° experiments, the initial look of the surface of the shale was not totally changed, when it was extracted with benzol, it yielded 0.29-0.30% of extract.

This slight output of extract indicates that under these test conditions the change in the constitution of the organic matter was extremely slight.

When higher temperatures are used, the yield of bitumen becomes higher; the quantity of gaseous products is also increased under these circumstances. The appearance of methane in the gas indicates that along with the bitumization of the organic substance, a reaction takes place, in which the bitumen is cracked; the velocity and intensity of these processes is proportional to the test temperature.

At temperatures up to 350°, the surface appearance of the shale remains unchanged by the heating. At 360°C. a large amount of bitumen is formed, causing a perfect change in the initial look of the shales. The substance discharged from the autoclave looks like a conglomerate of solid lumps which are very hard to break up.

The decomposition of the shale at 375° is not only accompanied by a greater yield of bitumen, but also by increasing amounts of methane in the gas. The increase in the evolution of methane indicates that the rate of decomposition of the bitumen under these experimental conditions is more intensive than in the previous experiments. The material discharged from the autoclave is of softer consistency than that obtained at 350°, thanks to the presence of cracking products of the bitumen.

In the experiments with temperatures up to 385°C., the gas pressure in the autoclave remained unchanged from beginning to end. The conclusion may be therefrom drawn that the quantity of hydrogen which had been consumed in the process, had been compensated for by the formation of gaseous products from the decomposition of the organic substance in the shale.

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Since we took into consideration that the complete conversion of the organic substance of the shale into bitumen might take place when the temperature is further increased to a very unimportant extent, we conducted the following experiments with 10° intervals, e.g., at 385°. A 10° increase in the temperature was mirrored to an extraordinary extent in the character of the decomposition of the organic material. An abrupt increase in the yields of methane, the amount of which amounts in the said test to 16.89/kg. of shale, is an indication of the intensity of the cracking reaction which the bitumen undergoes.

A decrease in the hydrogen partial pressure at the end of the experiment indicates that the velocity of the hydrogenation reaction is increased with higher temperatures. The hydrogen absorption reaches a ratio of 52.04 liter of hydrogen per 1 kg. of shale. In the experiment, the Berginization product consisted of a dark-colored liquid with the characteristic odor of petroleum products.

For the quantitative determination of the bitumen and of its cracking products, in this experiment as well as in the subsequent experiments, which were made at still higher temperatures, the following method was observed.

A weighed portion of the decomposed shale was placed into a small iron retort, which was heated by means of an electrical air bath. The fractions up to 200°C. are distilled off, the distillation residuum was extracted with benzol in a soxhlet apparatus. When the extraction was terminated, the benzol was distilled off, while the residuum was dried at a temperature of 105° and weighed once more. In this manner, the benzine fractions and the higher boiling hydrocarbons, extant in the bitumen mixture, were accounted for.

In the 385° experiment, the hydrocarbons with boiling points up to 200° amounted to 3.47% on the basis of the shale, and the benzol-soluble bodies to 29.09%. The extraction product is a dark substance, viscous at room temperature.

Table 2

No. of Tests	Temperature °C.	Yield of Benzine % of Shale	Spec. Grav. of Benzine	Sulfur in benzine	Aromatics in Benzine %	Bromine Number
9	385	3.47	0.752	0.25	-	35.98
10	420	9.20	0.754	0.24	10	20.91
11	450	14.90	0.759	0.21	13	18.63

In the subsequent experiments, which have been carried out at temperatures of 420 - 450°, the berginizate looks like a liquid in which some mineral body is dispersed, and may readily be decanted from the autoclave.

With this increase in temperature, the quantity of benzine goes up, whereas the output of benzol-soluble substances decreases correspondingly. But the sum total (benzine plus bitumen) is smaller in comparison with test No. 9, because of the increase in gaseous and coke-like products.

The benzine obtained in tests No. 9, 10, 11 is not of great stability; when it stands in the light, it becomes yellowish. Table 2 contains the results of the benzine analysis.

On the basis of our experiments it is obvious that the organic constituents of the shale begin to undergo a change when the working-up temperature has attained 200°C. When the temperature is further increased, the deploymerization velocity increases, reaching its maximum at 385° C. Hand in hand with the depolymerization process goes the cracking of the bitumen, causing deeper reaching changes in the deploymerization products of the organic substance, whereby liquid and gaseous products are formed. That means that the intensity of the cracking process is determined by the test temperature. Up to 375°, as Table I. shows, only a very unimportant quantity of methane is formed, and this amount is nearly constant in the several tests. Since there are no intense cracking reactions, the hydrogen consumption is also rather inconsiderable.

The disintegration of sulfur compounds increases with rising temperatures, as Table 3 demonstrates, where the sulfur-content analysis data are given for shale which has undergone a thermal treatment.

Table 3

Test temperature °C.	Sulfur content in shale after Berginization %
Starting material	2.59
200	2.32
225	2.27
250	2.17
275	2.05
300	1.97
325	1.90

At 375° much greater amounts of methane begin to evolve, due to the increasing velocity of the cracking reaction. At this temperature, the decomposition of the bitumen does not only result in the formation of gaseous molecules, but also of liquid substances.

The formation of liquid substances influences the consistency of the bitumen, which becomes softer than in the prior experiments. The first intensive cracking reaction occurs at the 375 - 385° interval. In the range of this interval the amount of methane evolving increases steeply, and the shale is converted into a liquid. The liquefaction process consumes a considerable amount of hydrogen.

When the temperature is raised still higher, the velocity of the cracking reactions goes up, and consequently the output of liquid products and the hydrogen consumption, but the sum total of useful products goes down, because of the formation of coke. The first step in the intensive cracking of bitumen is not only reflected in a higher consumption of hydrogen, but also in the heat effect of the reaction. In the course of the experiments it has been established that the rise of temperature inside of the autoclave goes smoothly up to 385°. Afterwards, the temperature inside of the autoclave remains constant for about one hour, even though the intake of heat in the autoclave may go on at a constant rate. Then, it goes up a few degrees in a very short time. Then follows a period of smoothly rising temperature rates, up to 440° C.

The last-mentioned temperature remained constant for the same length of time, one hour (confer fig. 1).

In the case in question, the retardation in the rise of temperature reflects the effects of the cracking reaction, which is of a highly endothermic character.

The fast rise which follows the period of retardation, points out the exothermic character of the reactions which take place at that time. A similar phenomenon has also been observed by Kogerman at the thermal decomposition of Esthonian shales. (1)

While the Berginization of shale at 385° C. and its bituminization under the usual conditions, give identical results with respect to the conversion rate of the organic substance, those tests which are carried out at the temperature of pure cracking in the presence of hydrogen exhibit a considerably higher conversion rate of the organic substance, than can be achieved in a low-temperature carbonization process.

Hydrogen, introduced into the reaction zone, saturates unsaturated compounds, which are obtained as products of the bitumen cracking process, and prevents the formation of coke in this way. The 420-450° tests show that the greatest susceptibility for a complete liquefaction of the organic substance exists at 420° C. At that temperature the losses suffered in the yield of liquid products can be accounted for by the evolution of gaseous products.

In order to eliminate losses of organic substance by the evolution of gaseous products, it is necessary to operate at a higher partial hydrogen pressure.

A All the tests which we made in order to investigate this factor, have been conducted at a constant temperature of 420°. But the initial hydrogen pressure has been varied; from 10 up to 100 atm. at intervals of 10 and 20 atm.

In conducting these experiments, we followed the methods and maintained the experimental conditions which we shall now discuss. The Berginization Product was analyzed with regard to its benzine content (the fraction up to b.p. 200°) and with regard to its benzol-soluble residue after distilling off the light fractions. Table 4 gives the results of the tests.

It is noteworthy that during the processing, shales will take up the hydrogen in different fashions. In the Test No. 6, the maximum pressure of 200 atm. had been reached at 386°; thereafter, the pressure began to drop and at 388° it had gone down to 183 atm. When the temperature was further raised to 420° C., the pressure rose by 7 atm. and thereafter, when the said test temperature had been maintained for two hours, it dropped to 182 atm.

We may therefrom draw the conclusion that the optimum assimilation of the hydrogen takes place in the first stage of intensive bitumen cracking, that is, at the moment, when the organic matter is completely liquefied. The rise and subsequent drop of the hydrogen partial pressure at the period when we operate at 420° C. are combined with the recracking of the products of the bitumen dissociation and with a re-hydrogenation of the hydrocarbons formed. At this stage, the velocity of the hydrogenation reaction is greater than the velocity of the cracking reaction, thus occasioning the drop of the hydrogen pressure.

The magnitude of the hydrogen partial pressure, determines also the character of the dissociation of the organic matter.

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(1) Oil shales and their technical exploitation, p. 268.

Table 4 shows also that an increase in the initial hydrogen pressure is accompanied by a decrease in the quantity of methane produced. If the hydrogen pressure is high, the character of the dissociation reaction changes, the rupture of the molecules takes place closer to the very centre, new bodies being formed, which belong to the liquid phase. Consequently, it is necessary to conduct the process under a high hydrogen pressure, the height of which determines the amount of methane formed, if we want to avoid losses due to the conversion of organic matter into gaseous products. (Table 4.)

A high hydrogen pressure makes it also possible to rupture sulfur compounds and to convert the organic sulfur into a gas of the form of H_2S. The quantity of H_2S formed, depends also upon the quantity of hydrogen which has been absorbed, and this amount is determined by its partial pressure (Table 4.).

It is thus obvious that the quantity of H_2S will reach 4.3 l/kg at 100 atm., while at the first test, under an initial pressure of 10 atm., 1.24 litre H_2S had been formed.

The Berginizate, which we obtained in the Tests No. 1,2,3,4, and 5, is a black mass, ressembling soft asphalt; the berginizate obtained in the experiments No. 6 and 7, is a liquid mass, in which a mineral solid was dispersed.

The color of the berginizate obtained in the two last-mentioned experiments, differs from that of the berginizate obtained in all the previous tests: it has a clearly noticeable green coloring. If it is exposed to light and air, the green coloring changes gradually into brown and will finally turn black.

In all tests, the berginizate was distilled, whereby the fraction with boiling points up to 200° C. was withdrawn. The distillation residue was extracted with benzol in a Soxhlet apparatus. Table 5 shows the quantities of the different products obtained in the berginization process.

Table 5

No. of experiments	Amount of benzine if shale, %	Amount of benzine in organic matter %	Benzol-soluble bodies, on basis of shale, %	Benzol-soluble bodies, on basis of organic matter, %
1	8.35	19.4	19.9	39.3
2	9.25	19.6	20.0	42.4
3	9.73	20.4	21.1	42.6
4	9.95	20.7	21.8	44.2
5	10.0	20.8	21.8	45.3
6	11.2	23.2	23.8	47.3
7	12.2	25.3	25.2	49.8

The increase in the quantity of benzine and benzol-soluble residue is proportional to the quantity of absorbed hydrogen.

The fact that the yields of liquid bodies are lower with a low hydrogen partial pressure, may be explained by the intensive formation of coke, which takes place because of the condensation and polymerization of the unsaturated compounds,

which had been formed in the cracking reaction.

The benzine which had been formed in the course of these experiments has been dried with sodium sulfate; thereafter, its specific gravity has been determined and the sulfur and aromatic compound contents. Freshly-distilled benzine is colorless, but in the course of time it turns slightly yellow.

Table 6 gives the characteristic data for the benzine and the benzol-soluble bodies in the residuum.

In inverse proportion to the rate of hydrogen absorption the sulfur content in the benzine and in the extract decreases. The substance, which we obtain when we extract the residue after the benzine has been distilled off, looks like soft asphalt.

When the initial hydrogen pressure was low, the extract is a highly viscous mass; in the experiments No. 6 - 7, it is of a completely liquid consistency.

In this fashion, the quantity as well as the quality of the products obtained by cracking the organic substance, is dependent upon the rate of the hydrogen partial pressure.

Table 6

No. of tests	Spec. Grav. benzine	Content aromatics %	Sulfur content in benzine %	Sulfur in extract %
1	0.7611	12.5	0.37	0.62
22	0.7585	12.0	0.35	0.61
3	0.7580	11.2	0.34	0.59
4	0.7580	11.0	0.34	0.56
5	0.7575	10.5	0.30	0.47
6	0.7540	9.2	0.25	0.33
7	0.7520	7.2	0.23	0.29

The highest hydrogen pressure offers the optimum condition for the conversion of the organic shale substance into liquid products.

Table 7 gives the results of the analysis which determines the quantity of the organic residuum in the Berginizate, which is left after removing benzine and the benzol-soluble bodies.

In general, the amount of organic shale material recovered goes up with higher hydrogen pressures and reaches a maximum at 100 atm. Under these conditions, one tenth per cent of organic material remains in the shale. Consequently, an initial hydrogen pressure of 100 atm. and the temperature of 420° offer the optimum conditions for the conversion of the organic matter contained in Gdov shales into fuel oil.

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Table 7

Initial hydrogen pressure	Amount of organic matter, on basis Of shale, %
10	6.3
20	5.8
30	3.2
40	2.5
60	1.5
80	1.1
100	0.63

In order to increase the output in the benzine fraction and to obtain a more complete desulfurization of the liquid products, we carried out experiments with the rehydrogenation of the berginizate. The method applied was as follows.

The berginizate and the gas which had been formed in the first berginizations were submitted to the above-mentioned analysis. The berginizate from which the benzine had been removed was, thereafter, charged to an autoclave and subjected to another berginization under the same conditions, that is, at 100 atm. hydrogen pressure and 420° C.

The data obtained in these experiments established the fact that the sum total of the amounts of hydrogen absorbed in these two subsequent berginizations, amounts to 194 litres, or 3.7 % in toto, reckoned on the basis of the organic shale material.

When we compare this rate of hydrogen absorption with that of shales Obshsheye Sirta and from Kashpir, it is obvious that Gdov shales are most satisfactory.

Gdov shales give a higher output of fuel oils with a lower content of sulfurous compounds and consume less hydrogen, an important feature in view of the fact that the rate of hydrogen consumption determines to a large extent the economic profitability of the berginization process.

The total output of benzine obtained in the multi-step berginization, is 17.4% calculated on the basis of the shale, or 36% calculated on the basis of the organic matter.

The residue left over after distilling off the benzine had a liquid consistency; it could be used for re-berginization. In the first berginization step, 12.2% of benzine were obtained with a sulfur content of 0.23%, and in the second step, 5.2% of benzine with a sulfur content of 0.07%. The destruction of the sulfur in the course of the berginization of shales takes pre-eminently place in the first step.

In the two-step experiment, we obtained 3.8 litres of hydrogen sulfide, disregarding the interaction with the material of the autoclave equipment and disregarding the amount of H_2S which has been dissolved in water. In the first step, we obtained 3.2 litres and the other 0.6 litres in the second step. Thus, it is possible that in the third step we should obtain a benzine with a minimum sulfur content. The benzine yields can be considerably increased, when the berginization process is conducted at a higher temperature.

The second berginization step at 420° indicates that at this temperature the recracking of the pyrolyzate is comparatively not very deep. This observation is corroborated by the low rate of the benzine output and of the hydrogen absorption -- 40.41 per kg of shale. When we compare these results with the results obtained by the destructive hydrogenation of coal and other kinds of solid fuels, we can see that the Gdov shales are also easy to liquefy since they are sapropelites, too.

The abovementioned discussion makes it possible for us to draw the following conclusions:

1.) The dissociation of the organic material starts at 200°, and the quantity of bitumen, which is obtained at that temperature, has been determined to be one tenth of a gram.

2.) The velocity of the depolymerization and of the cracking reactions is a function of the temperature. A temperature of 350° C. is the limit for the depolymerization reaction. Higher temperatures produce an intensive cracking of the bitumen.

3.) The first step of intensive bitumen cracking occurs in the temperature interval of 375 - 385° C., at which temperature the shales are liquefied. The liquafaction process is accompanied by hydrogen absorption.

4.) At 385 and at 420° C. the cracking process is accompanied by the absorption of a great amount of heat (zones of endothermic reactions).

5.) The decomposition of the shales under hydrogen pressure at 385° and the bituminization of the shales under normal conditions give identical results regarding the utilization of the organic matter. At pure-cracking temperatures, considerably higher conversion rates are obtained for the organic matter and of the hydrogen, than in low-temperature carbonization.

6.) At the multi-step berginization 36 % of benzine are obtained (the fraction up to 200°), calculated on the basis of the organic matter, representing 17.4% on the basis of the shale. The yield of benzine can be increased in another berginization step by means of the destructive hydrogenation of the benzine-free residuum.

7.) The liquefaction of the organic substance contained in the Gdov shales is accompanied by hydrogen consumption, therate of which is determined by the hydrogen partial pressure. At an initial pressure of 10 atm., 10 litres of hydrogen are absorbed; at 100 atm., 153.6 litres, and at the berginization stage, 194 l/ kg of shale . This is in proportion to the organic substance present: 0.2, 2.3 and 3.7 %.

8.) By raising the hydrogen pressure to 100 atm. we succeeded in reducing the sulfur content in the benzine to 0.23%. In the multi-step hydrogenation, benzine and a heavy residue left over after extracting the benzine-free pyrolyzate with a 0.07% sulfur content, are produced.

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TABLE I

Number of Experiments	Temperature °C.	Charge of shales g	Hydrogen pressure cold		Gas (l/kg of shales)			Berginization products in % (per shales)		
			P_M	P_K	H_2 absorbed	CH_4 evolved	H_2S formed	Benzine (sic) solubility of bodies %	Benzine fraction 1-200°	Total amount of products
1	200	500	50	50	-	-	-	0.29	-	0.29
2	225	500	50	50	-	-	-	0.30	-	0.30
3	250	500	50	50	-	-	-	1.02	-	1.02
4	275	500	50	50	-	1.41	-	1.06	-	1.06
5	300	500	50	50	-	1.72	-	3.20	-	3.20
6	325	500	50	50	-	1.72	-	8.30	-	8.30
7	350	500	50	50	-	1.74	-	27.2	-	27.2
8	375	500	50	50	-	3.87	-	29.65	-	29.65
9	385	500	50	45	52.04	16.89	2.20	39.09	3.47	42.56
10	420	500	50	40	71.00	27.02	3.30	29.30	9.20	38.50
11	450	500	50	35	136.90	41.72	3.38	16.10	14.90	31.00

TABLE 2

Number of Experiments	Temperature °C.	Initial pressure	Maximum pressure	Cold end pressure	Amount of H_2 absorption l/kg shales	Amount of CH_4 form. l/kg shale	Amount of H_2S form. l/kg shale
1	420	10	100	15	21.3	27.2	1.24
2	420	20	111	21	33.9	24.0	1.75
3	420	30	112	22	79.6	22.6	2.35
4	420	40	128	28	107.7	21.6	2.50
5	420	60	161	45	110.0	20.7	3.10
6	420	80	200	57	141.9	20.0	3.80
7	420	100	238	78	153.6	19.6	4.30

MD:mbb

SINCLAIR REFINING COMPANY
RESEARCH AND DEVELOPMENT DEPARTMENT

Translation Book No. 212
API-TOM Reel No. 72
Item 78
(6 Drugs.

November 22, 1948

SR-7

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Preparation of Octyl Acetate and of Acetic Esters of Secondary Alcohols with more than Eight Carbon Atoms

A. In our Report on the experiments concerning the preparation of amyl alcohol, we have demonstrated that amyl alcohol can be prepared by stirring the pentan-pentens fraction with aqueous sulfuric acid under suitable conditions. According to data given in the scientific literature (Ellis, The Chemistry of Petroleum Derivatives, I. 382) the same operating conditions may be applied to the hexane-hexene fraction, (b.p. 60-70°) and heptane-heptene fraction (b.p. 90-100°), on increasing the concentration of the aqueous sulfuric acid to 85%. Sec. hexyl alcohol and sec.-heptyl alcohol are obtained; these data were verified by tests of our own. On stirring the octane-octene fraction (b.p. 120-130°) with aqueous sulfuric acid, however, only a 15% yield of alcohol will be obtained, even under the most favorable operating conditions; the other 85% of octane being polymerized (Ellis, The Chemistry of Petroleum I, 386). If olefins with more than eight carbon atoms in their molecules are stirred with sulfuric acid, the principal reaction will be polymerization, too, and the yield of alcohol will be minute. If we take into consideration that the polymerization reaction proceeds via the sulfuric acid ester, we may conjecture that polymerization might be preventable by a rapid conversion of the sulfuric acid ester to another substance. It was obvious for us to apply to this reaction the re-esterification of acidic acid ester with a fatty acid, such as acetic acid. If acetic acid is introduced into a mixture of olefin and sulfuric acid only acetic ester is formed from the olefin and acetic acid, and next to no polymerizate. Thus, it is possible, indeed, to prepare alcohols from olefines with more than eight carbon atoms, via the corresponding ester (Procedure of Bertran, German Patent 67,255 (1893), confer. Houben, The Methods of the Organic Chemistry, 3rd ed. vol. 2, 98). Recently, Americans too, have chosen this path for preparing amyl acetate (Ind. and engin. Chem. (1938) 35).

B. Preparation of sec.-octyl acetate

1. Preparation and testing of the starting material

Octane and Octene have been obtained by distilling light benzine in Raschig ring columns, two metres high. The fraction of between 120 and 129° contains the octane and one or several octenes. We did not determine which and how many of the isomers were present. The density of the fraction at 20° was 0.710, iodine number 59-62, corresponding to 26.1% - 27.4% of octene.

2. Composition of the reaction mixture

The reaction mixture consists of five substances: octane, octene, acetic acid, sulfuric and water. Two other substances appear among the reaction products: octyl acetate and polymerizate. Octyl alcohol could not be determined in any case.

Just as when iso-propyl alcohol, sec. butyl alcohol and amyl alcohol are prepared, the mixed reactants form two layers. That means that the reactions occur in a two-phase heterogeneous system.

In order to obtain an accurate understanding into the course of the reaction, all the mixing ratios possible have been determined.

(a) Composition of the reaction mixture before the conversion.

A triangle diagram (Fig. 1) represents all the mixing ratios possible for the starting material: octane, octene, sulfuric acid and acetic acid. The course of the binodal curve shows what range is homogeneous and what range is heterogenous. Moreover, from one given point and the corresponding conode, the composition of the two phases and their weight ratio can be read off directly. (Confer below a more detailed discussion). In order to determine the triangle diagram, mixtures of octane, octene, acetic acid and sulfuric acid have been prepared, the total composition being known. These mixtures separate into two layers which are withdrawn. By determining the volumes and densities of the layers, the weight ratio of the layers has been ascertained. By titrating the upper layer, we find the percentage of acetic acid contained in the upper layer. From these three data, the composition of the top and bottom layer can be computed, since the sulfuric acid is contained in the bottom layer and only traces of this substance are dissolved in the top layer. Moreover, the acid number of the bottom layer may be determined, and the acetic acid content may be directly computed by deducting the amount of lye consumed by the sulfuric acid. This method is particularly satisfactory, when only a small amount of acetic acid is contained in the top layer. The slight differences in solubility exhibited by octane and octene in the two layers have been disregarded.

(b) Composition of the reaction mixture after the conversion.

The starting material has been converted by heating it to 90-100° under continuous stirring. By virtue of the reaction, the composition of the layers and thus their properties are altered. As an instance, we shall tabulate the changes in the percentage content of the layers, the density and acetic acid percentage of a reaction mixture, consisting of 6 parts each of octane-octene and acetic acid and one part of concentrated sulfuric acid.

Table I

		Vol.%	Weight %	d_4^{20}	% CH_3COOH at 20°	% CH_3COOH at 100°
Before conversion	Top layer	71	61	0.7694	16	23
Before "	Bottom "	29	39	1.1853	29	22
After "	Top "	79	73	0.8069		24
After "	Bottom "	21	27	1.2259		18

Table I shows that in the course of the reaction, the acetic acid concentration increases in the top layer and decreases in the bottom layer.

Determination of the Composition by means of Quantitative Analysis

In order to determine the amounts of acetic acid and of sulfuric acid contained in both layers, a sample of each has been titrated. After the titration, the sample has been acidified with diluted nitric acid and the sulfuric acid precipitated in the form of barium sulfate. The difference: total amount of the layer (acetic acid and sulfuric acid) gives the weights of octane, ester, octene and water.

After neutralizing the layer, octane, octene and ester can be driven off with steam and salted out of the distillate with K_2CO_3. The iodine and saponification numbers of the dried salt mixture are determined, and the ester and octene amount may be computed therefrom. The amounts of water and octane may be found by two differential calculations. In this manner, the following compositions of the reaction mixtures and for both layers of it have been found at 100° for the above ratio of 6 : 6 : 1, after the conversion had taken place.

Table II

Weight %	CH_3COOH	H_2SO_4	Octane	Octene	Ester	Water	%
Top layer (Rect. Mixt. 100%)	24.1	0.04	30.4	10.67	7.68	0	73
Bottom layer (React. mixt. 100%)	18.1	7.2	0.1	0.03	0.17	10	27
React. mixture	42.2	7.24	30.5	10.70	7.85	10	100
Top layer (Top Layer = 100%)	33.2	0.05	41.7	14.6	10.5	0	
Bottom layer (Bott. layer = 100%)	68.0	27.1	0.38	0.11	0.64	3.8	

III.) Determining the optimum reaction conditions

(a) The effect of the quantitative ratio of the two phases and of the stirring period upon the yield of esters.

We mentioned already that each mixture which is represented in the inhomogeneous range of the triangle diagram (Fig. 1) by some point, separates into two phases, the composition of which can be read off at the two ends of the conodes going through P. (1) The conode divided by this point is separated into two straight lines, the proportional length of which correspond to the proportional weight of the two phases. The kg i : kg J = P J : P i. The bottom line Pi represents the bottom layer, the top line PJ, the amount of the top layer. On the other hand, the lower point i indicates the composition of the top layer, the top point J the composition of the bottom layer. It has been found the output of ester, expressed in a percentage of the theory, that is, quantity of ester. 100% of the theoretically possible amount of ester) in compositions represented on the same conode, is always the same, provided that the reaction is permitted to proceed to the end equilibrium.

(1) For details confer Eucken, Chemie Ingenieur III, 3. part Pp. 226.

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This result is demonstrated in Table 3, where the data are given for three tests, the individual phases of which are of the same composition.

TABLE III

Exp. No.	Compos. of Mixture		% of octene feed is ester %	Stirring Period, hrs.
	Top layer %	Bottom layer %		
125	28	72	39.3	3
126	76	24	38.1	3
91	76	24	26.3	1

Exp. No.	Composition of the layers					
	Top layer			Bottom layer		
	CH_3COOH %	Octane Octene %	H_2SO_4 %	CH_3COOH %	Octane Octene %	H_2SO_4 %
125	19.2	80.8	0	76.0	1.0	23.0
126	19.2	80.8	0	76.0	1.0	23.0
91	19.2	80.8	0	76.0	1.0	23.0

In experiments Nos. 125 and 126, the quantities of the two phases differ and the stirring period is equal. In experiments Nos. 126 and 91, the quantities of the two phases are equal and the stirring periods differ. The output of ester is the same in experiments No. 125 and 126. In experiment 91, the stirring period is shorter than in experiment 126, and the ester output likewise. When the compositions of the mixture and the stirring velocities are equal, the ester output depends only upon the stirring period, as is also shown by the experiments given in Table 4.

TABLE 4

Relationship between ester output and stirring period, bottom layer: top layer = 1 : 1

Experiment No.	53	51 & 65	55	54	34
Time in hrs.	1/4	1	1-1/2	2	4
Ester output % of theory	13	30 & 28	29	37	36

Experiments No. 103, 90, and 104 demonstrate that the final equilibrium is more rapidly attained by increasing the proportional volume of the bottom layer, the compositions of the layers being equal.

0399

TABLE V.

No.	Stirring Period hrs.	Vol.top:Vol.bottom	Wt.top : wt. bottom	% of octenes fed is ester
103	1	1 : 1-1/2	1 : 0.733	29
90	1	1 : 1	1 : 1.47	37
104	1	1 : 2	1 : 3.3	41

(c) Relationship of the ester output to the compositions of the top and bottom layers.

1.) The conversion of octene with acetic acid takes place in a homogeneous system according to the mass effect law up to an equilibrium, which is only dependent upon the concentration of the reactants, temperature and nature of the solvent. By varying the concentration of the reactants, the ester output can be changed. The output may be calculated when the equilibrium constant K is known.

Determining the equilibrium constant.

The equilibrium constant for the conversion of octene with acetic acid to ester may be calculated from the initial and final concentrations of the reactants. It is

$$\frac{C_{\text{acetic acid}} \; C_{\text{octene}}}{C_{\text{octyl acetate}}} = K$$

By titrating the homogeneous reaction mixture in the course of the reaction, the decrease in the acetic acid concentration may be calculated under the assumption that the sulfuric acid present in the mixture acts only as a catalyst.

A mixture consisting of 80 g of glacial acetic acid (1.332 mol), 17 g of pure octene (0.151 mol) and 3 g of concentrated sulfuric acid has been heated to 100°, and the acid number has been continuously determined. After three hours it stops changing, as has been found by a titration made after another three-hour period. Initial acid number 779, final acid number 694. That means, 0.135 mols acetic acid have reacted with 0.135 mol octene. K is

$$\frac{(1.332 - 0.135)\;(0.152 - 0.135)}{0.135} = 0.15$$

That is, by feeding equimolecular amounts of acetic acid and octene, 0.68 mol ester are formed.

A mixture consisting of 87 g of acetic acid, 7 g of octene and 6 g of concentrated sulfuric acid gave K = 0.35 (56% of the theor. amount of ester, the stock consisting of equimolecular amounts). That means, K is dependent upon the rate of sulfuric acid concentration.

0400

Reaction velocity

With a mixture of 3% of sulfuric acid, 80% of acetic acid and 17% of octene, reaction equilibrium was reached in three hours. A mixture consisting of 6% of sulfuric acid, 87% of acetic acid and 7% of cetane, requires two hours for reaching a rate of equilibrium.

(2) Also in a heterogeneous system, the mass-effect law determines the course of the reaction in the phase where it takes place.

Since, however, in the course of the reaction a new substance is formed, the composition of this phase changes, and the phase composition is shifted in general, so that K does not remain constant, even if the temperature is unchanged. By virtue of the constant interface action of the two phases a direct change in concentration of the reactants takes place, according to the distribution theorem of Berthelot.

Example:

The mol-ratio of acetic acid to octene to ester was in the bottom layer:
before reaction: 1.132 : 0.00447 : 0 = 254 : 1 : 0
after the reaction: 0.767 : 0.000905 : 0.00372 = 778 : 1 : 3.78

Table VI

	CH_3COOH %	Octene %	Octane %	Ester %	H_2SO_4 %	Water %	%
Before reaction							
Top layer	25	55	20	0	0	0	40
Bottom layer	78.5	1.5	0.5	0	17.8	1.7	60
Mixture	46.1	34.3	12	0	6.8	1.0	
After reaction							
Top layer	32.2	41.7	14.6	10.5	0.05	0	73
Bottom layer	63.0	0.38	0.11	0.64	27.1	3.8	27
Mixture	42.2	30.5	10.7	7.85	7.24	1.0	

From the data given in Table VI we may compute that before the reaction started, 17.5% of the acetic acid were in the upper layer, but 56.4%, after the equilibrium had been reached.

While the bottom layer contained 1.132 mols of acetic acid at the beginning, finally, there were only 0.767 mol; 0.0454 mol. had been consumed for the formation of ester; that is: 0.32 mol of acetic acid (28% of the amount introduced) had been distracted from the chemical reaction by dissolution in the top layer, and not owing to chemical conversion. Nevertheless, the acetic acid excess in the bottom layer is still of such magnitude that a 90% conversion of the octene ought to take place, the reaction constant being 0.15 (at 100°).

Table VI shows that the H_2SO_4 concentration of the bottom layer increases from 17.8% to 27.1%. Now, it has been found that by doubling the H_2SO_4 concentration (from 3% of H_2SO_4 to 6% H_2SO_4) K increases from 0.15 to 9.35, that means, on reacting 1 mol CH_3COOH with 1 mol. octene, the ester output is 68%, that is, 56% of the theory. With increasing sulfuric-acid concentrations, the equilibrium constant

increases, and the theoretically possible yield decreases. This statement applies, however, only to the bottom layer of the heterogeneous system. The amount of sulfuric acid is of importance for the total output of ester, that is, the output of ester in both phases, whenever considerable amounts of the reactants are dissolved in the bottom layer. In this case (Table VI) only slight amounts, about 4%, of the total octene are dissolved in the bottom layer. The sulfuric acid content influences thus only the more or less complete conversion of 4% of the total octene content. The concentration of octene and water in the top layer takes place in accordance with the law of mass distribution.

(d) Effect of the water content upon the ester output.

The rate of output of esters is much more affected by the rate of concentration of water than by the concentration of acetic acid. Table VII shows that even a slight increase of the percentage of water contained in the mixture (from 4.2% to 5.4%) was sufficient to effect a decrease in ester output (from 17.8% to 5.6%). Moreover, Table VII shows that the maximum output of ester is obtained with 1.2% of water, it deteriorates again with 0% of water and goes down still further, when acetic acid anhydride is added.

Table VII.

Relation of the octyl acetate output to water content

No. of exp.	46	47	50	48	42	49	34	52
% octene/octane	46.1	46.1	46.1	46.1	46.1	46.1	46.1	46.1
% acetic acid	23.1	38.5	40.5	43.0	45.0	44.0	44.8	46.1
% sulfuric acid	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
% water	23.1	7.7	5.4	4.2	2.7	2.2	1.4	0
Ester % of theor.	0.6	2.3	5.6	17.8	28.3	33.7	36.1	34.4

The initial proportion of top to bottom layer is between 1 : 1 and 3 : 2. Since stirring continued for four hours at each of the tests, the terminal reaction equilibrium has always been reached.

(e) Effect of temperature upon ester output.

Experiments where the terminal temperature was 100°, yielded a maximum of ester output. Lower temperatures yielded poorer rates of output, higher temperatures (up to 120°) effected no further improvement.

Table VIII

Interrelationship of rate of output of ester and temperature
Composition of the feed stock

	Acetic acid %	Octane/octene %	H_2SO_4 %	%
Top layer	25.0	75.0	0	61
Bottom layer	78.7	2.0	19.3	39
Mixture	46.15	46.15	7.7	100

Stirring period: 2 hours								
Exper. No.	66	69	70	67	71	54	72	68
°C	50	60	70	80	90	100	110	120
Ester output % of theory	2.2	3.7	11.8	21.0	21.0	29.0	37.1	32.7	34.0

(f) Polymerization

We have already mentioned that the addition of acetic acid prevents the polymerization of octene. Polymerizate is only formed when the amount of sulfuric acid required for the catalyzation of the reaction is exceeded several times. Table IX shows that such extreme conditions may result in high-grade polymerization.

Table IX

Experiment No.	122	117	124	118	119	120
% of octane/octene	38.4	36	34	32	28	24
% acetic acid	19.2	18	17	16	14	12
% sulfuric acid	38.4	36	34	32	28	224
% water	4.0	10	15	20	30	40
Reacted % of theor.	57.5	21.5	21.7	19.7	6.9	5.8
% in ester	6.3	10.8	17.5	12.9	2.9	2.9
% in polymerizate	51.2	10.7	4.2	6.8	4.0	2.9

In most of the other experiments the sulfuric acid content in the feed stock did not exceed 15%, and the minimum content of acetic acid was 30%. It is advisable to add water to the sulfuric acid, since water affects a considerable reduction in the oxidizing effect of the concentrated sulfuric acid. The ratio of sulfuric acid to water does not influence the rate of polymerization, however, as may be seen from Table X; only a high-grade H_2SO_4 concentration affects the rate of polymerization.

TABLE X

Experiment No.	34	122	49	117	42	124
%octane/octene	46.1	38.4	46.1	36	46.1	34
% acetic acid	44.8	19.2	44.0	18	45.0	17
% sulfuric acid	7.7	38.4	7.7	36	7.7	34
% water	1.4	4.0	2.2	10	2.7	15
% water in the sulfuric acid	15.4	9.4	22.2	21.8	26.0	30.6
Converted % of theor.	36.1	57.5	33.7	21.5	28.3	21.7
% in ester	36.1	6.3	33.7	10.8	28.3	17.5
% polymerizate	0	51.2	0	10.7	0	4.2

(g) Synopsis of the optimum conditions for the formation of sec. octyl acetate.

Optimum yields are obtained by stirring for 4 hours at a temperature of 100°C. a mixture consisting of 46 parts of acetic acid, 41 parts of octane-octene, 9.8 parts of H_2SO_4 and 3.2 parts of water. The yield of octyl acetate is 47% of the theory. The top layer of the reacted mixture contains about 10% of ester at the termination of the reaction.

IV. Working-up of the reaction mixture.

(a) By diluting with water.

For the purpose of processing, the reaction mixture has been poured into a tenfold quantity of water under stirring, and the octane-octene, the ester and the acetic acid have been distilled with part of the water. The distillate has been neutralized, salted out with K_2CO_3, the upper layer withdrawn and dried. It contains a mixture of octane, octene, octyl acetate and a slight amount (about 5%) of polymerizate. The mixture is fractionated. At a temperature range of from 120-130° C. the octane and the octene go over; in the residue we find octyl acetate and, sometimes, polymers. By distilling the residue with first runnings up to 180°, a main fraction of from 180-200° and a slight residue of 98% octyl acetate can be obtained.

(b) By direct distillation of the top layer

At the termination of the reaction almost all of the octyl-acetate content is contained in the upper layer of the reaction mixture. The main part of the sulfuric acid is in the bottom layer. It is also possible to neutralize the slight quantities of sulfuric acid present in the top layer by means of sodium acetate and to distill the top layer. At 135°, glacial acetic acid, octane and octene go over; in the residue, we find the ester, some polymerizate and some sodium sulfate. The ester is easy to purify by steam distillation. The yields are at least as good as those obtained with the first-mentioned method, and there is the further advantage that the bottom layer remains undiluted and can be used for another reaction. Since the octane-octene-acetic acid mixture, which has been distilled off from the ester can be reused for another reaction, too, this working-up method achieves a thorough conversion of octene into ester. By refeeding the same octane-octene fraction three times, a 67% of the theor. output could be achieved.

V. Continuous Production of sec. octyl acetate.

By a suitable arrangement of the equipment it is possible to carry out a continuous octene-acetic acid reaction. The equipment consist of a stirring vessel (7) equipped with a separator (8), a washing apparatus (10) with separator (11), (the washing apparatus is also provided with a stirring device) and a distillation column (13).

(a) Description of the reaction in the apparatus.

(Confer the diagram)

The conversion takes place in the reactor (7) which is equipped with a stirrer. A part of the two-layer product is pushed out by the incoming feed stock (octane, octene and acetic acid) and gets into the separator (8), where the two

layers of the reaction mixture are separated. The bottom layer, which may be considered to be the catalyst, is recycled into the stirrer-equipped-flask (7). The top layer which contains the octyl acetate, flows via the storage vessel (9) into the washer (10). Here any sulfuric acid residues which may be present are washed out with sodium acetate. When all the sulfuric acid is consumed, the browncolored solution turns yellow and dry Kongo-paper is no more colored blue. In the course of the washing process again two layers are formed. The bottom layer consists mainly of acetic acid, in which the sodium sulfate is suspended. It is separated out. The top layer, which contains the ester (about 8%) along with large amounts of octane, octene and acetic acid, is fed into the distillation column (13). The distillate, which consists of octane, octene and acetic acid can be refed to the stirrer-equipped vessel (7) via the mixer (5). At the same time those substances which had been consumed in the reaction, i.e. acetic acid, octene and sulfuric acid, are replaced by fresh stock. As a compensation for the octane which is fed together with the fresh octene, the same amount of octane and a little octene is removed from circulation (receiver 15). That means, octane, octene, and acetic acid are fed to the apparatus and octyl acetate, polymerizate and octane lean in octene are discharged.

(b) Computing the sulfuric-acid amounts.

How to compute the amount of sulfuric acid necessary for a given capacity of the reactor and for the ratio of the volumes of the two layers (top layer : bottom layer = a : b), at a given ratio of the weights of octane, octene and acetic acid.

The capacity of the reactor V is given. The volume of the bottom layer is thus

$$\frac{V \cdot b}{a + b}$$

The composition of the bottom layer, which corresponds to a given ratio of the weights of (octane + octene)/acetic acid may be read off from the triangle diagram (Fig. 2) at the upper end of the conode. The composition of the octane-octene-acetic acid mixture if unknown, is easy to determine by means of titration. From the H_2SO_4 percentage in the bottom layer, the density of the bottom layer can be read off from fig 3. Then,

$$\frac{d : V : b}{a + b} = \text{weight of the bottom layer and}$$

$$\frac{b \cdot d \cdot V \cdot \% H_2SO_4}{(a + b) \cdot 100} = \text{the weight of the sulfuric acid, which we were looking for.}$$

(c) Examples.

Experiment 1 (6% sulfuric acid, 50% acetic acid in the feed).

	Octane-octene g	Acetic acid g	Conc. H_2SO_4 g
Feed stock (initial content of the reactor	1,700	1,701	176
Throughput (additional feed during the test)	2,920	2.920	

The acetic acid fed was 98 - 100%. The octane-octene mixture contained 28.1% of octene.

The throughput takes place in 330 minutes, about 21 cm^3/min. The reactants averaged a residence of approx. 1-1/2 hours.

The mixture was at first washed with a 4 - 40% aqueous sodium acetate solution. In order to avoid excessive water enrichment, a solution of sodium acetate in glacial acetic acid which can be prepared either by dissolving aqueous sodium acete ($CH_3COO\ Na\ .\ 3H_2O$) was used in the later experiments, or solid sodium hydroxide and glacial acetic acid. When sodium hydroxide is dissolved in glacial acetic acid only 1 mol water corresponds to 1 mol sodium acetate.

Yields: 23.1% of the octene feed are converted into ester
65.0% of the octene stock are unchanged
0.0% of the octene stock are polymerized
11.0% of the octene stock are loss.

A large part (3/4) of the loss are probably esters which remained in the column and are deemed losses. In the course of the experiments, 33 g of the sulfuric acid fed have been consumed, i.e. 5 - 6 g per 1000 g of reaction mixture.

Experiment 2

Feed stock and throughput, like in Test 1; in the course of the run, however, 30 g of sulfuric acid have been added. Moreover, the acetic acid in the stock was entirely anhydrous.

In the course of the reaction, samples have been withdrawn. From the nature of the samples one may conclude that the output reached about 30% of the theoretical. In fact, the output recovered approximated only 16% of the theory. The deficiency in washing solution caused poor rates of output. In consequence thereof sulfuric acid entered the distillation flask, re-decomposing a part of the octyl acete into the starting material and coking another part. The amount of washing solution had been computed on the basis of the data of Example 1. This quantity, however, proved to be unsufficient, because the solubility of sulfuric acid in the top layer of an anhydrous reaction mixture is considerably greater than in a reaction mixture which contains slight quantities of water. This assumption has been verified in a test: octane/octene : acetic acid : sulfuric acid = 6 : 6 : 1. In the anhydrous top layer we found dissolved 0.7% of H_2SO_4. On adding 10% of water to the reaction mixture, the solubility of sulfuric acid in the top layer drops to 0.1%.

Test 3 (81% sulfuric acid, 36.6% acetic acid in the feed stock.

	Acetic acid g	Octane-octene g	Conc. 96% H_2SO_4 g
feed	1,540	748	204
Throughput	7,600	13,178	

The acetic acid of the feed stock was 97% conc. the acetic acid of the throughput was anhydrated, that is 100% conc. The octane-octene mixture contained about 26.6% of octene.

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That means, the feed stock contained

60% CH_3COOH
30 % octane-octene
7.9% sulfuric acid
2.1% water — 81% sulfuric acid

The throughput consisted of 24.5 l of octane-octene-acetic acid mixture (with 36.6% acetic acid), 43 cm^3/min., corresponding to an average residence of 40 minutes.

Yield is 14% of the theory. The samples withdrawn in the course of the test, show a yield of 18-20% of the theory.

During the reaction, the bottom layer was about 28 vol %. The volume of the layer in which the reaction takes place, is too small, the residence being 40 minutes; that is why the output is so slight. In the course of the test, 45 g of H_2SO_4 have been consumed, i.e. 22 g H_2SO_4 per 100 g of reaction mixture.

Test 4 (79% sulfuric 27.6% of acetic acid in the feed stock.)

Composition of the feed stock before the test

	Acetic acid %	Octane octene %	H_2SO_4 %	Water %	%
Top layer	27.6	72.4	0	0	33.4
Bottom layer	76.8	3.2	15.74	4.26	66.6
Mixture	60.2	35.0	10.6	3.2	

Weight of feed stock 2,588 g (top layer: 580 g, bottom layer 2,008 g with 316 g sulfuric acid.)

In order to accelerate the reaction, a feed stock has been selected the bottom layer of which was of sufficient volume (66.6%).

Throughput in 595 minutes:

3,680 g acetic acid (100%)
9,640 g octane-octene (with 26.3% octene)
13,320 g

The mixture put through contained 27.6% of CH_3COOH. Average residence of the reactants 35 minutes. The ratio of the layers was altered in the course of the test from 33.4 : 66.6 to 52.4 : 47.6 parts by weight.

The yield of ester was 30 - 32 % of the theory, as shown by the samples withdrawn in the course of the experiment. On working up the mixture, only 23.4% of the theor. of ester has been found; a part of the ester has obviously been lost in working up. The polymerizate amounted only to 0.7% of the octane introduced.

In the course of the test 62 g of sulfuric acid have been consumed, i.e. 4.0 g of sulfuric acid per 1000 g of reaction mixture.

Test 5 (79% sulfuric acid, 24.8% acetic acid in the feed stock)
Composition of stock like in Test 4.

The octane-octene-acetic acid mixture fed, contained 24.8% of acetic acid. 11,140 g of reaction mixture, containing 62.6% of octane, 12.6% of octene and 24.8% of acetic acid were introduced.

We investigated particularly carefully the change in the ratio of the layers in the course of the test. At the start of the run it was: top layer: bottom layer = 32 vol.% : 68 vol. %. After the mixture had been stirred for an hour, without throughput, it changed to a ratio of top : bottom = 54 vol % : 46 vol %. This shift in the ratio of the layers is occasioned by the formation of ester, which increases the solubility of the acetic acid in the top layer from 29% of the acetic acid in the top layer from 29% of CH_3COOH (before starting the run) to 48% of CH_3COOH (after an hour of stirring without throughput). When the throughput starts, the acetic acid concentration is continuously diluted by the inflowing mixture which contains less acetic acid, so that finally even the acetic acid concentration in the bottom layer is reduced. This occasions also a reduction in the output of ester. 22-24% of the theory of ester has been found.

4.7 g H_2SO_4 has been consumed per 1000 g of reaction mixture.

Test 6 (79% sulfuric acid, 50% of acetic acid in the feed stock).
Composition of the feed stock as in Test 4.

In the course of 4 hours, 2,500 g of acetic acid and 2,500 g of octane-octene mixture with 26.3% of octene have been put through.

Average residence of the reaction mixture: 48 minutes. In Table 11 the compositions of the overflow samples which have been withdrawn from time to time, have been recorded.

TABLE XI

No.	Withdrawn after throughput of cm^3	CH_3COOH %	Octane %	Octene %	Water %	% of octene are in ester
1	0	39.3	49.8	4.5	6.4	47.0
2	1000	46.5	41.5	5.6	6.4	42.6
3	1750	48.5	37.3	6.8	7.4	41.4
4	3000	49.0	36.8	6.9	7.3	40.7
5	5000	48.9	34.8	8.2	8.1	39.1
6	6000	48.9	34.5	8.2	8.5	40.5

That means, the yield of ester is approx. 40% of the theor. The maximum amount of ester in the top layer is 8.5% of ester. Per 5,000 g of reaction mixture 48 g of H_2SO_4 have been consumed, i.e. 9.6 g of H_2SO_4 per 1,000 g of reaction mixture.

Test 7 (80% sulfuric acid, 30% of acetic acid in the feed stock.
Composition of mixture as in Test 4.

The concentration of the water was somewhat lower, that of acetic acid somewhat higher.

Table 12 records the composition of the top layer of the reaction mixture during the reaction.

TABLE XII

No.	Withdrawn after throughput of cm³	CH_3COOH %	Octane %	Octene %	Ester %	% of octene are in ester
1	0	39.0	51.7	4.4	4.9	42.0
2	1000	40.0	50.5	4.9	4.6	38.7
3	1750	38.5	50.7	6.0	4.8	34.0
4	2500	38.5	47.0	8.4	6.1	32.2
5	3250	37.0	46.8	9.3	6.9	32.4
6	4000	35.1	47.0	10.5	7.4	31.3
7	4750	33.1	47.6	11.1	8.2	32.4
8	6000	33.5	47.2	11.0	8.3	32.9
9	6750	31.9	48.2	11.9	8.0	30.4
10	7750	30.7	50.0	12.2	9.1	32.6
11	8500	29.4	49.4	12.4	8.8	31.7
12	8675	26.2	52.6	12.6	8.6	30.9

Table XII demonstrates the maximum concentration of ester in the top layer at a 8-9% content of ester. A higher percentage of ester does not cause an increase in the ester concentration.

In Test 7, 7 g of H_2SO_4 have been consumed per 1000 g of acetic acid octane-octene stock.

(d) Synopsis of the Examples and Conclusions

On comparing Table XI with Table XII, we see that the higher yields, expressed in percents of the theoretically possible amounts, are contained in the reaction products when a higher percentage of the stock consisted of acetic acid.

If the output of ester is expressed in terms of g of ester contained in 100 g of reaction mixture, however, the increase of the acetic-acid concentration in the top layer beyond 25% of acetic acid fails to result in an increase of the ester concentration. With 49% of CH_3COOH in the outgoing reaction mixture (Table 11) approx. 9 g of ester are contained in 100 g of reaction mixture (Table 11); and with 30.7% in the outgoing reaction mixture, there are also approx. 9 g of ester (Table 12) It is therefore necessary to take into consideration not only the theoretical yield but also the reaction capacity available. A higher acetic concentration in the top layer increases the output, to be sure, but decreases the reaction capacity.

The sulfuric acid consumption varies between 2 and 10 g of H_2SO_4 per 1000 g of acetic acid-octane-octene mixture. It increases with an increase in the acetic acid content in the reaction mixture. This fact, too, makes it advisable not to select too high an acetic acid percentage.

Along with the ester output the processing method plays a decisive role for the choice of the rate of acetic acid concentration in the feed stock. Since acetic acid and octene-octene form an azeotropic mixture, which boils at 105° C and consists of equal weight parts of acetic acid and octane-octene, in recycling the acetic acid, it is necessary to reintroduce at least the same amount of octane-octene as of acetic acid. If the octyl acetate is to be prepared in a continuous process, fresh octene must be continuously introduced and octane must be discharged. It is therefore necessary to operate with a mixture containing less than 50% of acetic acid and allowing for a sufficient addition of fresh octene.

On the basis of all these considerations we may draw the conclusion that an octane-octene-acetic acid mixture containing 25-30% of acetic acid, is to be reacted in continuous operation in the presence of 80% sulfuric acid. But since the commercial concentrated acetic acid is only 98-99% concentrated, concentrated sulfuric acid will be used together with this acetic acid, in order to avoid an excess of water. 90 g of ester are obtained per 1000 g of reaction mixture. In replacement thereof, 31.5 g of fresh 100% acetic acid or 32.2 g of fresh 98% acetic acid must be introduced. From 2 to 10 g of H_2SO_4 have been consumed; in order to form an 80% conc. acid an amount of 0.4-2.4 g of water is needed. Along with the acetic acid, 0.7 g of water have been introduced. In continuous operation, it is therefore possible to use 98-98% acetic acid and concentrated sulfuric acid. We must only take care that the water content of the acetic acid-octane-octene mixture does not reach a magnitude which would cause separate layers to be formed. Fig. 4 indicates, at what percentage the layers would separate.

Since water excess must be avoided, a solution of anhydrous sodium acetate in glacial acetic acid must be used as a washing solution. When the washing solution has been prepared by dissolving sodium hydroxide in glacial acetic acid, with 1 mol of sodium acetate per 1 mol of water, about one fourth of the water will go over with the acetic acid-octane-octene-ester mixture when the sulfuric acid is washed out from the reaction mixture. Water come into contact with acetic acid in the stirring vessel; And an undesirable increase in the water content would result therefrom.

C. Preparation of acetic esters of the secondary alcohols with more than eight carbon atoms in the molecule.

By using the method developed for octyl acetate, we can also prepare nonyl acetate, decyl acetate, undecyl acetate, dodecyl acetate, tridecyl acetate, tetradecyl acetate, and pentadecyl acetate from the corresponding olefins and acetic acid. Products ranging from octyl to undecyl acetate, yield always 30% of the theor. or more; but starting with dodecyl acetate the rate drops with increasing molecular weights. With pentadecylene, only 10% of the theor. could be obtained in one step, while 85% of the olefin stock remained unconverted. Further tests will be made in order to clarify whether the slight yield of esters made from alcohols with more than eleven carbon atoms is caused by the chemical nature of the starting material or by the operating method used.

1. Di-isobutylene and acetic acid.

As an example for the fact that not all the olefins can be converted with fatty acids according to the method in question, we give the result of an attempt to react di-isobutylene with acetic acid.

When a highly branched octene contained in the polymer benzine of the alcohol plant (di-isobutylene or one of its isomers), is reacted with acetic acid by the same method used for the octene obtained from light benzine, only 1-2% of ester, i.e. next to no ester, are obtained. This result indicates that certain branched olefins can not be converted by the method in question, and not even when we use 100% olefin. Branched olefins of this type are easy to distinguish from the unbranched type. For this purpose, the method would have to be developed some more.

II. Preparation of higher sec. alcohols from the esters.

In order to obtain alcohols, the esters are saponified by boiling with sodium hydroxide under continuous stirring. Acidic saponification is not advisable, for, water may be split off from the alcohols. Since the higher alcohols are water-

indissoluble, all that is needed after the alkaline saponification, is to separate and rectify them. The alcohols thus produced are of a high degree of purity.

The theory of the conversion process

We have already mentioned that sulfuric acid may be assumed to be added initially to the olefin, forming sulfuric ester. The sulfuric ester is immediately converted into acetic ester, since a large surplus of acetic acid is present. Thereby the sulfuric acid is re-liberated and can be reacted once more.

1. $H_2SO_4 + C_nH_{2n} = HO_3SOC_{cn}H_{2n+}$;

2. $HO_3SOC_nH_{2n+1} + CH_3COOH = CH_3COOC_nH_{2n+1} + H_2SO_4$

The addition of equation 1 and equation 2, gives:

3. $C_nH_{2n} + CH_3COOH = CH_3COOC_nH_{2n+1}$

Olefin Acetic-acid Ester

Regardless of whether the esterification goes via Equation 2, Equation 3 gives a correct representation of the reaction. It has been proved, moreover, that the reaction takes place only under the catalytic action of the sulfuric acid. Pure acetic acid does not react with olefins, not even at higher temperatures. Phosphoric acid failed to display a catalytic activity under equal conditions, as we ascertained, in contradiction to statements contained in the literature. Whether other acids exhibit catalytic action, we shall investigate later on.

According to Equation 3, the ester output would be a function of the olefin concentration. But experiments showed that the ester output is 1/3 to 1/2 of the theor. whatever the rate of concentration of octene. This fact indicates that in this heterogeneous system the chemical equilibrium is decisive and other influences, in particular distribution equilibria are effective along with it (1). Several physical and chemical processes take place at the same time.

1. Top-layer octene is dissolved in the bottom layer.

2. The bottom-layer octene is in chemical equilibrium with acetic acid and octyl acetate, according to Equation 3.

3. The acetic-acid distribution varied in the course of the reaction, with an increase in the amount of ester in such a manner that the acetic-acid concentration increases in the top layer and decreases in the bottom layer.

4. The octyl acetate is formed in the bottom layer and is thereafter distributed between both layers according to the law of distribution.

The interrelationship of these reactions may be represented by the following scheme:

Octane, ⇣⇡ Acetic acid, ⇣⇡ octyl acetate . . . m. top layer

Octene + acetic acid (H_2SO_4) octyl acetate . . . . . bottom layer

(1) Ind. and engin. Chem. 1938, pp. 55.

The top layer contains next to no sulfuric acid. The reaction can therefore take place only in the bottom layer. As Table 2 and Fig. 3 show, the bottom layer will at all times contain only slight quantities of octene and acetic acid, in chemical equilibrium. In the chemical equilibrium of the bottom layer, about 60% to 90% of the octene are converted into octyl acetate. The steady state prevailing in the bottom layer can be disturbed only by diffusing octene into this bottom layer from the adjacent phase and diffusing out octyl acetate. This diffusion or solution process will take place until equilibrium is reached in the heterogeneous system. For the attainment of this equilibrium, the diffusing powers of the octene, on the one hand, and of the octyl acetate, on the other hand, are of decisive importance. The yield of octyl acetate is thus determined by the distribution equilibria of the octene and the octyl acetate in the two phases. If we should succeed in finding a heterogeneous system, in the top layer of which octene would be very hard to dissolve and octyl acetate very easy, a quantitative conversion of octene to octyl acetate could be obtained.

This scheme and the additional explanation indicate that it is not only possible to make octyl acetate from octene and acetic acid, but that it ought to be possible, too, to prepare octene from the ester. Indeed, pure octene is obtained by heating pure sec. octyl acetate with glacial acetic acid and sulfuric acid. This observation is not only of theoretical but also of practical importance, since only in this manner it is possible to prepare pure olefins from hydrocarbon mixtures via the esters. Paraffins and olefin of the Fischer Tropsch systhesis, in a mixture which could not be separated by any of the hitherto known methods, can be quantitatively separated in this manner.

Preparation of pure olefins

Paraffin + olefin ---------- paraffin + ester

The paraffin is distilled off, the ester is left in the distillation residue.

$$\text{Ester + fatty acid} \xrightarrow{H_2SO_4} \text{olefin + fatty acid.}$$

The fatty acid is needed as a diluent in order to avoid polymerization. Olefins and fatty acids can be separated either by means of distillation or by washing with lye.

By distilling mixtures of octyl acetate, acetic acid and sulfuric acid and processing the distillate in an adequate manner, 100% octene could already be prepared yields: 80%. 100% nonene has been obtained from nonyl acetate with the same rate of output.

M. Beth

MB:mbo

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A. E. Miller (25)

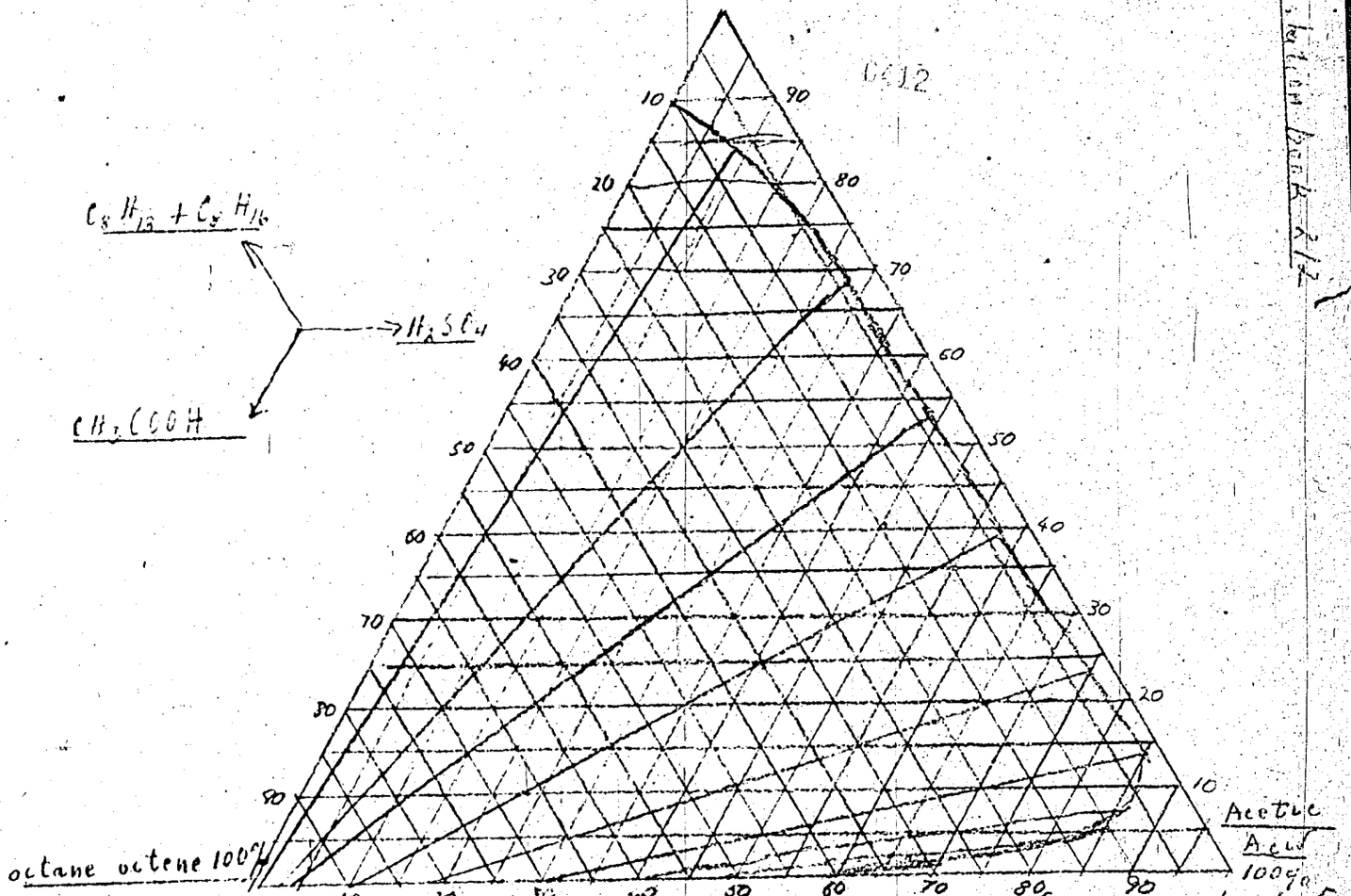

Fig 1 — Composition of the octane – octene – acetic acid – concentrated sulfuric acid mixture.

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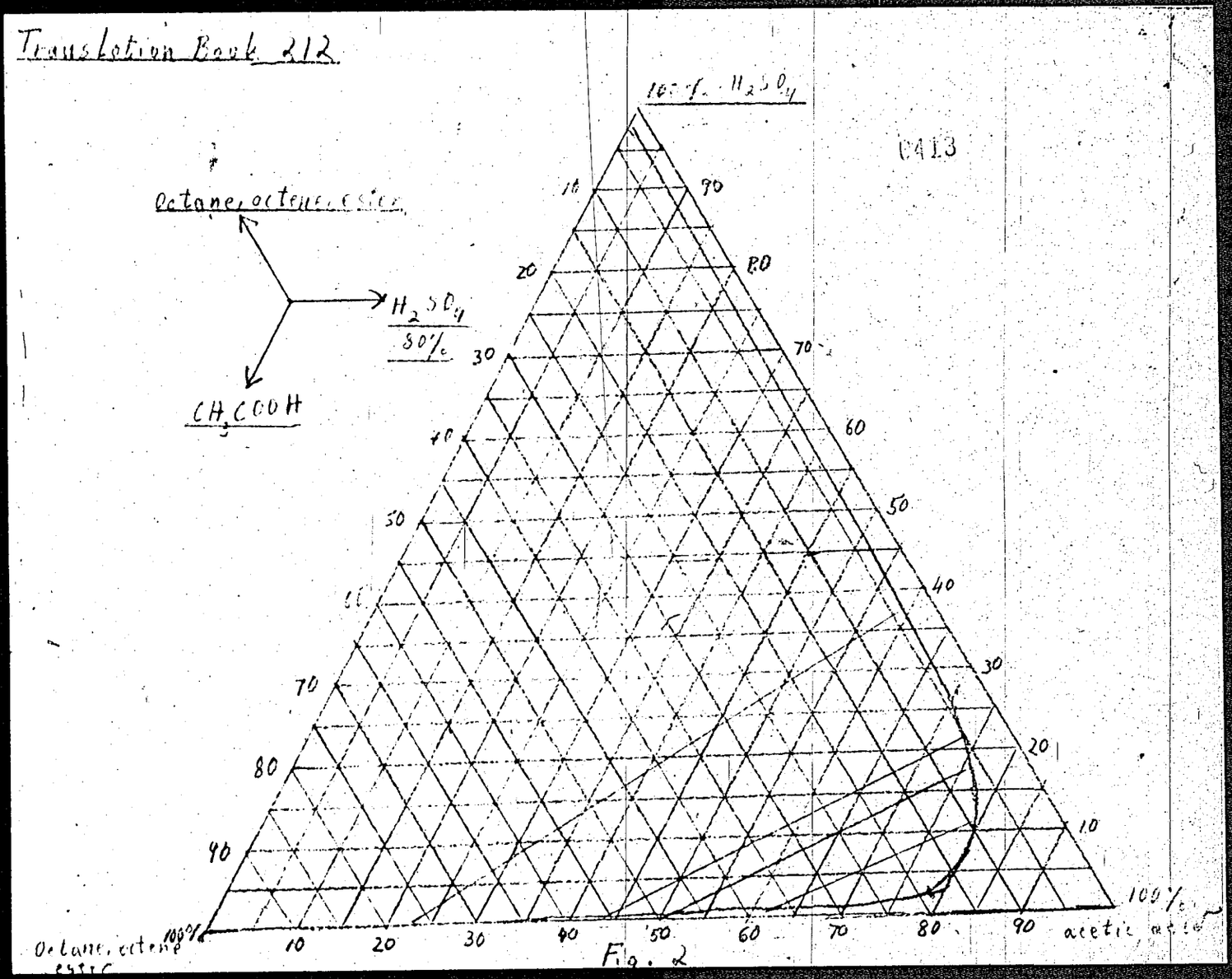

Fig. 2

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Fig. 3

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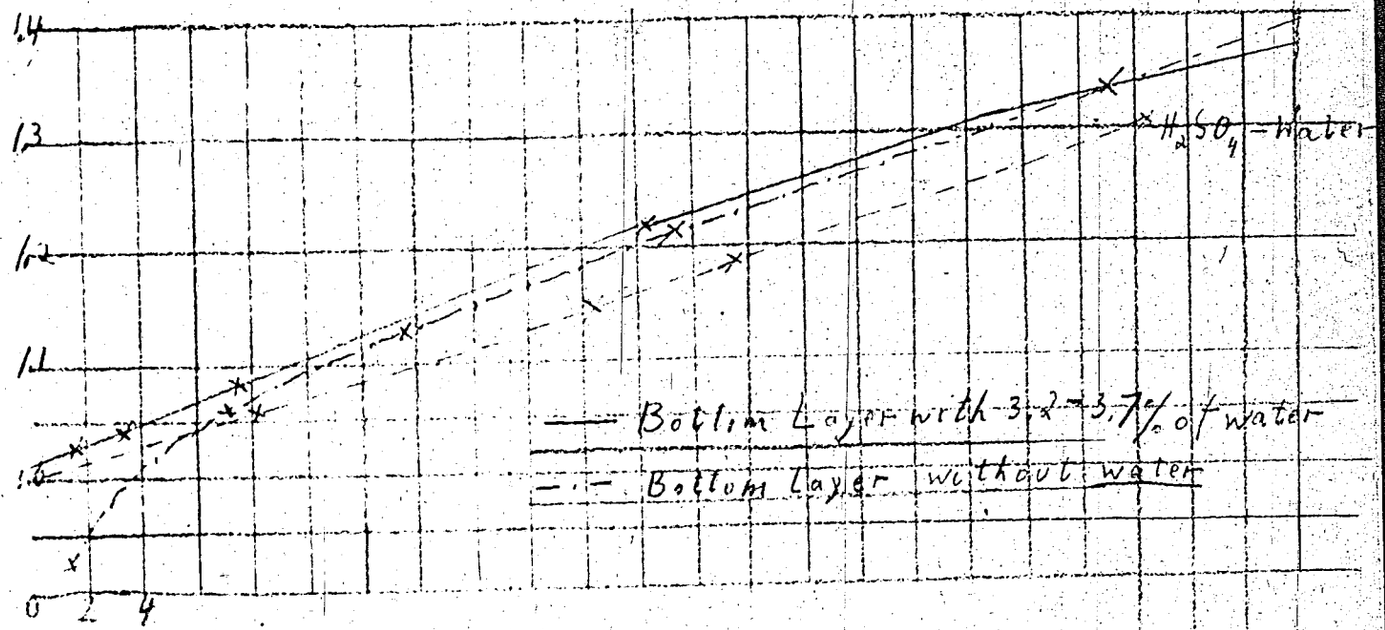

Change in Density in Bottom Layer in Proportion to Percentage of H_2SO_4

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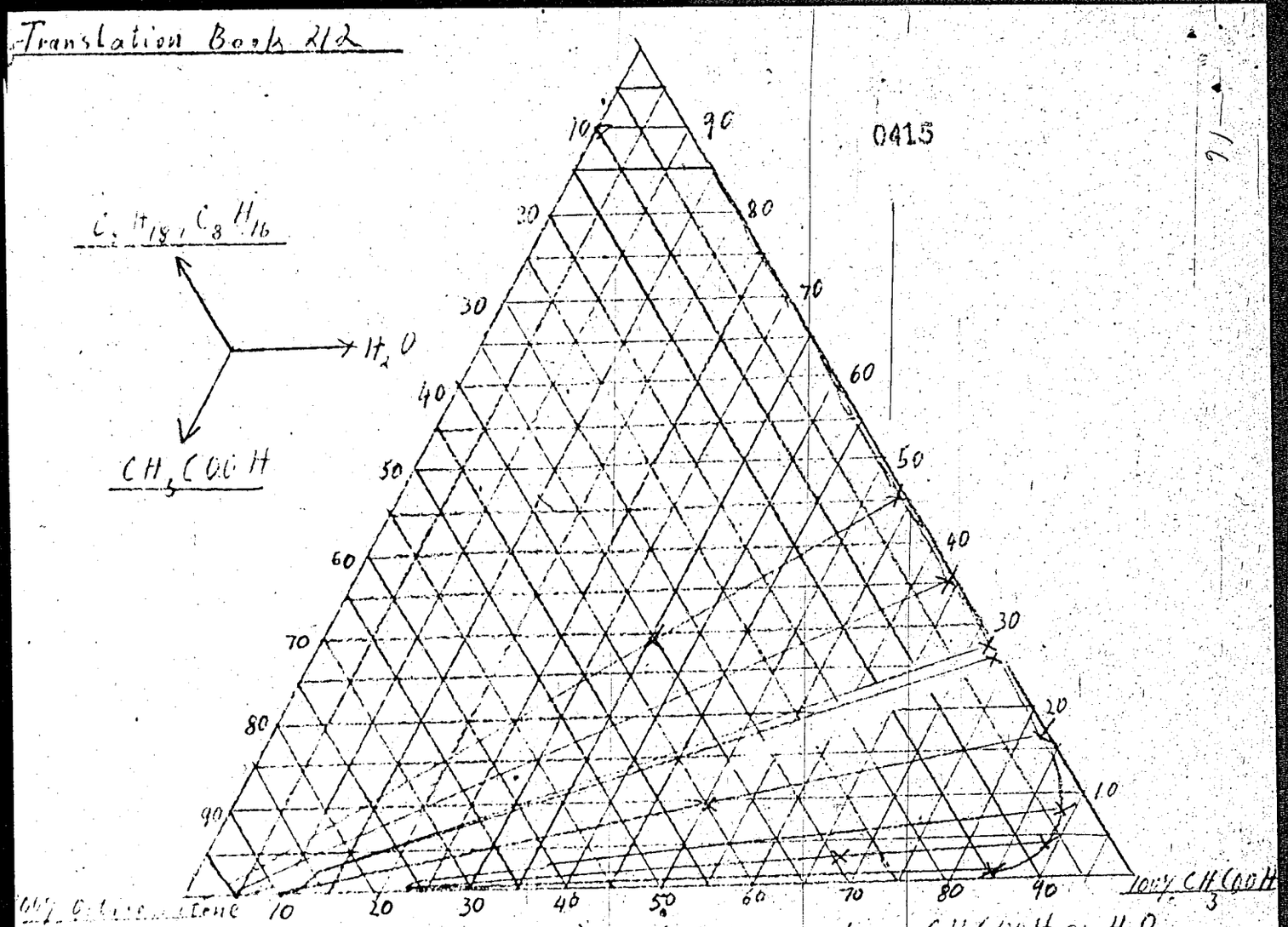

Fig. 4. Compositions of Mixtures of Octane, octene, CH_3COOH & H_2O

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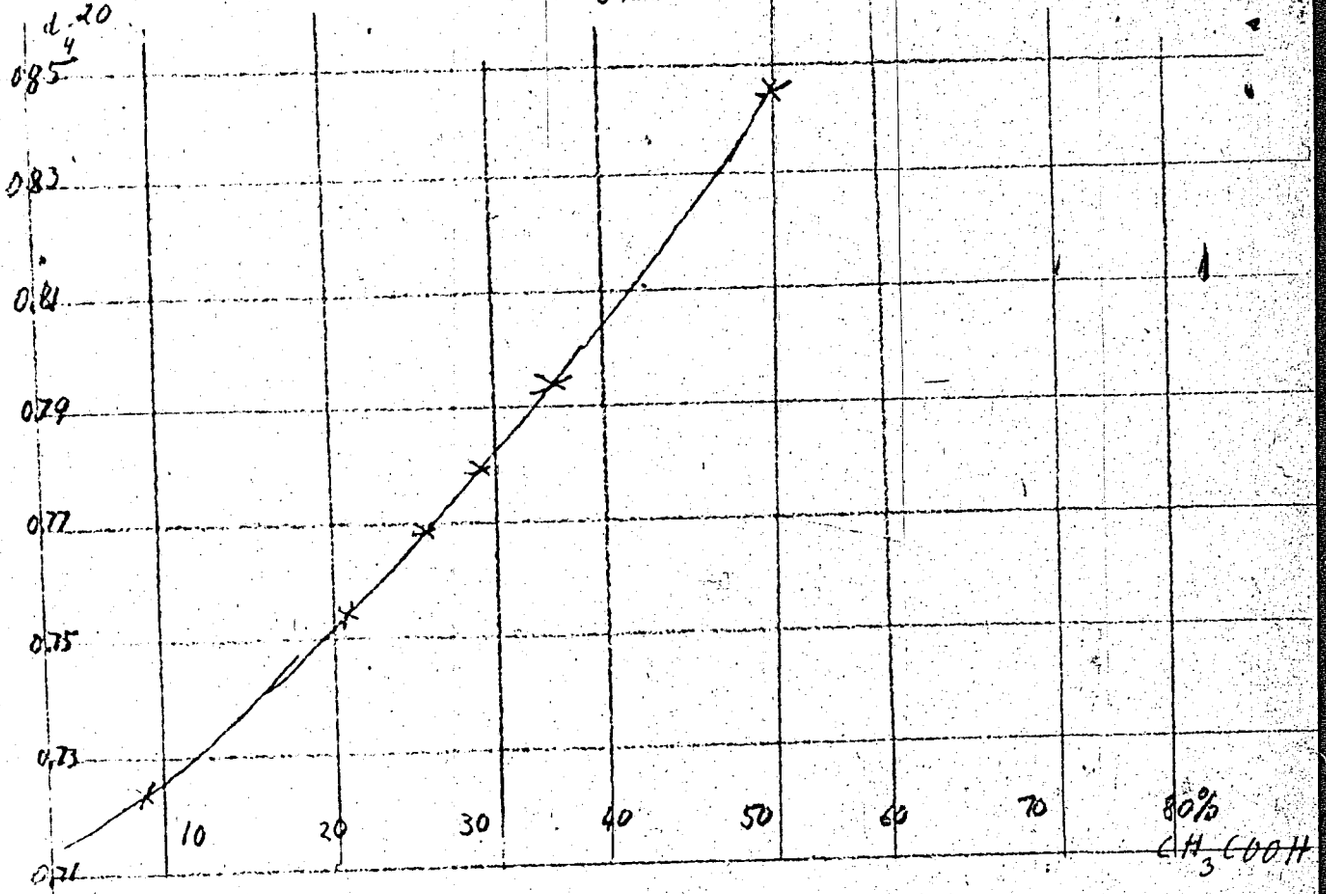

Fig 5 Density of Acetic Acid - Octane - Octene Mixtures at 20°C.

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FLOW SHEET: CONTINUOUS PRODUKTION

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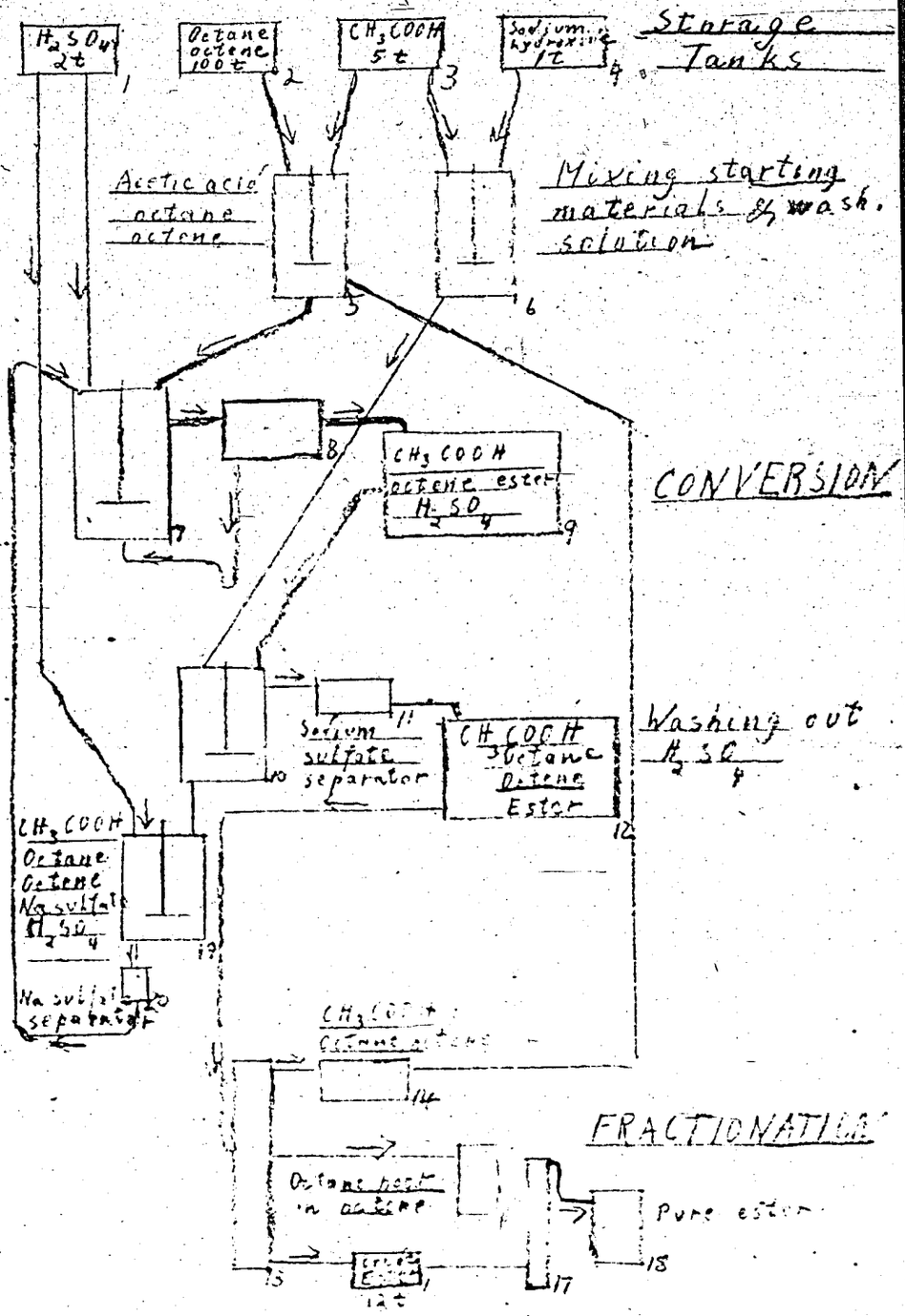

SINCLAIR REFINING COMPANY
RESEARCH & DEVELOPMENT DEPT.

Translation Book No. 216
API-TOM Reel No. 21
Bag 3045-25
Frame 25000451-484

December 10, 1948
SR-8

0418

The Interaction of the Sulfonic-Acid Chlorides, Formed by means of Sulfochlorinating Aliphatic Hydrocarbons with Ammonia and Ammonia Derivatives.

by
Dr. Asinger, Dr. Ebeneder, Dr. Boeck, Dr. Schmidt
January 1941

I. General Part

Introduction.

The preparation of sulfonic-acid chlorides by means of sulfochlorination (simultaneous action of sulfur dioxide and chlorine under the influence of light) from hydrocarbons which are gaseous at normal temperature (ethane, propane, butane) and liquid hydrocarbons (in particular mepasin), has already been treated in prior reports.

Equally elaborate reports have been made on the conversion of sulfochloride with alkali hydroxide solutions into sulfonates, and on the properties of the products of this reaction.

This study is a synopsis of those experiences, which have been gained in the laboratory and in the pilot plant, when we tried to convert the said sulfochlorides with ammonia or ammonia derivatives. Moreover, a detailed description of the analytical methods of testing said sulfamides and an enumeration of their properties and uses are included in this report.

Starting materials for the sulfamidation reaction.

A. Sulfochlorides.

There were available for the conversion pure, defined sulfochlorides, such as ethane, propane, and butane monosulfochlorides, which, however, were not always free of isomers, and the sulfochlorides of the higher hydrocarbons (pethane-eikosane); to be sure, we did not know the location of the sulfochloride group in the molecule. Mixtures of higher-molecular monosulfochlorides, such as Mersol E [1] have been also processed.

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(1) Mersol E is obtained by extracting Mepasin half-sulfochloride with liquid SO_2; it is a mixture consisting mostly of monosulfochlorides C_{12}-C_{19}, of a mean C-number of about C_{15}.

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By means of the sulfochlorination reaction, di- and multisulfochlorides, e.g. propane disulfochloride and butane disulfochloride and disulfochlorides of higher hydrocarbons and hydrocarbon mixtures, e.g. Mepasin disulfochloride, have become accessible and can be converted with ammonia and ammonia derivatives like monosulfochlorides. Finally, there were mixtures of sulfochlorides available, which contain certain portions of neutral oil along with monosulfochlorides and disulfochlorides, and which had been obtained by means of the sulfochlorination of higher hydrocarbons with sulfur-dioxide and chlorine in amounts calculated for monosulfochlorination, e.g. Mersol D (1).

2. Ammonia and its derivatives.

The conversion products of the interaction of the above named sulfochlorides with ammonia, monoethylamine and dimethylamine, were of the greatest interest, since these materials are manufactured at Merseburg on a commercial scale. Later on, we carried out tests, reacting them with other aliphatic amines which are also manufactured at Merseburg, such as isobutylamine, diisobutylamine, isohexylamine, isoheptylamine, etc. We tested also amines of the aromatic series, (aniline, methyl aniline and ethyl aniline) and of the hydroaromatic series (cyclohexylamine).

THE MECHANISM OF THE CONVERSION REACTION OF THE SULFOCHLORIDES WITH AMMONIA AND ITS ALKYL DERIVATIVES AND THE CHEMICAL PROPERTIES OF SULFOAMIDES.

A. Main Reaction.

The conversion of the aliphatic sulfochlorides with ammonia and its derivatives progresses exactly like that of aromatic sulfonic-acid chlorides. In order to bind the hydrogen chloride gas set free by the reaction, 2 mols of ammonia or amine must be added per one mol of sulfochloride.

$$RSO_2Cl + 2\,NH_3 \longrightarrow RSO_2NH_2 + NH_4Cl$$

According as the sulfochlorides are reacted with ammonia proper or with monoalkylamine or dialkylamine, sulfamides of different chemical natures are formed.

The reaction with ammonia yields sulfamides which have two disposable hydrogen atoms at the amino group. Such products are soluble in lye, since they are able to go over into an azi-form, excited by the negative SO_2 function.

$$R - S(=O)(=O) - NH_2 \longrightarrow R - S(-OH)(=NH)(=O)$$

$$R - S(-OH)(=NH)(=O) + NaOH \longrightarrow R - S(-O\,Na)(=NH)(=O) + H_2O$$

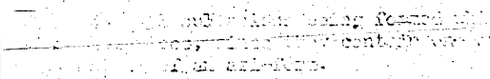
---

(1) Mersol D is a mixture, consisting of about 50-60% of monosulfochlorides, 20-30% of disulfochlorides and 20% of neutral oils of the C-number C_{12}-C_{19} and an average mol. weight corresponding to about $C_{13}H_{31}SO_2Cl$.

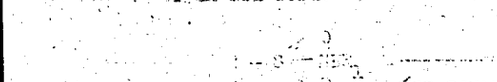
Even when the water-soluble alkali salts of the aci-form of the sulfamides are acidified with very weak acids, such as carbonic acid, the sulfamides are formed once more, since the free aci-form is not stable. This goes to show that the sulfamides are not soluble in a soda solution, which is of importance in view of the productive use of mopesin sulfamides as textile plasticizers (Mühlspinnweichmacher).

The sodium salts of sulfamides, whose carbon-chain is of sufficient length to cause capillary-chemical reactions when it is dissolved in water, are [illegible] foaming, wetting and washing capacity for wool and cotton and of no interest in this respect.

The sulfamides are of remarkable stability towards alkali hydroxide solutions. They are more easily hydrolyzed by acids. When they are heated with concentrated sulfuric acid, they are readily transformed into sulfonic acid and ammonium sulfate. The reaction of sulfochlorides with primary amines takes place according to the following equation:



[illegible] easily formed white [illegible] soluble in [illegible] sodium hydroxide [illegible], [illegible] contain the hydrogen atom, which permits the formation of aci-form.



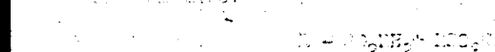
The sodium salts of [illegible] are likewise water soluble and of [illegible] to [illegible] sulfamides.

[illegible] with [illegible] amines:

[illegible] and [illegible] in [illegible].

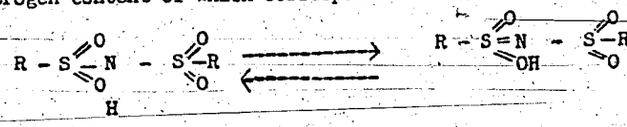
[illegible]

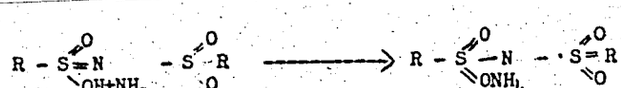
[illegible] reactive [illegible] and [illegible] when the process [illegible] with [illegible]. Anhydrides may be formed, which [illegible] the [illegible] of [illegible] previously formed molecule [illegible]:



Obviously, this reaction will be apt to occur when there is a deficiency of amines which are reacting more quickly than sulfamides. In order to prevent this side-reaction or, at least, in order to repress it, it is necessary to operate in the presence of an excess of amines.

The ammonia-derived disulfides are soluble in lye and can also be dissolved by soda, in contradistinction to the sulfamides. This is comprehensible, since the dissociation constant of the azi-form of the disulfimide is considerably greater than that of the sulfamide, due to the presence of two negative SO_2 groups. For this reason, at least a part of the disulfimide appears as a salt of ammonium of the azi-form, the nitrogen content of which corresponds to that of the sulfamide.





Since the salt of ammonium of the azi-form of the disulfimide is soluble in water, it is easy to see why mepasin sulfamides are comparatively easy to emulsify with water. Mepasin sulfamides free from disulfimides do not emulsify.

Disulfimides derived from primary amines, are not soluble in lye, since there is no available hydrogen atom left.

THE SULFAMIDE REACTION

A. The conversion of aliphatic sulfochlorides with ammonia and its derivatives in liquid ammonia or amines used as a solvent.

It is not possible to convert sulfochlorides by introducing gaseous ammonia, because in this case there would be an excess of sulfochloride in proportion to the ammonia or amines, so that the formation of disulfimides would be considerably favored. The conversion of sulfochlorides with amines liquid at normal temperature, is preferably carried out in such a fashion that the sulfochloride is made to flow into an excess charge of amines, whereby a part of the amine charge acts as a solvent and diluent. It is suitable to operate in like manner when ammonia or methyl amine is used in the conversion, passing under stirring the sulfochloride at low temperature or under pressure into the stock of liquid amine, present in excess.

After evaporating the amine excess we obtain a mixture of finely distributed hydrochloride and sulfamide, which can be separated on a heated filter by means of filtering with suction. This mode of operation is not applicable to low sulfamides (ethane,- propane- and butane sulfamide), since these compounds are soluble in water. It is also unsuitable with mepasin sulfamides even though they are insoluble in water, per se, since they contain water-soluble compounds in the form of the salts of

ammonium of the disulfimides, which very easily emulsify the sulfamide in water. The water can be separated from sulfamides only by very wearisome operations. Furthermore, such a sulfamide, even though it may appear to be pure, will always contain a few per cents of residuary water.

But in reacting disulfochlorides of short-chain hydrocarbons (propane- and butane disulfochloride), this mode of operation can be used to advantage. For the mepasin sulfochlorides, however, a mode of operation turned out to be suitable where, by using solvents in which the sulfamide is readily soluble but the amine hydrochloride only poorly soluble, the two reaction products can be smoothly separated.

B. Sulfamidation in the presence of organic solvents.

1. Alcohols.

In the first experiments, alcohols, such as methanol and ethanol, have been used as solvents. The alcohols have been saturated with the gaseous amine and the sulfochloride has then been passed in dropwise, while the reactor was cooled and further amines were introduced. This mode of operation results in the formation of a very complex mixture of various reaction products, consisting from the salt of ammonium of the sulfo acid pertaining to the sulfochloride, the ester of the alcohols used as a solvent and the sulfo acid, the sulfamide, the alkyl chloride derived from the alcohol, the ether derived from the alcohol, and finally the amine hydrochloride.

For instance: 1.) $RSO_2Cl + RCH$ ------ $RSO_2CH+HCl$ (alkychloride and sulfo-acid formation)

2.) $RSO_2CH + NH_3$ ------ RSO_2ONH_4 (salt of ammonium formation)

3.) $RSO_2Cl + 2NH_3$ ------ $RSO_2NH_2+NH_4Cl$ (sulfamide and hydrochloride formation)

4.) $RSO_2Cl + ROH+NH_3$ ------ RSO_2OR+NH_4Cl (ester formation)

5.) $RSO_2Cl + 2ROH+NH_3$ ------ $RSO_2OR+ROR+NH_4Cl$ (ether formation)

By using higher alcohols as solvents (e.g. isobutyl alcohol and, in particular, butyl alcohol) the ester and alkylchloride formation could be repressed; this mode of operation has been discontinued, however, as being unsuitable. Only the use of tertiary butyl alcohol had some prospect of practical application.

2. Chlorohydrocarbon.

Among all the known, comparatively easily accessible and low-boiling solvents which contain chlorine, only chloroform is suitable for the conversion of low molecular sulfochlorides. The sulfamides of propane, for instance, are unsoluble in carbon tetrachloride or trichloride. On the other hand, carbon tetrachloride only is suitable as a solvent for mepasin sulfamides. This fact is important in this connection, since the higher molecular sulfamides will probably interact with chloroform in the presence of ammonia, forming some isonitrile-like bodies which cause the reaction product to be malodorous, even in small quantities. At any rate, with chloroform or carbon tetrachloride as a solvent, any range of molecules can be processed.

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3. Hydrocarbons.

While the low-molecular sulfamides are unsoluble in benzol as well as in petroleum ether, benzol will readily dissolve higher-molecular sulfamides, and petroleum ether n-alkyl sulfamides. Whenever for some reason or other, chloroform or carbon tetrachloride can not be used (e.g., whenever the amine hydrochloride is soluble in these compounds, such as dimethyl amine hydrochloride or isobutyl amine hydrochloride, which are soluble in chloroform, or diisobutyl amine hydrochloride which is soluble in carbon tetrachloride and chloroform) these two solvents can be successfully used.

4. Oxygenous solvents, excepting alcohols.

Acetone is an excellent solvent for sulfamides; but since it interacts with ammonia and amines, it is impracticable. Ether is very suitable, in particular for laboratory tests and preparations. The most suitable procedure passes a solution of sulfochloride in ether into a solution of liquid ammonia in ether.

C. The operating conditions of the sulfamidation reaction in a solution.

In practice the sulfamidation reaction is carried out in such a manner that the major part of the solvent provided for the sulfamide is first introduced into the reactor and then saturated with the gaseous amine at a minimum temperature. The cooling is then continued and the sulfochloride which had been dissolved in the rest of the solvent, is made to flow into the reactor in such a fashion that the temperature does not rise above the most suitable reaction temperature, which had been determined in preliminary tests. The introduction of gaseous amine is continued while the reaction takes place. After the termination of the reaction, the product is boiled for some time, in order to drive off the amine excess and to complete the reaction; then the product is separated from the aminohydrochloride, and the solvent is evaporated. The residuary solvent is easy to remove in the vacuum by blowing out the product with superheated steam. All aliphatic sulfochlorides, which have become easily accessible through the sulfochlorination processes can be readily and smoothly converted with ammonia and its alkyl derivatives in this fashion.

The Analysis of the Sulfamides

As we have previously mentioned, in the products of the interaction of sulfochlorides with ammonia and amines (in the following discussion we shall, for simplicity's sake, always consider products of the interaction of sulfochlorides with ammonia obtained in an anhydrous medium), the following compounds may be present:

1.) the sulfamide RSO_2NH_2 (I)

2.) the salt of ammonium of the azi-form of the sulfamide

$$R\,S(=O)(=NH)(ONH_4) \quad \text{(II)}$$

3.) the disulfimide $RSO_2\text{-}N(R)\text{-}SO_2R$ (III)

4.) the salt of ammonium of the azi form of the disulfimide

(IV)

5.) the hydrochloride of ammonia, in the special case in question, ammonium chloride (V)

6.) imperfectly converted free sulfochlorides (VI)

7.) solvent residues. (VII)

(I) is formed as the chief product, if the reaction is carried out under [illegible] conditions (amine excess).

Only minor quantities of (II) are formed, if any (some salt of ammonium [illegible] with benzol sulfamide), so that we may disregard its existence in the [illegible] discussion as well as that of any trisulfimides that may be formed: $(RSO_2)_3H$.

A rather considerable quantity of (III) is formed when the reaction is [illegible] with an insufficient amount of ammonia and at too high a temperature.

(Whenever (III) is present, (IV) will be present in considerable quantities, [illegible] the pseudo acid derived from the disulfimide is comparatively strong.)

(V) is a by-product, which can not be helped being formed and which is [illegible] in varying quantities in the sulfamide, according to the procedure chosen.

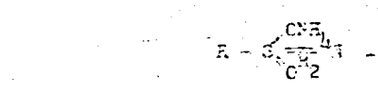
Whenever the reaction is carried directly, the final product ought to be free of sulfochloride (VI), [illegible], even though the conversion of the sulfochloride with ammonia, in particular with higher molecular products, does not [illegible] take place readily and rapidly as with alkali, for instance.

Solvent (VII) will be present, if the reaction product has not been completely worked out.

Determination of the individual constituents.

(I) The content of sulfamides may be calculated by means of the difference [illegible] titrimetrically determinable constituents from 100. For checking purposes, an additional [illegible] and nitrogen determination may be carried out.

(III) When the sulfamide is treated with dilute methanol at high temperature, the disulfimides are hydrolyzed to sulfamide and sulfo acid, while the [illegible] of ammonium of the azi-form are transformed into sulfamide and ammonium [illegible] (IV).



That means, when the reaction mixture is heated with water, free sulfo acid is formed by hydrolysis; it can be determined by means of titration. The percentage of acid x 2 gives the content of free disulfimide. By this hydrolytic process, (IV) is transformed into sulfamide and ammonium sulfonate. The ammonium-sulfonate content is easy to determine by formol titration. The formol-titration procedure is based on the principle of treating salts of ammonium with formaldehyde in an aqueous solution, producing hexamethylene tetramine, while the acid contained in the ammonium salt is set free and can be titrated.

$$4\ RSO_2ONH_4 + 6\ CH_2O \longrightarrow (CH_2)_6N_4 + 4\ RSO_2OH$$

The percentage of acid which has thus been determined multiplied by two, gives the content of salt of ammonium of the azi-form of the disulfimide, and the sum total of the acid content (with or without formol titration) multiplied by 2, gives tht total percentage of disulfimide. The values obtained by formol titration must be subjected to a correction, since ammonium chloride may be present in the reaction product, setting free hydrochloric acid when it interacts with a formalin solution. This correction is made after the content of ammonium chloride has been determined by means of a Volhard titration of the chlorine ion.

The content of ammonium chloride or aminohydrochloride (V) is determined by means of a Volhard titration of the chlorine ion which appears on treating a sulfamide sample with dilute nitric acid in an acetone solution.

The percentage of the non-converted sulfochlorides (VI) present, if any, can not be determined by a hydrolysis of the reaction products with alkaline potassium lye at a high temperature and by the determination of the chlorine ion, since this mode of operation would also include chain chlorine. On the other hand, chloroform or tetra if they are used as solvents, would react with alkaline potassium lye, chlorine ions being formed. For this reason, non-converted sulfochloride must be determined by dissolving the sulfamide in anhydrous methanol and adding an amount of normal sodium methylate solution in methanol sufficient for reddening phenol phthaleine. The methylate reacts with the sulfochloride extant, immediately forming a sulfo ester and splitting off the sulfochloride chlorine in the form of NaCl, while chain chlorine and any chloroform or tetra which may be present, remain unchanged. Thereafter, methylate solution in excess is added, acidified after a few minutes with dilute nitric acid 1 : 1, and titrated if necessary with a $\frac{n}{20}$ silver nitrate solution, according to the Volhard method, in the presence of acetone. The content of ammonium-chloride chlorine must be deducted from the value thus obtained. The accuracy of this method of sulfochloride determination has been checked; we used mixtures of pure sulfochloride-free sulfamide and pure sulfochloride, containing a known percentage of chlorine which can be determined by methyl titration, and have found the method to be fool proof. In this context, we may point out that in determining the disulfimide and the salt of ammonium, the presence of sulfochloride in the sulfamide results in erroneous (too high) values, because in the hydrolysis a major or minor part of the sulfochloride is split into sulfo acid and hydrochloric acid.

Analytic Procedure.

1. Determination of the disulfimide content.

a.) Free disulfimide.

One of the substances in question is dissolved in 25 cc of methanol; 75 cc. of distilled water are added, and the resulting emulsion is heated for one hour under frequent shaking in a bath of boiling water. Then, it is cooled to 30° C. and the free acid titrated.

Calculation: $\frac{30 \times \text{cc } \frac{n}{10} \text{ sodium lye}}{10 \times \text{amount weighed}} = \%$ of free sulfo acid

% of free sulfo acid x 2 = % of free disulfimide

If non-converted sulfochloride is present it is also converted into sulfo acid and hydrochloric acid by this mode of operation and must therefore be deducted in this calculation.

b.) Salt of ammonium of anti-form of the disulfimide.

To the sample obtained in the reaction described in (a), 25 cc of a 40% formaline solution areadded and after 10 minutes the free acid is titrated. The titration value of the blank test must be taken into account. Likewise must be taken into account the ammonium chloride which liberates hydrochloric acid with formaldehyde.

Calculation:

$\frac{30 \times (\text{cc } \frac{n}{10} \text{ NaOH with formaline sol.} - \text{cc } \frac{n}{10} \text{ NaOH blank test})}{10 \times \text{amount weighed}}$

= Volhard chlorine from ammonium chloride titration x 8.45
= given % of sulfo acid after formol titration
% of sulfo acid x 2 = percentage of salt of ammonium of the anti-form of the disulfimide.

= % of total sulfo acid with formaline addition - % of sulfo acid with formaline addition
= % of total sulfo acid.
% of total sulfo acid x 2 = % of disulfide.

Examples of analysis data.

	% sulfo acid without formol	% sulfo acid with formol	ammonium chloride value deduced	% total sulfo acid	% disulfimide
[illegible]sulfamide					
[illegible] formol	5%	11 %	10.36%	15.4 %	30.8 %
[illegible] method	5.15	11.75	10.70	15.6	31.2
[illegible] determinations	5.8	11.30	10.6	15.4	30.8
[illegible]disulfamide					
[illegible] tetra	3.81%	5.1 %	5.0 %	8.81%	17.62%
[illegible] thiol	3.65%	4.95%	4.65%	8.5 %	17.00%
[illegible] termination	3.90%	5.3 %	5.70%	8.78%	17.56%
[illegible] free sulfamide					
[illegible] chloroform	3.9%	5.3%	3.8%	7.7%	15.48%

Determination of the ammonium chloride content

2-3 grams of the substance in question are dissolved in 100 cc of acetone and the chlorine ion is titrated according to Volhard.

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Calculation:

$$\frac{1.775 \times \text{cc spent } \frac{n}{20} \text{ silver nitrate solution}}{10 \times \text{amount weighed}} = \% \text{ of chlorine}$$

% of chlorine x 1.51 = % ammonium chloride

3. Determination of the content of sulfochloride.

10 g of sulfamide are dissolved in 25 cc of anhydrous methanol and an about 1-normal solution of sodium methylate in methyl alcohol reddened by the addition of phenol phthaleine, is added until the alcoholic solution of the sample is likewise red-colored. Thereafter, 5 cc of the methylate solution are added and allowed to stand for 5 minutes; thereafter the mixture is acidified with dilute nitric acid (1 : 1); acetone is added in order to dissolve the sulfamides; and the chlorine ion is titrated with silver nitrate according to Volhard. The ammonium chloride chlorine amount is deducted.

Calculation:

$$\frac{1.775 \times \text{cc used } \frac{n}{20} \text{ silver nitrate solution}}{10 \times \text{amount weighed}} = \% \text{ of chlorine}$$

% of chlorine - % of ammonium chloride chlorine - % of sulfochloride chlorine

% of sulfochlorine x 9 = % sulfochloride (with a molecular weight of 320 for Mersol E)

4. Determination of the solvent.

When chloroform or tetra has been used as the solvent, the amount of solvent retained by the products can be determined by determining the percentage of chlorine after saponification with alcoholic potassium lye, since in this operation, chloroform and tetra are practically quantitatively hydrolyzed. The sample is dissolved in acetone, and the split-off chlorine is thereafter determined according to the Volhard method.

For instance: % of tetra = % of chlorine x 1.085

% of chloroform = % of chlorine x 1.12

The contents of ammonium chloride and free sulfochloride must be taken into account. The split-off chain chlorine,, to be sure, is thereby not taken into account. Benzol and petroleum ether percentages are determined in such a manner that major samples are subjected to a distillation in a steam stream, using an efficient cooler, the solvent in the distillate being separated and weighed. Any neutral oil present, which is produced from the sulfochloride, does not distill over with this method.

The same methods can be applied to the analysis of the n-alkylsulfamides. These compounds may be changed into disulfimides, but not into salts of ammonium, since they can not develop an azi-form.

The interaction of sulfochlorides with secondary amines takes place quite specifically under the formation of n-dialkylsulfamides. Side-reactions of the type mentioned before, are excluded.

The Use of Commercially Manufactured Sulfamides to Date

A. Use of sulfamide compounds by themselves.

Several departments of the I.G. have tested the suitability of ethane and propane-sulfamide and of butane monosulfamide and butane disulfamide as plasticizers for artificial textile fabrics. Up till now, it has not been possible to use propane sulfamilide in the form of the technical mixture consisting of the two isomer propane monosulfochlorides, as a plasticizer for Novilith emulsions; for, in the light it is unstable. This property is not modified if anilide is replaced by chlohexyl amide. Mepasin sulfide has been directly used at Wolfen. It is a suitable spinning material plasticizer (Einspinnweichmacher) for viscose silk. This procedure is based on the fact that the sulfamide is soluble in sodium lye. It is directly added to the viscose mass; while diluted in the sulfuric-acid bath, it is retransformed from the sodium salt into the sulfamide form which is then very finely distributed in the fibre. Since the sulfamide, however, is insoluble in soda, it can not be leached out when the fibre is treated with soda solution. Mepasin sulfamide is also used as a linseed-oil substitute in the production of putty. Recently it has also been suggested to use Mepasin sulfamide at Wolfen as a fat-restoring agent in the preparation of washing agents for hands or skin, instead of the expensive undecane acid monoglycerogene ester.

B. Working up the sulfamide.

Of the low-molecular sulfamides, propane sulfamide only has been worked up. It is used at Wolfen for an important military purpose. Mepasin sulfamide is converted at Hoechst under suitable conditions with ethylene oxide to a polyglycol ether, which is of equal washing capacity as the Igepals. By introducing mepasin sulfamide as a base, the corresponding phenol fraction can be saved. The conversion of mepasin sulfochloride with glycokoll or Sarkosin yields products resembling medialan ("medialanartige Verbindungen"). The same type of compounds has been synthetisized at Hoechst from the sulfamide part, in such a fashion that the sodium salt of the aci-form of the mepasin sulfamide or methylmepasin sulfamide is converted with chloracetic sodium.

In the same manner, the preparation of the so-called sulfoigepons has been carried out, by converting mepasin sulfochloride with "taurines", starting from the sulfamide by means of the Cderaction (conversion of the sulfamide with formaldehyde bisulfite).

II. Practical Part

A. Laboratory Tests.

1. Conversion of low-molecular sulfochlorides with ammonia and its derivatives.

(a) Ethane sulfochloride derivatives.

Ethane sulfochloride, obtained by the sulfochlorination of ethane in a carbon tetrachloride solution, is a colorless, lachrymator of pungent fragrance. B.p. 15 mm. = 62° C.

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Ethane sulfamide.

A solution of 1 kg of ethane sulfochloride in 1 liter of ether has been slowly introduced drop by drop under stirring into 2 l of ammonia. The stirring has been continued for several hours. Then, the excess ammonia has been evaporated, and the residuary mass has been extracted with hot chloroform, the ammonium chloride remaining undissolved. Ethane sulfamide crystallizes in colorless fine needles (freezing p. 58° C.) and is readily soluble in water. Yields: quantitative.

N-methylethane sulfamide.

This derivative has been prepared in the manner described for ethane sulfamide; it is a yellowish liquid. Yields: quantitative.

N-dimethylethane sulfamide.

Prepared in the same manner. Yellowish liquid. Yields: quantitative.

N-cyclohexyl ethane sulfamide.

125 g of ethane sulfochloride dissolved in 1 liter of ether are poured into 2.8 l of diisobutylamine dissolved in 1 liter of ether. When the reaction is terminated boiling is continued for one hour under recycling. The excess amine has been washed out with dilute hydrochloric acid. Yellowish liquid. Yields: 65% of the theory.

(b.) Propane sulfochloride derivatives.

1. Monosulfochloride derivatives.

Commercial propane monosulfochloride, i.e. the product prepared by sulfochlorinating propane, is a mixture of the two possible isotopes propane-1-sulfochloride and propane-2-sulfochloride in a proportion of about 1 : 1.

Propane sulfamide.

A solution of 1 kg of propane sulfochloride in 1 liter of chloroform has been slowly poured into 2 l of liquid ammonia at 60° C. After evaporating the ammonia, the product is filtered and freed of chloroform. Yields: 97% of the theory. The commercial propane sulfamide is liquid and readily soluble in water. Among the usual liquids, which are non-reactive with ammonia or sulfochloride, only chloroform has solvent properties.

N-methylpropane sulfamide.

Preparation as above. Also benzol and tetra can be used as solvents. The product is liquid and less readily soluble in water than propane sulfamide. Yields: quantitative.

N-diisobutylpropane sulfamide.

Preparation as above. Benzol must be used as a solvent, since dimethylaminohydrochloride is soluble in chloroform. Yields: quantitative.

N-diisobutyl propane sulfamide.

1 kg of propane sulfochloride is dissolved in 1 liter of benzol and made to flow into a solution of 2.5 l of diisobutylamine in 1 liter of benzol at -5°. Excess amine is washed out with dilute hydrochloric acid. The product is liquid and unsoluble in water. Yields: 80 % of the theory.

Propane sulfanilide.

142 g of propane sulfochloride are entered drop by drop into a solution of 200 g of aniline in 200 cc of ether. When the reaction is terminated, the aniline hydrochloride and the excess aniline are washed out with dilute hydrochloric acid. Yields: 90% of the theory. The propane sulfanilide is an oil which starts crystallizing when it is allowed to stand for a longer period of time.

N-cyclohexyl propane sulfamide.

Preparation like that of anilide. Yields: 93% of the theory. The product is solid and melts at 56-62° C. (melting point of the isomer mixture: N-dicyclohexyl propane-1-sulfamide and N-cyclo-hexylpropane -2-sulfamide).

2. Propanedisulfochloride derivatives.

By the sulfochlorination of propane only, a disulfochloride derivative is formed, namely, the 1,3-propane disulfochloride (trimethylene disulfochloride). Colorless crystals, melting at 48° C.

1,3-Propane disulfamide.

1 kg of propane disulfochloride is introduced in portions into 2 liters of liquid ammonia at -60°C. Ammonium chloride is dissolved out with water, after distilling off the ammonia, and the trimethylene disulfamide is recrystallized from hot water. Colorless flakes. Freezing point: 177°C. The product is soluble in alcohols, acids, acetone, benzol, ether, etc.

N,N'-tetramethyl(1,3)-propane-disulfamide.

240 g of propane disulfochloride are introduced at -60° into 1 liter of liquid methylamine. Working up as above. Colorless flakes out of water. Melting point: 174-176°.

N,N'-diethyl(1,3)propane-disulfamide.

240 g of propane disulfochloride are introduced in 1.5 liter of liquid ethylamine. Colorless crystals from dilute alcohol (2.5 part of ethanol to 1 part of water). Freezing point 85° C.

3. Propane sulfochloride derivatives.

Monosulfochloride derivatives.

Like the technical propane-monosulfochloride mixture, the technical butane-monosulfochloride obtained by sulfochlorination of n-butane, is a mixture of two isomers. The percentage distribution of the individual isomers is not known, however. (Studies are under way.)

The preparation of the monosulfamides is like that of propane. All of them are liquids. Whereas propane monosulfamide is soluble only in chloroform, butane sulfamide is soluble in benzol, but not in tetra.

2. Butane disulfochloride derivatives.

One of the two isomer disulfochlorides which are formed in the sulfochlorination of butane, namely the isomer which melts at 83° C., has been recognized to be 1,4 butane disulfochloride. Its sulfanilide consists of colorless crystals; freezing point: 182°. The melting point of the disulfamilide is 188° (crystallization out of methanol).

3. The conversion of higher-molecular sulfochlorides with ammonia and its derivatives.

There were not any isomer-free sulfochlorides available among the higher-molecular sulfochlorides, either. For this reason, we failed to produce sulfamides in a crystallized form, but have always obtained more or less viscous oils.

The conversion has been made in a liquid amine solution as well as with other solvents.

The best products have been obtained, when the reaction was carried out in liquid ammonia, which has been used at the same time as the solvent; since with this mode of operation, the rate of disulfimide formation is very slight, due to the presence of a great ammonia excess. The separation of the ammonium chloride, which is obtained in a finely distributed form, is a difficult process and it is most suitable to use a heated filter for it.

In this operation, it may happen that ammonium chloride passes through the filter in a colloidal form. Working with liquid ammonia requires pressure vessels or very low temperatures; for this reason, we tested also other solvents.

Whereas for propane there is only one suitable solvent available (namely, chloroform)benzol, tetra, toluene etc., may be used for nepasin sulfamides and for some derivatives, also petroleum ether. This mode of operation suffers from the disadvantage that initially (as long as no sulfamides are present, either), the concentration of ammonia is at a low rater, so that the percentage of disulfides in the reaction product increases. These experiences made with ammonia may be directly applied to the interaction of sulfochlorides with alkyls or dialkylamines.

(a) Working with chloroform as a solvent.

In order to obtain a filterable form of ammonium chloride, a certain proportion must prevail between solvent and sulfamide. To be sure, the operation may be carried out at a greater rate of dilution. But this method ought to be avoided since it is an expensive proposition to evaporate large quantities of solvent. If we operate in an overly concentrated solution, it may happen that ammonium chloride or aminohydrochloride are obtained in a colloidal form and pass through the filter.

For Mersol E and chloroform, the optimum ratio of the stock is about 1 part of Mersol E per 2.5 parts chloroform per 0.4 parts of liquid ammonia (parts by weight). The chloroform is first brought into the reactor and cooled to -20° C.,

then, we add the necessary amount of liquid ammonia and introduce thereafter Mersol E, which contains some chloroform, in such a fashion that the temperature does not exceed -20° C. When all of the Mersol has been introduced the reactants are heated, while ammonia is passed, so that the reaction be completed. Thereafter, the ammonia flow is switched off and the mass is boiled under recycling, until the major part of the ammonia is driven off. After filtering off ammonium chloride, which is obtained in a finely granular, readily filterable form, the chloroform is distilled off.

Advantages of operating with a chloroform solution.

Chloroform solidifes only at -63° C; at -20° C., it will readily dissolve liquid ammonia; when the ammonia is driven off, the ammonium chloride will practically quantitatively separate out.

Disadvantages: The products obtained by the action of chloroform have a slight fragrance like isonitrile compounds.

Analysis of a sulfamide prepared with chloroform as a solvent from Mersol E:

ammonium chloride content	0.05%
total disulfimide content	10 %

In order to find the cause of the offensive odor, sulfamide has been boiled for four hours with chloroform and alcoholic potassium lye. It has been examined whether the sulfamide undergoes a transformation similar to the isonitrile reaction.

$$RSO_2NH_2 + CHCl_3 + 3\ KOH \text{ ------ } R\text{-}SO_2\text{-}N{\equiv}C + 3\ KCl + 3\ H_2O$$

The sediment contained potassium chloride with some potassium cyanide. When the reaction product was boiled with dilute sulfuric acid, formic acid failed to be found. The product was malodorous.

(b) Operating with benzol as a solvent.

Ratio: 1 vol. Mersol E: 2.5 vol. benzol.

Benzol is first brought into the reactor and saturated with ammonia at -6° C. Then the Mersol E is allowed to flow in while more ammonia is introduced. The solubility of ammonia in benzol is very poor. Therefore, the rate of velocity of charging Mersol is of decisive importance in this process. The slower the Mersol is fed, the less disulfide will be formed. Its rate is high anyway.

Advantages: The odor of the product is perfectly suitable. The ammonium chloride may be readily filtered.

Disadvantages: After the benzol has been distilled off, ammonium chloride continues to settle out.

Benzol solidifies at +6° C. and dissolves only slight quantities of ammonia. In order to obtain a fair product, Mersol E must be fed very slowly (within 8 - 10 hours). Benzol is very toxic and easily inflammable. High yields of disulfimide.

Analysis: Content of ammonium chloride 0.15 %
" " disulfimide 24 %

At a larger-scale experiment (10 kg of Mersol E) where the reaction had been carried out more quickly, a sulfamide of the following composition was formed:

ammonium chloride	0.16%
disulfimide	30 %

In the presence of benzol as a solvent it will therefore be suitable to operate under pressure in order to obtain a higher rate of ammonia concentration.

In order to study the sulfamidation reaction from another angle, a test has been made with benzol as a solvent at a higher temperature.

In boiling benzol, the ammonium chloride is always separated out in a colloidal form and can not be filtered. But when the reaction is carried out at 50° C., ammonium chloride may be readily filtered; but 50% of disulfimide are formed, hence the rate of ammonia concentration is very low.

Solubility of ammonia in benzol at 25° C.

At 25° 100 cc of benzol will dissolve 0.35g of ammonia
100 cc of a 15% sulfamide solution 0.44 g of ammonia
100 cc of 2% sulfamide solution 0.45 g of ammonia

Operating with Mersol as a solvent (procedure of working up Mersol E)

By passing Mersol H (Mersolin half-sulfochloride) into liquid ammonia at about -40°, a smooth reaction takes place, and after filtering off ammonium chloride, a light yellow, thinly viscous liquid is formed. Since the ammonium chloride is hard to filter, it may be removed by washing out with water. By introducing ammonia into Mersol H a workable product is obtained. (1)

Operating with carbon tetrachloride as a solvent.

Ratio of quantities: 1 vol. Mersol H : 3 vol. tetra.

Carbon tetrachloride is first introduced into the reactor and saturated with ammonia at -10°, and then Mersol H is introduced while more ammonia gas is passed in. Part of the tetra may also be used for diluting the Mersol. Ammonium chloride is readily filterable still evaporating the excess ammonia. After separating the tetra, some more ammonium chloride is separated out, so that the sulfamide contains still 0.6% of ammonium chloride.

Properties: Odor all right. Tetra is not inflammable, less toxic than benzol. Light-colored products.

Technical: The last residues of tetra must be driven out from the sulfamide by steam. Basic organic compounds have no effect on corrosion of metal in processing the sulfamide (ester) solution. Ferrous, nickel, and monel are indifferent.

In large-scale production, the last traces of tetra will be removed by steaming the reaction products with superheated steam in the vacuum.

(1) According to the most recent tests, however, the desired product may be obtained by means of this procedure, if the temperature is prevented from rising above 0° C. during the passing in of the ammonia.

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Analysis: ammonium chloride content 0.5%
hydr. chlorine, varying with the tetra content
disulfimide content 17%

In accordance with the variations in test conditions, the content of disulfimide varies between 15-17%.

(e) Operating with liquid ammonia as a solvent.

This mode of operation is carried out in such a fashion that the Mersol is permitted to flow slowly into liquid ammonia at 35-40° under cooling with CO_2 snow; or, we may choose to operate at a higher temperature under pressure, and the Mersol is slowly pressed into the water under stirring. This procedure gives the best products.

There are the disadvantages that after the termination of the reaction greater quantities of ammonia must be vaporized; the ammonia/under atmospheric pressure is a very slow process, for, otherwise, the reaction mass would constantly froth over. In large-scale production it would be necessary to operate in such a manner that the sulfochloride is pressed into an excess of liquid ammonia at about +10-15° C. under a pressure of about 7-8 atms., under constant stirring and maintaining a temperature of 10°. When the reaction is terminated, the ammonia is distilled off under pressure.

In the laboratory test it is possible to filter the ammonium chlorides which are very finely distributed in the sulfamide through heated filters; but this is a very slow process, too.

500 g of Mersol E have been fed dropwise at 40° C into 2 l of liquid ammonia during 6 hours. Since the reaction velocity of higher-molecular sulfochlorides is slight at this low temperature, the stirring has been continued for six hours more.

When the ammonia had been evaporated, a process which required about ten hours more, the thick sticky mass has been brought upon a heated filter and sucked off under suction. A light-colored honeylike liquid passed the filter, whereas the ammonium chloride remained upon it.

Analysis: ammonium chloride content 0.2 %
disulfimide content 10 %

Tests made with sulfochlorides prepared from low-boiling Mepasin fractions in tetra solution showed that the percentage of disulfimide in the reaction product goes up with a shorter chain length.

E.G. boiling range of the hydrocarbon fraction	% of disulfimide
140 - 160°	47%
160 - 180°	25%
180 - 200°	20%

But if a monosulfochloride obtained by sulfochlorination of undecane is converted in a solution of liquid ammonia in ether, a product is obtained which gives the following analytical data (100 g of undecane monosulfochloride have been entered dropwise into a mixture of 300 cc of ether and 500 ccm of liquid ammonia very slowly under stirring at a temperature of -35° C. The ammonium chloride has settled out at the walls of the flask in the form of tiny crystals.)

Analysis: ammonium chloride 0.18%
disulfimide 3%

N-alkyl mepasin sulfamides.

N-methyl mepasin sulfamide is prepared approx. in the same manner as the unsubstituted sulfamide. Benzol or petroleum ether must be used as a solvent, however, since some hydrochlorides of alkyl amines are soluble in chloroform or tetra. On the other hand, N-alkylated mepasin sulfamide is of higher solubility in benzol or petroleum ether, and this is an advantage. In converting sulfochlorides with dialkylamines, there are no side reactions and the reaction is not reversible. But since the reaction proceeds much more slowly, it must be carried out at higher temperature.

(1) N-methyl mepasin sulfamide.

1 vol. of Mersol E : 3 vol. benzol.

1.5 l of benzol are saturated with methyl amine at a temperature of + 6 to 10° C. The introduction of methylamine is continued and 0.5 l of Mersol E are entered under vigorous stirring in such a manner that the temperature does not exceed +10°. The excess amine is driven off by heating to 60° and the hydrochlorate is sucked off.

Analysis: nitrogen: 4.9% (calcd. for $C_{15}H_{31}SO_2NHCH_3$ 4.6%)
aminohydrochloride: 0.25%

(2) N-dimethyl mepasin sulfamide.

Ratio: 1 vol. Mersol E : 2.5 vol. benzol

1,000 g of Mersol E are slowly passed into 2.5 l of benzol at a temperature of 60-70°C., while dimethyl amine is introduced. When dimethyl aminohydrochloride has stopped separating out, the mass is filtered and the benzol distilled off.

Analysis: nitrogen = 4-1 % (calcd. for $C_{15}H_{31}SO_2N(CH_3)$ 4.3%)
aminohydrochloride: 0.05%

(3) N-isobutyl mepasin sulfamide.

Ratio: 1 mol Mersol E : 3 mol isobutylamine: 10 mol benzol.

Isobutyl amine is dissolved in benzol and Mersol E is entered dropwise under vigorous stirring into this solution at a temperature of +10° C. The excess amine along with the benzol is distilled off in the vacuum. Isobutylamine (b.p.69° C. at 760 mm.).

Analysis: nitrogen: 4.22% (calcd. for $C_{15}H_{31}SO_2NHC_4H_9$ 3.95%)
amino hydrochloride 0.5%.

(4) N-diisobutyl mepasin sulfamide.

(Ratio as in No. 3.)

The temperature in the vacuum has been increased to 100° C. in order to remove all traces of diisobutylamine.

Analysis: nitrogen : 2.9% (calcd. for $C_{15}H_{31}SO_2N(C_4H_9)_2$ —3.4 %)
aminohydrochloride 0.5 %

B. Pilot Plant Operation.

(1) Propane sulfamide.

Up to date, propane sulfamide only has been produced on a semi-technical scale as far as the low-molecular sulfamides are concerned.

Chloroform is the only solvent for propane sulfamide which can be used in practice.

The sulfamidation reaction has been carried out in an enamelled stirring apparatus. (Confer the flow sheet).

145 kg of chloroform have been introduced into the reactor II and indirectly cooled to -20° C. with liquid ammonia. Thereafter 23 l of liquid ammonia have been pressed into the chloroform from the pressure tank D. Under stirring, 36 kg of propane sulfochloride have been made to flow from the storage tank P 512 into this mixture in such a manner that the temperature did not exceed -15°. In 2-3 hours, the reaction has been terminated. Subsequently the stirring of the reaction mixture has been continued for 1/2 hour, and thereafter, the mass has been slowly heated to 60-70° in the stirrer-equipped vessell III in order to drive off the ammonia and complete the reaction (two hours). Then, the ammonium chloride has been filtered off on a stoneware suction filter; chloroform has been distilled in the evaporator IV at 80-90° and at a pressure of 100 mm. Since the propane sulfamide was not yet quite free of chloroform (after dilution with water, little chloroform drops would settle at the bottom of the container after the sulfamide had been allowed to stand for some time), the residual chloroform is removed by evacuating. In toto, six charges have been processed, yielding 230 kg of propane sulfamide instead of 248 kg. That is a yield of 94% of the theory. The ammonium chloride is a fine colorless dry powder of 96% purity (chlorine determination), after being cleansed (decken) once with chloroform.

The propane sulfamide thus obtained is a brownish-yellow oily liquid, which begins slowly to crystallize if it is allowed to stand for a longer period of time, in particular at a lower temperature. It can be mixed with water at any ratio, is readily soluble in chloroform, alcohol, tetra, carbon trichloride, ethylene chloride, and less readily soluble in ether.

Analysis:	d/20° = 1,2415	
	ammonium chloride content	= 0.15%
	chloroform	0.1 %
	disulfimide content	15 %
	nitrogen	10.5 %

(2) Mepasin sulfamide (Mesulfan)

For the semi-technical production of Mesulfan, the apparatus put up for the production of propane sulfamide has been used after a few changes had been made. We succeeded in obtaining a novel and simple reaction by using one of the reactants, i.e., ammonia, at the same time as a coolant for the exothermic reaction, by simply introducing liquid ammonia into the reactor at atmospheric pressure. By this device we complied with another important condition, namely, that of providing a large excess of ammonia (repressing the formation of disulfimide).

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Mode of Operation

196 l of carbon tetrachloride have been cooled in the reactor R to 0° C. by introducing liquid ammonia; under vigorous stirring, a mixture of 71 l of Mersol D (for want of Mersol E, the tests have been made with Mersol D) = 75 kg of Mersol D and 56 l of carbon tetrachloride has been fed in such a manner that the temperature did not exceed 0° C. The temperature was controlled by means of the intake of liquid ammonia; it was usually -2° C. The reaction was terminated in about 6 hours. Feeding velocity; 25 l of tetra-Mersol D mixture per hour).

In order to check the total ammonia consumption, the additional amount required for the carrying off of the reaction heat has been absorbed by a known amount of recirculated water (1200 l) in a bubble tower, packed with Raschig rings and thereafter titrated.

When the entire stock had been fed, the stirring was continued for an hour, while the temperature was slowly raised to 30° C., whereby the major part of ammonia had been driven off. Thereafter, the granular ammonium chloride, which contained also the disulfamide when Mersol D was used, has been removed by filtration and the tetra has been evaporated in vessel D at a subatmospheric pressure (500).

The last residues of solvent and the neutral oil present have been removed in a blow-out column with superheated steam at 30 mm pressure and a temperature of 105° C. The blow-out process made the sulfamide somewhat darker. The product had an acid reaction with litmus, but still an alkaline one with methyl orange.

For a pilot plant test with a feed stock of 75 kg of Mersol D, the apparatus had also been precooled with liquid ammonia; 9 kg of NH_3 have been consumed in the reaction and 63.7 kg of NH_3 have been recovered in the absorption tower. For the purpose of carrying off the heat of reaction, 72.7 kg of liquid ammonia had to be evaporated, i.e. 0.97 kg of liquid ammonia = 1.52 l of liquid ammonia per 1 kg of Mersol D. At another test, the apparatus was cooled to the reaction temperature by means of a brine, then the brine has been discharged and only the heat of reaction has been carried off by means of injecting liquid NH_3 into the reactor. The practical determination of the heat tone has been based on the data obtained in this test.

With a charge of 75 kg of Mersol D, 9 kg of NH_3 have been consumed in the reaction and 56.1 have been recovered in the absorption unit; that is, a total of 65.1 kg = 102 l of liquid NH_3, and 0.868 kg = 1.36 l of liquid NH_3 per 1 kg of Mersol D. The results of this test will be used as a basis for planning a plant for manufacturing 40 to/mo of Mesulfan.

The heat tone of the sulfamidation reaction.

Approximate theoretical calculation.

Since the heats of combustion of mepasin sulfochloride and mepasin sulfamide are not known, that amidation reaction which most closely ressembles an aliphatic sulfamidation reaction, namely, that of an aliphatic carboxylic acid chloride (i.e. the conversion of acetyl chloride with ammonia to acetanide) has been chosen as the basis for calculating the heat tone of the reaction in question.

	Heat of combustion in cal/mol
Acetyl chloride ammonia	242) 333 90.7)
Acetamide hydrogen chloride	283) 295 12.2)

According to the Hess theroem per mol 38 cal. were liberated

$CH_3COCl+NH_3 \longrightarrow CH_3CONH_2+HCl$	+ 38 cal
$HCl(gas.)+NH_3'gas.) \longrightarrow NH_4Cl$ (solid)	+ 42 cal.
Total heat tone	+ 80 cal/mol

That is per kg of Mersol D:250 cal.

Since the heat of vaporization is about 326 cal per kg of liquid ammonia at about -30°, 21,100 cal can be carried off by means of 65.1 kg of liquid ammonia, that is about 280 kcal per kg of converted Mersol D. Taking into account the loss in heat, the experimentally found value for the heat tone agrees satisfactorily with the theoretically ascertained value.

In the absorption tower we have also recovered about 10 l of tetra which has been entrained by the ammonia stream.

Blowing out the raw product with steam.

After distilling off the tetra, the raw product has been blown out with dry steam in a steam-column at a pressure of 40 mm. 6 l of raw product and the amount of steam corresponding to 4 l of liquid water have been passed per hour.

The product obtained is free of tetra and neutral oil, somewhat more viscous and of darker coloring. The p_H value of the mesulfan lies between 3 and 7.

The neutral oil has been separated out with the water, while the tetra was driven off at coolant temperature under the pressure in question.

If the flow rate of the raw product is reduced to 3 l per hour, maintaining the flow rate of the steam unchanged, the sulfamide is of a still darker color, but otherwise of unimproved quality.

After undergoing the blowing-out process, the raw product still contained 0.5% of ammonium chloride. In storage, the ammonium chloride settles out in the course of time, forming crystals at the bottom of the storage tank. After about 2-3 weeks of storage, mesulfan has a content of only 0.18% of ammonium chloride. The semi-technical product contained 18% of disulfamide.

The viscosity (Engler) has been determined for different temperatures.

Temperature	Degree Engler
100°	4.63
80°	24.4
60°	77.8

A control test has been made in the laboratory with 18 kg of Mersol E; the raw product has been treated with steam in the same column. The test has been made in a glass flask of 50 l capacity under exactly equal conditions (maintaining the temperature by injecting liquid ammonia). The temperature was 120° C. After being blown out, mesulfan contained 0.05% of ammonium chloride, 1.5% of disulfimide. The content of ammonium chloride was so low because the product had been held in storage for a longer period of time and had been freed from the settled-out ammonium chloride by decanting it.

M. Beth

M. Beth

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(Flow sheets may be issued upon request.)

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RESEARCH & DEVELOPMENT DEPT.

Translation Book No. 219 0440 December 9, 1948
API-TOM Reel 21
Frame 24000438

The Constitution of the Mepasin Sulfonates. SR-9

Dr. Asinger
October 29, 1941

In a previous investigation we have studied the mechanism of the sulfochlorination of normally gaseous hydrocarbons, such as methane, ethane, propane, n-butane and i-butane, and the constitution of the mono- and disulfochlorination products formed as well as the relative proportions in which the individual isomers appear. In this project, we studied the constitution of the sulfochlorination products of the higher-molecular hydrocarbons of the capillary active range.

Primarily two types of straight-chain hydrocarbons are to be examined, i.e., dodecane and hexadecane.

We wanted to establish how the sulfochloride function in the monosulfochlorides proceeds via the individual carbon atoms, i.e., in what relative percentage e.g. the six possible individual monochloride isomers of dodecane are formed.

Under the viewpoint of elucidating the capillary-chemical mechanisms involved, it was of particular importance to learn, with regard to the mepasin sulfonates, whether the major part of the sulfochloride groups are oriented towards the end of the molecule, or whether they are uniformly distributed all over the range of the molecule, so that neither substitution promotions nor substitution inhibitions occur at any place of the molecule with regard to the methyl groups.

The aliphatic sulfonic-acid chlorides which are formed by sulfochlorinating paraffinic hydrocarbons, e.g., mepasin, yield sulfonates which are not only of excellent chemical capillary properties but also very active in white-washing processes (cotton fabrics), when saponified withalkalies. For this reason, it had been initially conjectured (1937) that in the course of the sulfochlorination process the sulfonic-acid chloride groups are predominantly incorporated near the end of the molecule.

Up to that time the ideas prevailing in the field of alkyl sulfates (alcoho sulfates) assumed that type of alkylsulfate to be of the best washing properties which carries its lyophil group at the end of the molecule (sulfates of the normal primary alcohols).

But when a synthetic sulfonate with an undoubtedly terminal cetane sulfonate group, which had been prepared by sulfochlorinating cetane, was examined by capillary chemical and washing test methods, the striking fact has been established that the sulfonate with the terminal lyophil group was obviously inferior to the sulfonate mixture obtained by sulfochlorinating cetane with respect to its wetting, foaming and white-washing effects; its wool-washing effect was considerably inferior.

Thus it had been established for the first time that it is by no means desirable to incorporate the sulfochloride group at the end of the carbon chain in the sulfochlorination process, even if it were possible to do so.

In our studies devoted to the determination of the constitution of the mono- and disulfochlorides which are formed by sulfochlorinating gaseous hydrocarbons, it has been established that the relative proportions of the substitution products obtained by a monosulfochlorination process are the same as when the direct-chlorination method is applied. Thus, Hess' rule which states that whenever the primary hydrogen atom reacts with a rate of velocity 1, the secondary is substituted 3.23 times more frequently and the tertiary 4.45 times more frequently, has been confirmed still in another way, from the sulfochlorination side.

The tertiary hydrogen atom, however, makes an exception, since for steric reason it does not react at all in the sulfochlorination process even though its substitution proceeds smoothly in the chlorination process.

Whereas 50% of propane 1-sulfochlorides are formed from propane, only 33% of terminal sulfochlorides are formed from n-butane and 23.5% from n-pentane. This means, the longer the hydrocarbon chain, the more methylene groups present, the lower the percentage of terminal sulfochlorides, in contradistinction to the internal ones, which are of secondary substitution.

On the basis of the assumption that the Hess rule is also valid for higher Molecular hydrocarbons (exact determinations have been made only up to the n- and i-pentane resp., since the various isomer hexyl chlorides can not be separated any more by means of rectification) the sulfochlorination or chlorination of n-dodecane would yield only 8.5 mol %, that of n-hexadecane only 6.2 mol % of terminal sulfochlorides or chlorides.

The distribution of the other mol percentages of sulfogroups ought to take place uniformly along the entire molecular range, since two methyl groups are each time equivalent to one another.

Whereas 8.5 mol % are placed at the end of the dodecane molecule, 18.3 mol % may be conjectured to be linked to carbon atom 2, 3, 4, 5, and 6.

Correspondingly, 6.2 mol % of the sulfochloride groups would be found at the end of the cetane molecule and 13.4 mol % at the carbon atom 2, 3, 4, 5, 6, 7 and 8.

These substitution regularities ought to be the same in the sulfochlorination and chlorination processes.

Both relationships could be clarified in this study. Thus another contribution has been made to the substitution problem of the higher molecular aliphatic hydrocarbons.

The data refer only to the onosubstitution processes.

Direct chlorination as well as sulfochlorination yield equimolecular mixtures consisting of all theoretically possible isomers of monochlorides and monosulfochlorides resp., that means, the substituent is uniformly distributed over all methyl groups, in accordance with the Hess rule as adapted to higher-molecular hydrocarbons.

The percentage of substitutions occurring in the terminal methyl group is lower than in the methylene group, ie., the primary hydrogen atom reacts less frequently. It can not be accurately established whether the proportion of relative reaction velocities of the primary: to the secondary hydrogen atom is again 1 : 3.25; indeed, this datum is not important for the ultimate result. It may however be conjectured that this proportion is also the same with higher-molecular hydrocarbons, all other circumstances being equal. These facts havebeen experimentally ascertained for dodecane as well as for hexadecane.

The following scheme shows what methods were applied:

I. Sulfochlorination products.

a.) Half-sulfochlorination : $2RH + SO_2 + Cl_2$ ---------- $RSO_2Cl + RH + HCl$.

b.) Removal of the neutral oil by means of extraction with liquid SO_2 or with water vapor in the vacuum.

c.) Removal of the disulfochloride portion by means of liquid SO_2 or of pentane at -35°.

d.) Sedulation of the monosulfochloride mixture to form a mixture of alkyl chlorides RSO_2Cl --------- $RCl + SO_2$.

e.) Dechlorination of the alkyl chloride mixture, by means of the silver stearate method, without causing the double bond to shift.

f.) Ozonification of the olefin mixture and quantitative oxidative splitting of the ozonides into acids.

g.) Separation of the acid mixture by means of vacuum rectification.

h.) Collection of the acid fragments.

There is another way of treating sulfochlorination products: the monosulfochloride mixture obtained in step c.) is saponified and the sulfonates transformed into the olefin mixtures by means of a caustic potash fusion, since this does not result in a noticeable shifting of the double bond, as has been ascertained recently. The further treatment of the olefin mixture is like under f.)

Ad I c.) The disulfochloride portion may be removed by means of the pentane method as well as by diluting the half-sulfochloride with a large quantity of pentane and treating it thereafter with liquid SO_2, thus separating out the disulfochlorides which are selectively dissolved in liquid SO_2. This mode of action is repeated until the SO_2-extract analysis shows pure mono-sulfochloride. There is no selectivity of the SO_2 with respect to the various monosulfochloride isomers.

Ad I e.) A special method had to be developed for the dechlorination of the alkyl chloride without shifting the double bond. The chloride is reacted with silver stearate in a solvent at 200° C., the stearic-acid ester of the alcohol which belongs to the alkylchloride being formed; it is decomposed into stearic acid and olefin upon being distilled under somewhat reduced pressure. The double bond is not shifted thereby.

Ad I f.) The olefin ozonification proceeds smoothly. Up to date, however, there were no methods available for a quantitative splitting of the ozonides to carbonic acids. A suitable method had to be developed; the ozonide is dropped into an alkaline silver-oxide suspension at 90°, resulting in a quantitative acid formation.

Ad I g.) It is impossible to distil the acid mixture in such a fashion that uniform individuals are obtained; indeed, when 10° fractions are separated, we find most always mixtures of two acids, the relative proportions of which have been calculated on the basis of the mixing rule. Since a residue results in every distillation, and since in th s case, the said residue corresponds to the highest-molecular carbonic acid possible in each case, the last fraction can not be determined exactly any more, because the residue does not consist of the pure acid but of certain quantities of resinous bodies. Unless differently specified, this residue has been uniformly calculated as consisting of a pure acid.

Ad I h.) The amounts of acids calculated by the mixing rule, are tabulated according to C-numbers and the respective quantities in grams, are divided by the mol weight of the acid in question. In practice, the same quotient has always been obtained, proving that the splitting of the olefins resulted in equimolecular proportions of acids being formed. This indicates that also the olefins and ultimately the chlorides or sulfochlorides are present in an equimolecular proportion.

II. The direct-chlorination products.

a.) Half-chlorination (50% conversion).

b.) Rectification for the purpose of obtaining a pure monosulfochloride.

c.) Dechlorination of the monochloride, without shift in the double bond.

d.) Processing the olefin mixture as before.

Experimental

A.) The sulfochlorination product obtained from n-dodecane.

1.) Desulfation of the monosulfochlorides and dechlorination of the dodecyl chlorides.

Eight litres of pure dodecane were reacted for about two hours with 200 g chlorine gas and 200 g of SO_2 each per hour while being irradiated with ultraviolet light (One-third sulfochlorination).

The dodecane one-third sulfochloride was mixed under stirring at -20° with a twofold amount of pentane and an equal amount of liquid SO_2.

The layers separated, the bottom layer containing practically all of the disulfochlorides which were formed in the one-third sulfochlorination process. Thereafter, the same amount of SO_2 as before was added to the top layer which consisted of a pentane solution of the monosulfochlorides. The other (bottom) layer was practically free of disulfochloride. Sulfur dioxide and pentane was removed from the top layer, and the dodecane removed by means of steam distillation.

The residual pure dodecane monosulfochloride mixture is analyzed as follows:

Prec. hydr. chlorine	13.4 %, calc. 13.6%
" total chlorine	14.2 %
Thus, chain chlorine	0.8 %
Neutral oil acc. to Fahrion	2.2 %

A sample of this was mixed with a tenfold quantity of pentane and chilled to -35° C. We did not observe indications that disulfochlorides were precipitated.

1000 g of the dodecane monosulfochloride mixture was mixed with xylene and boiled for sixteen hours under recycling, the temperature being 144° C. When the xylene was distilled off, 610 g of substance was left, i.e. 71% of the theory. Therefore, the xylene cut was distilled thru a column. This yielded 183 g of the same product. That is, in toto 793 g of alkylchloride mixture was obtained, or 94% of the theory.

Analysis:	
Total chlorine prec.	16.2% theor. 17.2%
Hydr. chlorine "	0.98% " 0.00%
iodine number "	7.5 " 0.00%
Spec. weight/20	0.8841

The crude desulfation product was rectified in a tripartite Widmer column.

At 15 mm we obtained:

at 34 - 80°	1.6% of the stock
at 80 - 110°	10.0% " " "
at 110 - 128°	87.0% " " "

The fraction of boiling range 110 - 128° was separately subjected to another rectification and at 15 mm we obtained 65 % of a fraction of boiling range 125 -128°, the analysis of which gave the following values, (after removing small quantities of unsaturated compounds, which had remained in the product after purification with phosphorous pentoxide sulfuric acid).

Iodine Number	0.9
$d_{20°}$	0.860
Chlorine	17.35 %

Two hundred cc of octadecane was added to 200 g of the dodecylchloride mixture, and 400 g of silver stearate were introduced into this mixture under stirring. The stirring was continued for fifteen hours at a temperature of 200°. Thereafter, the reaction mixture was diluted with benzol and 50 ccm of sulfuric acid in a 1 : 2 ratio was added. The clear benzol solution was poured off and the residue was washed out with benzol several times, until evaporated benzol did not leave any residue. The benzol was distilled off over a column and the residue heated in an air bath until the octadecane began to distil. At this temperature the major part of the stearic acid decodecyl ester mixture decomposes. Finally, the distillation was carried out at a pressure of 600 mm, until stearic acid (which was immediately solidified in the cooler) distilled over.

The distillate was rectified in a tripartite Widmer column. At 15 mm, 95-98°, 142 g of dodecylene mixture was obtained, i.e., 85% of the theory. Iodine number : 150.

0445

100 g of the said dodecylene was dissolved in 400 ccm of carbon tetrachloride and ozonified at 0° (ozone content: 7 g l). The ozonification was terminated after about four hours. When the carbon tetrachloride was removed in a gaseous form, 130 g of ozonide was obtained. Theory: 129 g.

The ozonide was added dropwise in the course of one hour to a suspension of 280 g silver oxide in 500 ccm 10% soda lye at a temperature of 90° under stirring, and the stirring was continued for three hours. Thereafter 400 ccm conc. nitric acid was added, whereby all the silver or any silver oxide was dissolved. After cooling, the fatty-acid layer was separated, the sour water was shaken out several times with pentane and the pentane solutions were blended. The fatty-acid layer was also blended with the pentane solutions, and the entire solution was neutralized with alcoholic soda lye. After adding a quantity of water such that the alcohol became about 50% dilute, the layers separated. The pentane layer contained the non-acidic constituents, about 2.8 g. After evaporating the alcohol and acidifying the alcoholic soap solution with pentane, the water-unsoluble fatty acids were extracted. Eighty-seven grains of fatty acids with an acid number of 370 were obtained.

290 g of these acids were distilled at 13 mm with a Raschig column 35cm long. Boiling started at 67°.

Fraction	Weight	Acid No.	Calc. by the mixing rule	Total Yield g	Molecular Weight of acid
67-80°	10.6 g	519	5.15g C_5 + 5.45g C_6	38.15 g C_6	33.0
80-90°	20.5	500	5.20g C_5 + 15.3g C_6	43.9 g C_7	33.8
90-110°	22.0	472	17.4g C_6 + 4.6g C_7	49.7 g C_8	34.4
110-120°	30.5	430	30.5g C_7	51.5g C_9	32.6
120-130°	33.5	400	8.8g C_7 + 24.7g C_8	55.3g C_{10}	32.2
130-140°	54.3	370	25.0g C_8 + 29.3g C_9	30.0g C_{11}	16.1
140-150°	36.5	343	22.2g C_9 + 14.3g C_{10}		
150-160°	54.1	320	41.0g C_{10} + 13.1g C_{11}		
Residue	25.0	203	therefrom acc. to acid no. 16.9 g calc. as C_{11}, the rest as resin without acid no.		

This distillation result indicates unequivocally that this acid mixture consisted of an equimolar mixture of fatty acids, i.e., that also the olefins and chlorides and ultimately the sulfochlorides formed an equivalent mixture of identical nature.

0446

2.) Potassium fusion of dodecane sulfonate.

300 g of this dodecane sulfochloride was saponified and the sulfonate dried and thereafter melted in a copper flask together with 400 g of caustic soda and 400 g of caustic potash in an air bath at a pressure of 15 mm. The distillate was rectified, and 170 g of dodecylene of a boiling range of 96-98° obtained at 15 mm. D_{20}°: 0.762; iodine number: 147.

100 g of this olefin mixture was ozonified and split up to acid as usual by oxidation with silver oxide.

79.6 g of fatty acids with an acid number of 388 was obtained.

64 g of this acid mixture was rectified at 6 mm with a Raschig column of 35 cm length. Boiling start: 67°.

Fraction	Weight	Acid No.	Calc. by the mixing rule	Total Yield g	Mol. Weight of acid
67-85°	3.7g	515	1.8g C_5 + 1.9g C_6	7.98g C_6	69.0
85-100°	6.8	488	0.72g C_5 + 6.08g C_6	9.00g C_7	69.0
100-110°	8.4	427	7.6 g C_7 + 0.8g C_8	10.1 g C_8	70.0
110-120°	4.9	401	1.4g C_7 + 3.5g C_8	11.45g C_9	72.0
120-130°	12.7	370	5.8g C_8 + 6.9g C_9	12.30g C_{10}	71.5
130-140°	12.7	336	4.55g C_9 + 8.15g C_{10}	6.25g C_{11}	34.0
140-150°	10.4	311	4.15g C_{10} + 6.25g C_{11}		
Residue	2.0				

The alkali fusion of the sulfonates and the conversion of the olefins into acids yielded the same results as was previously obtained, namely, we find the formation of an equimolecular mixture of sulfonates, in which the group joined to the end of the molecule is represented in a smaller proportion than that which is linked to the secondary carbon.

B.) Chlorination product of n-dodecane.

N-dodecane was subjected to a half-chlorination under irradiation with ultraviolet light, and the reaction product rectified in the vacuum with a Raschig column 75 cm long, at 15 mm.

Boiling point: 15 mm 128-130°; chlorine content 16.95%, theor. 17.2%

The mixture of monochlorododecane isomers were processed with phosphorus pentoxide/sulfuric acid and thereafter dechlorinated by means of silver stearate, and the dodecylene isomers split up into carboxylic acids as above.

56.7 g of the acid mixture with the acid number: 390 was distilled in the usual fashion. Pressure 5 mm; Boiling started at 75° C.

Fraction	Weight g	Acid No.	Calc. by the mixing rule	Total Yield g	Molecular weight of acid
75-85°	1.7	564			
85-95°	3.75	520	2.0g C_5 + 1.65g C_6	7.41g C_6	63.5
95-105°	5.80	466	3.9g C_6 + 1.90g C_7	8.05g C_7	62.0
105-115°	6.90	445	1.86g C_6 + 5.04g C_7	9.06g C_8	63.0
115-125°	6.65	396	1.11g C_7 + 5.54g C_8	10.14g C_9	63.0
125-135°	8.20	369	3.52g C_8 + 4.68g C_9	10.47g C_{10}	61.0
135-145°	13.90	337	5.46g C_9 + 8.44g C_{10}	4.37g C_{11}	23.0
145-155°	3.90	314	2.03g C_{10} + 1.87g C_{11}		
Residue	2.5		Calc. as C_{11}		

This distillation result shows unequivocally that also in the direct chlorination of dodecane, an equimolar mixture of all theoretically possible isomers is formed, among which the primary chloride represents the lowest proportion, owing to the lower reaction velocity of the primary hydrogen atom.

N-hexadecane

A.) Sulfochlorination products of n-hexadecane

The cetane was obtained by the catalytic reduction of n-cetyl alcohol with hydrogen over contact 118 at 200 atm. pressure and a temperature of 320° C., and was purified by rectification in a Widmer column.

The main fraction boiled at 3 mm at 125-126°. A small sample of it boiled at 765mm at 289-290°. d_{20}: 0.7718.

Ten litres of the hexadecane were subjected to a one-third sulfochlorination, as described for dodecane; this product was extracted eight times with liquid SO_2 and thus deemed to be exhaustively extracted for all practical purposes. The first two extracts which contained all the disulfochlorides, were kept separate. The small amount of monosulfochlorides still present in the refined product, was saponified, and the sulfonate was subjected to the caustic-potash fusion. The major part of monosulfochlorides was desulfated, as described for dodecane. The desulfation product was purified by means of rectification and subsequent treatment with phosphorus-pentoxide sulfuric acid. Its boiling point at 2.5 mm was 145-150°: it contained 13.7% of total chlorine. Theory: 13.65%.

The dechlorination was carried out according to the silver stearate method, undecane being used as a solvent. The cetylene mixture's boiling point at 15 mm pressure was 154-157°. d_{20} : 0.772, iodine number 110 (instead of 113.)

100 g of this cetylene mixture was ozonified as usual and split up to form acids.

76 g of the acid mixture of the acid number 324 was rectified at 2 mm with a small Raschig column. Boiling start: 70°

Fraction	Weight g	Acid No.	Calc. by the mixing rule	Total g	Yield mol. weight of acid
70-80°	2.5	515	1.22g C_5 + 1.28g C_6	4.66g C_6	40.2
80-90°	4.0	475	3.38g C_6 + 0.62g C_7	5.81g C_7	44.0
90-100°	4.65	427	4.20g C_7 + 0.45g C_8	6.40g C_8	44.5
100-110°	3.30	403	0.99g C_7 + 2.30g C_8	6.98g C_9	44.0
110-120	4.25	384	3.64g C_8 + 0.61g C_9	7.35g C_{10}	42.5
120-130°	7.20	350	6.17g C_9 + 1.03g C_{10}	7.62g C_{11}	41.0
130-140°	5.60	327	0.20g C_9 + 5.40g C_{10}	8.94g C_{12}	44.5
140-150°	7.70	304	0.92g C_{10} + 6.78g C_{11}	9.69g C_{13}	45.0
150-160°	8.80	282	0.84g C_{11} + 7.96g C_{12}	10.13g C_{14}	44.5
160-170°	8.80	264	0.98g C_{12} + 7.82g C_{13}	4.5g C_{15}	18.5
170-178°	12.00	248.5	1.87g C_{13} + 10.13g C_{14}		
Residue	4.5				

This means, the sulfochlorination of hexadecane yields also the various theoretically-possible sulfochlorides in an equimolar proportion.

Alkali Fusion of the cetane sulfonate.

We have already mentioned that the sulfochloride which remained in the refined product when cetane one-third sulfochloride was extracted with liquid SO_2, was saponified with soda lye and that the sulfonate solution was thereafter evaporated and dried. 300 g of this cetane sulfonate was converted into olefins by means of the caustic potash fusion, as previously described with reference to dodecane. The yields were practically quantitative. 100 g of the cetylene mixture which was obtained in this manner and purified by distillation was transformed into oxides by ozonofication and oxidative splitting up of the ozonides. 66.2 g of the acid mixture thus obtained was rectified at 2.5 mm. Boiling start: 60°.

Fraction	Weight	Acid No.	Calc. by the mixing rule	Total Yield g	Molec. weight of acid
60-70°	0.6	514	0.281g C_5 + 0.319g C_6	3.95g C_6	23
70-80°	1.7	504	0.54g C_5 + 1.16g C_6	4.30g C_7	33
80-90°	2.87	472	2.26g C_6 + 0.61g C_7	5.06g C_8	35
90-100	2.98	433	0.11g C_6 + 2.87g C_7	5.28g C_9	33.5
100-110°	4.90	396	0.82g C_7 + 4.08g C_8	5.47g C_{10}	32
110-120°	4.90	361	0.98g C_8 + 3.92g C_9	6.16g C_{11}	33
120-130°	4.77	334	1.36g C_9 + 3.41g C_{10}	6.65g C_{12}	33
130-140°	5.74	310	2.06g C_{10} + 3.63g C_{11}	7.00g C_{13}	33
140-150°	5.80	289	2.48g C_{11} + 3.32g C_{12}	7.63g C_{14}	33
150-160°	6.00	272	3.33g C_{12} + 2.67g C_{13}	6.60g C_{15}	27
160-170°	8.67	254	4.33g C_{13} + 4.33g C_{14}		
170-180°	9.90	236	3.33 g C_{14} + 6.6 g C_{15}		
Residue	4.18		Residue was resinified and and was taken into account.		

The picture is the same as in all the other distillations.

B.) The chlorination product of n-hexadecane.

Hexadecane was subjected to direct chlorination and the monochlorides were obtained by rectification with a Raschig column of 75 cm length at 5 mm pressure. The fraction boiling at 156-158° contained 12.8% of chlorine.

It was dechlorinated acc. to the silver stearate method with phosphorus pentane sulfuric acid. The cetylene mixture b.p. at 15 mm was 155-157°, d_{20}°: 0.773, iodine no.: 108.

As usual, 100 g of the dechlorination product was converted into carboxylic acid. 80 g of the acids was rectified at 2 mm over a small Raschig column.

Fraction	Weight g	Acid No.	Calc. by the Mixing Rule	Total Yields g	Molecular weight of acid
63-73°	1.0	540			
73-83°	5.0	482	5.0g C_6	5.00g C_6	43
83-95°	4.8	430	4.8g C_7	5.47g C_7	42
95-105	4.7	395	0.67g C_7 + 4.03g C_8	5.70g C_8	40
105-115°	4.5	367	1.67g C_8 + 2.83g C_9	6.68g C_9	42
115-125°	4.5	350	3.86g C_9 + 0.64g C_{10}	6.94g C_{10}	40
125-135°	6.5	326	4.95g C_{10}	7.60g C_{11}	41
135-145°	8.4	305	1.35g C_{10} + 7.05g C_{11}	8.45g C_{12}	42
145-155°	5.8	282	0.55g C_{11} + 5.25g C_{12}	8.77g C_{13}	41
155-165°	11.5	267	3.20g C_{12} + 7.30g C_{13}	10.23g C_{14}	45
165-175°	11.7	248	1.47g C_{13} + 10.23g C_{14}	5.2g C_{15}	23
Residue	10.4	half of it calculated as C_{15}			

Even when cetane is directly chlorinated, all the monochloride isomers which are theoretically possible are formed in an equimolar proportion.

Summary

1.) The monosulfochlorides formed by means of the sulfochlorination of higher-molecular weight aliphatic hydrocarbons, contain the sulfochloride group in uniform distribution all along the hydrocarbon chain. That means, all the monosulfochloride isomers which are theoretically possible are formed in an about equimolecular proportion. Only the terminal sulfochloride which is formed by the substitution of one hydrogen atom in the CH_3-group, is formed at a lower rate of yield.

2.) The same proportion is also found when higher-molecular weight hydrocarbons are directly chlorinated.

3.) The rule of Hass and Weber, which is applicable to the formation of the monosulfochloride isomers formed by sulfochlorinating gaseous hydrocarbons, as we have found in a previous study, is also valid for the higher-molecular weight hydrocarbons.

4.) The monosulfonates of the type of Mesapon N. which are formed by alkaline saponification of the sulfochlorides, are thus mixtures of all the isomers which are theoretically possible in equimolecular proportions.

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RESEARCH AND DEVELOPMENT DEPARTMENT

Translation Book 222
APL-TOM Reel 21
Frame 486-504

December 27, 1948

0451

SR-10

Preparation, Character and Capillary-Chemical Properties of Hexadecane Sulfonates and Sulfates.

Dr. Asinger, Dr. Eckhardt, Dr. Ebeneder.

Project: This investigation aims at ascertaining whether the esterification of the easily accessible oxo-alcohols with sulfuric acid yields substances of more desirable capillary-chemical properties than the direct sulfation of the olefins, assuming that alcohol and olefin are of the same carbon number. We are moreover including the sulfonates, which are easily accessible via the sulfochlorination of saturated hydrocarbons of equal C-number.

For a certain length of time, white-washing agents, and in particular wool-washing agents (fine-washing agents) have been produced by esterifying higher-molecular alcohols with sulfuric acid. For wool-washing purposes, the sulfuric-acid esters of the lower-molecular alcohols have been used, e.g. lauryl alcohol (Fewa), whereas, the higher-molecular alcohol esters, of the octadecyl-alcohol type (Sekurit), are more suitable for white-washing purposes.

Lately, the Ludwigshafen Chief Laboratory has again devoted intensive studies to the production of wool-washing and white-washing agents by sulfating olefins (converting them into sulfuric acid esters). Two novel products (Lm 3/111a and Lm 3/112) have been developed. Hitherto, higher-molecular alcohols were produced by reducing fatty acids or fatty-acid esters. By means of the Oxo-reaction they are now comparatively easily accessible. The starting material of the Oxo-reaction are olefins of a very narrow boiling range (10-13°). For this reason, it is necessary to fractionate the commercial products by means of a very accurate rectification into several fractions. This fractionation is necessary, because hitherto all olefins, whatever their origin, contain about 40-50 percent of paraffins or other saturated hydrocarbons. If a wider boiling range would be used as feed stock, the boiling points of the alcohols obtained from the low-boiling olefinic fractions would mix with the boiling points of the higher-boiling saturated hydrocarbons.

The alcohols produced would contain neutral oil components; such products are practically useless, as big manufacturers, e.g. Henkel, have stated.

The complex work involved in distilling alcohols obtained by this synthetic mechanism, made it doubtful from the very start whether this method is suitable for the production of washing agents, if there is a possibility of subjecting the starting-material olefins to a direct sulfonation, even though the products thus obtained should be of somewhat inferior washing value than the alcohol sulfates.

However, at the present time, the amounts of olefins available for the production of oxo alcohols or for the direct sulfation, do not suffice as the raw-material basis for a mass-production article, like nekpsin, which is manufactured from easily accessible, saturated, preferentially straight-chained hydrocarbons.

In order to make an approximate comparison of the foaming, wool-washing and white-washing capacities of the sulfonation products prepared from the alcohols or the olefins and of those of the products made from the abundant saturated hydrocarbons, eight C$_{16}$ sulfonates and sulfates, the constitution of which was either well-known or known with great probability, have been prepared and compared with one another.

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The comparative testing of these samples was supposed to show which method yielded optimum products, and whether the expense in labor and material necessary for producing such a washing agent is economically profitable, in comparison with that of products obtained by different methods, even if the former product is of superior quality.

Selection of the starting material.

The capillary-chemical properties of sulfonates (salts of true sulfo acids with the characteristic bond C-S) or of sulfate salts of the sulfuric-acid semi-esters of alcohols with the characteristic bond C-O-S) depend mainly upon the length of the carbon chain, and also upon the position of the sulfo-group in the molecule. For this reason, the very same carbon structure, namely, hexadecane (cetane: $C_{16}H_{34}$) has been chosen for this comparative investigation.

The Oxo-reaction is a "carbon synthesis," which proceeds according to the following general reaction mechanism under formation of aldehydes which are then directly converted into primary alcohols by means of a reduction mechanism.

For instance,

$$R\text{-}CH{=}CH\text{-}R \xrightarrow[\text{Catalyst}\ 120\text{-}130^\circ\ 200\ \text{atm.}]{CO + H_2} R\text{-}CH_2\text{-}CH(R)\text{-}C(=O)H$$

$$RCH_2\text{-}CH(R)\text{-}C(=O)H \xrightarrow[\text{Catalyst}\ 180\text{-}190^\circ\ 200\ \text{atmos.}]{H_2} R\text{-}CH_2\text{-}CH(R)\text{-}CH_2OH$$

Since in the course of the synthesis, the hydrocarbon-chain length is increased by one carbon atom, a pentadecene fraction which was finally converted into a hexadecyl alcohol had to be chosen as the olefinic starting material. Two technically accessible processes are to-day available for procuring higher-molecular olefins which lie in the capillary-active range. Both of them, however, yield olefins mixed with about 50% of paraffins or of other saturated hydrocarbons of the same boiling range.

Procuring the starting material

The pentadecene fraction used for preparing oxo-hexadecyl alcohol, or the hexadecene fraction (cetene fraction) used for the direct sulfonation, have been obtained by distilling cracking olefins produced at Ruhrchemie (they are recovered with a 40% olefin content), or from the primary olefin mixture which is formed in the catalytic reduction of carbon monoxide over iron catalysts at a pressure of 20 atmos. and a temp. of about 230-250°C. Consideration of the reaction kinetics permits us to conjecture that the primary olefins have a terminal double bond; the same statement has been made by Ruhrchemie with regard to the cracking olefins, but definite confirmation is still lacking. The oxo-reaction, moreover, does not yield products of uniform constitution, but an isomer mixture. Consequently, whenever there is a Δ 1,2 olefin present, the newly formed primary alcohol group can be attached at carbon atom 1 as well as at carbon atom 2, and it is most probable that both of the possible isomers are formed at ratios which depend upon the actual constitution of the olefin. We however, needed a uniform product on which to base the comparative analysis of the alcohol-sulfate products. Therefore, pure hexadecanol (1) has been esterified with sulfuric acid.

The same consideration applied to the olefin sulfonates prepared from the cetene fraction. In this case, too, a $\not\sphericalangle$ 1.2 cetene has been prepared by dehydrating and sulfating hexadeconol (1).

The cetane sulfonate, obtained by sulfochlorination and saponification (the sulfo group is probably attached at carbon atom 3 or 4), has been directly produced from cetane. The cetane had been prepared by the catalytical reduction of hexadecanol (1).

For control purposes, cetane sulfonate (1) has also been prepared synthetically via n-cetyl chloride (1).

Summary of the Products Tested

A. Sulfonation products made from C_{16} alcohols.

1) Cetyl alcohol sulfate made from hexadecanol (1). Position of the sulfo-group definitely established (carbon 1).

2) Cetyl alcohol sulfate from hexadecanol, prepared from a pentadecene fraction by the oxo synthesis. The pentadecene fraction was cut from a primary olefin mixture.

3) Cetyl alcohol sulfate from hexadecanol prepared from a pentadecanol fraction by means of the oxo reaction. The pentadecene fraction came from a cracking olefin mixture of Ruhrchemie.

B. Sulfonation products prepared from C_{16} olefins.

4) Sulfonation products made from $\sphericalangle$ 1,2 cétene, obtained by dehydrating hexadecanol.

5) Sulfonation products made from a cetene fraction prepared from the primary olefin mixture obtained by the hydrocarbon synthesis.

6) Sulfonation products of a cetene fraction obtained from the Ruhrchemie cracking olefin mixture.

C. Sulfonation products of C_{16} saturated hydrocarbons.

7) Cetane sulfonate (1) from n-cetyl chloride ⟶ n-cetyl rhodanide ⟶ n-cetyl sulfochloride ⟶ n-cetane sulfonate (1).

8) Cetane sulfonate made by sulfochlorinating cetane. Position of sulfo groups unknown.

Preparation of the Individual Products

1. Sulfate from hexadecanol (1). Commercial cetyl alcohol (F.p. 44°, OH number 207) was purified by a twice repeated fractionated vacuum distillation in a Claisen flask with column; about 15% have been removed as first runnings, and 40% of higher boiling substances. The main fraction boils at 200-212° at 23 mm.

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Sol. p. 49° (literature 50°)
OH-no. 226-232, corr. 97.5%, i.e. 100% of theoretical.

Fifty grams of this purified cetyl alcohol was dissolved in 100 g. of anhydrous ether, and this solution was added dropwise into a solution of 27 g. of chlorosulfonic acid in 50 g. of anhydrous ether in the course of 20 minutes, so that the temperature would not exceed 10-15°. Thereafter, stirring has been continued for 30 minutes. Two hundred grams of water-ice was added to the solution. It was neutralized with 90 cc of 30% sodium lye. A thick paste originated. After the sublimation of the ether, 250 cc of isopropylalcohol suspended in one liter of water was added, and the mass shaken out several times with ether, in order to separate out unsulfated parts. It is also possible to proceed in such a manner that the mass is extracted with ether after drying the unsaponifiable components.

Yields: 86 g of alcohol sulfate, 11 g of unsulfable.

The anorganic salts were removed by means of isopropyl alcohol extraction.

Analysis: $C_{16}H_{33}SO_4Na$ calc.: C 55.76% H 9.64 % S 9.29 %
exper.: C 55.47% H 9.56 % S 9.00%

2. Sulfate from the hexadecanol, obtained from the pentadecene fraction of the primary synthetic olefins by means of the oxo reaction.

a.) The pentadecene fraction (C_{15} fraction) came from the products obtained in the hydrocarbon-synthesis experiments at Leuna and had a boiling range of 260-280°C.

Boiling analysis (Engler):

260	270	280	285
10 %	53 %	93 %	98 %

$d_{20}^{20°} = 0.797$

mol. weight : 210; 213 (calc. for pentadecene 210)
Bromine No. = 343 mg Br/g substance, corresponding to a 45-% content of olefins.

b.) The Oxo-reaction. Three kilograms of olefins are mixed with 200 g. of Ruhrchemie-contact (the same catalyst as that used for the Fischer synthesis) and heated to 115° in a rotatory autoclave; thereafter 190 atmos. of water gas 1:1 is pressed on. After 75 minutes, the reaction was terminated (aldehyde formation). The autoclave pressure was thereafter released and 200 atmos. of hydrogen pressed on—keeping the catalyst—and heating continued for 4 hrs. to 185-190°C. (alcohol formation through aldehyde reduction).

The alcohol was then purified by a twice-repeated fractionated vacuum distillation.

B.p.=200-210° at 23 mm
OH-no. = 230, corresponding to about 99% of alcohol
Sol. p.=23-30°C.

c.) The sulfation and working up of the reaction product was carried out in the same fashion as with hexadecanol (1), as described under 1.).

3. Sulfate from hexadecanol obtained from the pentadecane fraction of Ruhrchemie cracking olefins through the Oxo-reaction.

a.) The pentadecene fraction was taken from the Ruhrchemie cracking olefin mixture and had a boiling range of 270-280°.

Boiling analysis (Engler):

277	278	282	283	284
5 %	36 %	86 %	95 %	98 %

d_{20} = 0.783
mol weight = 212 (calc. for pentadecene 210)
Olefin content = 38%.

b.) The oxo-reaction and working-up was carried out exactly as described under point 2.

Hexadecanol boils at 200-212° at 23 mm.
OH no. = 215, corr. to 92% of the theoretical.
Sol. p. = 40-45°.

c.) The sulfation and working up of the reaction product acc. to the method described under 1.

4. Sulfonation product of △ 1,2 cetene.

a.) △ 1,2 cetene has been obtained by dehydrating cetyl alcohol in the presence of an alumina-kaolins catalyst (Kont.163) at 390°. The reaction product was twice subjected to a fractionated vacuum distillation. The main fraction boiled at 160-175° at 23 mm.

d_{20} = 0.780
Bromine no. = 730 mg Br/g of substance, calc. for cetene 715 mg Br.

b.) Sulfation with acetyl sulfuric acid.

188 g. of acetyl sulfuric acid (mixed at 0° from 98 g of monohydrate and 90 g of acetic acid anhydride) was fed to 200 g of cetene, maintaining a temp. of 0-to + 5°. The stirring is thereafter continued for sixty minutes at the same temperature. Two hundred grams of ice water were added and the stock neutralized with 350 cc of 30% sodium hydroxide. The reaction product separated out in the form of a paste. It was dried and freed from the non-sulfated portion by means of ether. The anorganic salts were extracted with isopropyl alcohol.

5. Sulfonation product of the synthesis cetene fraction.

a.) The cetene fraction boiled from 280-300°.
Boiling analysis (Engler)

280	285	290	300°
10 %	46 %	72 %	95 %

d_{20} = 0.787
mol. weight 227 (calc. for hexadecene 224)
Bromine no. = 305 mg Br.g substance corr. 45% of olefin

b.) The Sulfation. Nine hundred grams of this synthetic cetene fraction was mixed with 170 g of acetyl sulfuric acid at 0° in the course of 40 minutes. Three hundred grams of water-ice was added, and the stock neutralized with 960 cc of 20% sodium hydroxide. A neutral-oil layer separated out. 1500 cc of water and 300 cc of isopropyl-alcohol methanol were added to this layer, separating out the neutral oil. The aqueous alcoholic solution was shaken out several times with petroleum ether and then evaporated until dry. The salt-free product was obtained by an isopropyl alcohol.

6. Sulfonation product of the cetene fraction from the Ruhrchemie cracking-olefin mixture.

a.) The cetene fraction boils between 280-295°.

Boiling analysis (Engler)	280	285	290°
	5 %	80 %	96 %

d_{20} = 0.787
mol. weight = 225 (calc. for hexadecene 224)
br. no. = 228 mg Br/g substance corr. 31% olefins.

b.) The sulfation and working up of the reaction product is carried out as described under 5.)

The sulfonation products of cracking olefins are distinguished by the feature that they contain about 10% of constituents which are not readily soluble in cold water, but crystallize in lustrous colorless flakes from hot water; their analysis does not disclose any difference of these crystals from the normal cetane sulfonate. Whether this fraction's existence is due to the presence of olefin isomers in the cracking-olefin fraction, cannot be stated, but probably that is what happened.

7. Cetane sulfonate (1) from n-cetyl chloride (1)

Cetane sulfonate (1) has been produced by the alkaline saponification of cetane (1). Cetane (1) sulfochloride has been synthesized by transforming an alkyl chloride into the resp. alkyl rhodanide and treating the latter with chlorine in an aqueous suspension, converting the rhodanide into a sulfochloride.

a.) Cetylrhodanide (1). One hundred fifty grams of cetyl chloride (1), (Cl-content 12.7% theor. 13.6%) was boiled jointly with 140 g of potassium rhodanide (2 mols) and 1.2l of methanol for twenty days with recirculating. Potassium chloride was filtered off. Then, the major part of the alcohol was distilled off and the residue was distilled in a water-vapor stream. The rest of the alcohol and the oily parts (neutral oils) distill over thereby. The residue left in the flask was dissolved with ether, dried with sodium sulfate and treated with animal charcoal. The ether was distilled off. A light-yellow oil was left which solidified if kept over conc. sulfuric acid. Yields 140 g.; sol. p. 38°. Achromatic crystals of sol. p. 46° were obtained by recrystallization from an ether-methanol mixture. Repeated recrystallization from petroleum ether did not result in raising the melting point.

Analysis: exper. S: 11.45 % calc. S 11.6%
N 4.88 % N 4.95 %

b.) Cetyl sulfochloride (1). Sixty grams of cetylrhodanide (1) was suspended in 1 liter of water, and a vigorous chlorine current passed in at room temperature; the temperature rose gradually to 40°. Reaction period 2 hours. When no additional chlorine was absorbed (green coloring) the stock was shaken out with ether, the ethereal solution washed with aqueous bisulfite solution for the purpose of removing the dissolved chlorine, and finally dried with molten calcium chloride. When the ether was distilled off, cetane sulfochloride (1) was left, an achromatic mass of crystals, which melts at 52-53°, after being recrystallized from petroleum ether.

Analysis	Exper.	S	10.2 %	Calc.	S 9.85 %
		Cl	10.78 %		Cl 10.9 %

c.) Cetane sulfonate (1)

The pure salt-free cetane sulfonate (1) was obtained by saponifying the above sulfochloride with the calculated amount of 10% sodium hydroxide, evaporating and extracting with methanol.

8. Cetane sulfonate from the sulfochlorination of cetane.

a.) Cetane. Cetane was produced by the catalytic reduction of cetyl alcohol in the presence of K 118 at 200 atmos. and 320° and purified by fractionated vacuum distillation.

d_{20} = 0.769

Boiling analysis (Engler)

280	284	288
3 %	50 %	96 %

b.) Cetyl sulfochloride. 1000 cc cetane were treated with a stream of gaseous chlorine (50 g) and SO_2 (50 g) per hour for 80 minutes, and irradiated with ultra-violet light, so that the conversion rate was limited to about 25 %, in order to avoid the formation of disulfochlorides.

Analysis	d_{20}	= 0.821
	hydr. Cl	2.6 %
	sulfur	2.2 %
	Total Cl	2.9 %

c.) Cetane sulfonate. By saponifying the "cetane one-fourth sulfochloride with the theoretical amount of 2-% sodium hydroxide at 90-95°, separating the neutral oil, evaporating the sulfonate solution and drying it cetane sulfonate was obtained. It was extracted with methanol to remove the salt.

Properties of the Individual Sulfates and Sulfonates.

A. Appearance. The alcohol sulfates are achromatic powders. The cetane sulfonate (1) is a light yellow crumby mass, whereas the olefin sulfation products are of a pasty, sticky character and of a yellow to brownish coloring. The sulfonate obtained by the sulfochlorination of cetane settled in yellow scales having a greasy luster.

B. The solubility in water. The alcohol sulfates are very difficultly soluble in water. Cetane sulfonate (1) is more readily soluble, and the olefin sulfation products and the cetane sulfonate obtained by sulfochlorination are very readily soluble. In hot water, the alcohol sulfates are readily soluble, too.

C. Hygroscopicity. The individual products differe widely with regard to their hydroscopic properties. Alcohol sulfates are practically non-hygroscopic. Cetane sulfonate (1) is of little hygroscopicity. All the olefin sulfation products are of a highly hygroscopic character, whereas the products obtained by sulfochlorinating cetane, deliquesce if left standing in the air. The position of the sulfo groups of the sulfates as well as of the sulfonates affects thus the intensity of their hygroscopicity. The products tested have been of 100% purity, and since they can not be powdered and undergo different increases in weight in accordance with the size of their granules, we did not measure the rates of hygroscopicity.

D. Hardness stability. The hardness stability of the alcohol sulfates could not be determined at room temperature, because they are not readily soluble.

At 70°C. and 30° S.H. (?) the alcohol sulfates are superior to all other products. The poorest performance is exhibited by cetane sulfonate (1). The olefin sulfation products are of satisfactory stability. The sulfonate obtained by the sulfochlorination of cetane is of intermediate value, poorer than olefin sulfation products and better than cetane sulfonate (1).

E. The capacity for disperging calcium soaps does not appear in any of the products.

F. The wetting effect. It has been determined at 20 and 70 degrees. It was necessary to determine the wetting capacity at high temperatures, because the alcohol sulfates are of poor solubility at 20°C., so that it is not possible to achieve exactly that concentration of wetting agents required for sinking a little disk of cotton (diameter: 3 cm) in 120 sec. The following table arranges the the products, according to their wetting effect at 20° in such order that the best products are put first, the less satisfactory ones last. The tabulation with respect to numbers is kept in the same sequence as established in the preceding text.

No.	Starting Material	Wetting value at 20° g/l	Wetting value 70° g/l
1.)	Sulfate from n. cetyl alcohol	-	0.048 g/l
2	Sulfate of the alcohol from hydrocarbon synthesis olefins	-	0.048 "
3	Sulfate of the alcohol from cracking olefin	-	0.048 "
8	Cetane sulfonate of the sulfochlorination of cetane	0.33 g/l	0.05 "
4	Sulfonation product of Cetene 1,2.	0.34 "	0.05 "
6	Sulfonation product of cracking olefin	0.48 "	0.05 "
5	Sulfonation product of hydrocarbon synthesis olefin	0.59 "	0.05 "
7	Cetane sulfonate (1)	0.91 "	0.08 "

9.) Foaming capacity. (one thousand cc capacity of measuring cylinder, 20 hits with perforated plate, temperature 70°). We determined the foaming capacity in the following manner. Two hundred fifty cc of a sulfonate solution of 1 g/l, and 0.5 g/l or 0.25 g/l resp. are introduced into a measuring cylinder of 1000 cc capacity and made to foam by pushing up and down a perforated brass stamp twenty times. The height of the foam has been measured 30 sec., 2 min.,

and 5 min. resp., after terminating the pushing action. In the subsequent table, the products are once more arranged in accordance with their foaming capacity, in such a manner that the foaming capacity exhibited at a 0.25 g/l concentration has been chosen as the standard capacity. In the higher concentration, the foaming capacity of the individual sulfonates and sulfates does hardly exhibit any differences:

No.	Starting Material	Height of foam in cm. 1 g/l	0.5 g/l	0.25 g/l
2	Sulfate of the alcohol obtained from hydrocarbon synthesis olefins.	10.90	990	930
		950	860	760
		770	730	710
1	Cetyl alcohol sulfate (1)	1160	1080	910
		1000	850	640
		820	780	680
8	Cetane sulfonate obtained by sulfochlorination	1140	1020	780
		1000	860	800
		830	745	570
5	Sulfation product of hydrocarbon synthesis olefin	1090	990	740
		940	860	610
		790	730	500
6	Sulfonation product from cracking olefin	1100	1000	670
		940	850	570
		800	730	500
3	Sulfate of the alcohol made from cracking olefin	1060	990	740
		940	860	610
		790	730	500
4	Sulfonation product from cetene-1,2	1060	970	560
		880	790	480
		700	630	390
7	Cetane sulfonate (1)	1030	820	340
		820	680	280
		780	580	220

There is hardly any difference in the foaming values at 1 or 0.5 g/l. There is a difference apparent in the foaming values exhibited at the lowest rate of concentration, proving once more that cetane sulfonate (1) is the least effective of all products compared.

H. Washing efficiency

a.) Cotton washing (white-washing)

Cotton which had been soiled with 3 g of tallow, 1.5 g of mineral oil and 15 g of dirt from the street (cheesecloth 445) was washed three times with 1 g/l of 100-% salt-free substance each time, without adding soda. The degrees of whitness obtained were measured with the Zeiss leukometer.

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Since after washing cotton three times only, where there is not any grey discoloration of the fabric to be expected, the white-washing values found are for all practical purposes a gauge for the dirt dissolving capacity in the absence of soda. In the following table, the products are once more arranged in accordance with their washing efficiency.

No.	Starting Material	Degree of Whiteness %
1	cetylalcoholsulfate (1)	73.5
3	sulfate of alcohol from Ruhrchemie olefins	72.0
5	sulfonation product from hydrocarbon synthesis olefins	70.9
2	sulfate of alcohol from hydrocarbon synthesis olefins	69.7
4	sulfonation product from cetene Δ1,2	69.5
8	sulfonation product from cetane	67.2
6	sulfonation product from Ruhrchemie olefins	66.6
7	cetane sulfonate (1)	64.6

Whitewashing tests have been made at Leuna. The cotton was washed once in the presence of 1 g of soda in one liter of washing liquor with a rate of concentration of 2 or 4 g of substance per liter. The following data were obtained:

Concentration: 2 g/l + 1 g soda/l

No.	Starting Material	Degree of Whiteness %
3	Sulfate from alcohol made from Ruhrchemie olefins	72
4	Sulfonation product of cetene Δ1,2	71.5
8	Sulfochlorination product from cetane	71.3
1	Cetyl alcohol sulfate (1)	70.9
5	Sulfonation product from hydrocarbon synthesis olefins	70.8
6	Sulfonation product from Ruhrchemie olefins	70.8
7	Cetane sulfonate (1)	70
2	Sulfate from alcohol made from hydrocarbon synthesis olefins	69.8

Concentration 4 g/l + 1g soda/l

No.	Starting Material	Degree of Whiteness %
1	Cetyl alcohol sulfate (1)	74.5
3	Sulfate from alcohol from Ruhrchemie cracking olefins	74.0
6	Sulfation product from Ruhrchemie olefins	73.3
5	Sulfation product from hydrocarbon synthesis olefins	72.3
2	Sulfate from alcohol from hydrocarbon synthesis olefins	72.1
8	Sulfochlorination product from cetane	72.1
4	Sulfonation product from cetene Δ 1,2	72.0
7	Cetane sulfonate (1)	71.0

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The differences in the dirt dissolving effect are considerably lower in the presence of soda.

The sulfates of cetyl alcohol and of the alcohol made from the Ruhrchemie washing-alkyls turn out to be of superior effect in white washing. The alcohol sulfate from the hydrocarbon synthesis olefins did not stand up as well in both of the test series. The olefin sulfonation products and equivalents as the olefin sulfates and inconsiderably poorer than the alcohol sulfates.

The cetane sulfochloride product is superior to cetane sulfonate (1). This part is of interest in view of the previous ideas concerning the behavior of capillary active substances with terminal and non-terminal lyophil groups.

As hardness builders, the cetane sulfates are inferior to the olefin sulfonation products on the whole as builders in white washing. In the presence of soda as builder, the effect in whitewashing, the differences are slight. The [illegible] conclusion that there is no important [illegible] olefin sulfation products and sulfonates [illegible] when the materials are compared.

[illegible] (Wäschenähte 36) impregnated with olive oil [illegible].

[illegible] the first time 0.5 g of [illegible] 1 g of soda per liter and 1 g the [illegible] then measured. The [illegible] percentages.

[illegible] of soda/l

	% of Remission
[illegible]	69
[illegible]	68
[illegible]	53
[illegible]	43
[illegible]	43
[illegible]	42
[illegible]	36
[illegible]	4

[illegible] 1 g/l - 1 g/l of soda

	% of Depressing
[illegible]	86
[illegible]	80
[illegible]	69
[illegible]	67
[illegible]	60
[illegible]	55
[illegible]	54
[illegible]	39

In wool washing there appear considerable differences in the behavior of the individual sulfates and sulfonates. Cetyl-alcohol sulfate and the sulfate of oxo-alcohol produced from Ruhrchemie cracking olefins are excellent. The olefin sulfonation products are poorer than the alcohol sulfates of the primary alcohols. The hydrocarbon synthesis olefins yield better products when they are directly sulfates than when they are converted into alcohol of the same carbon number. It is very striking that the cetane sulfonate lacks almost entirely a degreasing capacity. The cetane sulfonate, obtained by the sulfochlorination of cetane is much better. The difference in the efficiency of the terminal alcohol sulfate in comparison to that of therterminal sulfonate of equal chain length is striking.

These findings are conformant with the experience made at Heinze-Oppau, where it was also established that the wool-washing effect of terminal alcohol sulfates is considerably superior to that of the terminal sulfonates.

It is of importance for evaluating the satisfactory behavior of the mepasin sulfonate to find that the sulfonate obtained by the sulfochlorination of cetane, which consists probably preeimently of non-terminal sulfo groups, exhibits a much more satisfactory degreasing effect than cetane sulfonate (1).

Whereas cetane sulfonate (1) at 0.5 l of substance has only a 4-% effect, the mixture of sulfonate isomers obtained by the sulfochlorination of cetane, exhibits a 43-% efficiency. At a concentration of 1g of substance per liter, the ratio is 39:60.

It will be an important contribution to our knowledge of the behavior of mepasin sulfonates, if we shall learn to understand the behavior of cetane sulfonate, moreover, where the positions of the sulfo groups in the molecule vary, and moreover, the capillary chemical properties of mixtures of such sulfonates.

In this context, we may mention that the shifting of the sulfo group of sulfates from the position 1 to the position 2, that is from a primary alcoholic hydroxyl group to an adjacent secondary hydroxyl group causes important changes in the wetting efficiency. The wetting number of octadecane sulfate (1) is 4g/l, of Ampho-soap (octadecane-2-sulfate, sulfation product of octadecylene 1,2) under equal conditions and at the same temperature is only 0.4/l. That means the wetting efficiency is tenfold.

Summary

1.) The alcohol sulfates, olefin sulfonation products and cetane sulfonates are nearly equal in wetting and foaming capacity (the wetting capacity of the alcohol sulfate in the cold can not be exactly determined since they are not readily soluble in cold water.) The least effective among all the products tested is the cetane sulfonate (1).

2.) Important differences in the dirt dissolving capacity were observed, when the products were used in white-washing in distilled water without soda addition. The n-cetyl alcohol sulfates and the oxo-alcohol sulfates from Ruhrchemie cracking olefins were best.

3.) In the presence of soda in distilled water, there were not any important differences in the white-washing capacity of the individual products. The effects of additives such as pyrophosphate, silicate, tylose, etc. were not tested.

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1.) In the presence of soda, there were considerable differences in the [illegible] in the wool-cloth washing process. The n-cetyl alcohol [illegible], and the hydrocarbon-olefin oxo-alcohol sulfates turned out to be most suitable. [illegible] olefin-sulfonates previous and the sulfonates were decidedly inferior. Cetane [illegible] (2) is [illegible] effective.

3.) It is a remarkable fact that in white-washing as well as in wool [illegible], the sulfation product made from hydrocarbon-synthesis olefins is superior [illegible] made from the oxo-alcohol of the hydrocarbon-synthesis pentadecene [illegible].

4.) The effect of salts, e.g. sodium sulfate, upon the behavior of the [illegible] has not been examined.

5.) The fact that sulfonates with a terminal lyophil group were found to [illegible] unfavorable proper capillary-chemical properties than the desirable sulfo-[illegible] probably, which probably predominantly an interior sulfo group, [illegible] for explaining the desirable behavior of the nopasin sulfonate.

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SINCLAIR REFINING COMPANY

RESEARCH & DEVELOPMENT DEPT.

Translation Book No. 223
API-TOM 255
Chemistry of Solid Fuels
Vol. IV, No. 5, p. 459-469

January 3, 1948
SR-11

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Stabilization and Refining of Shale-Tar Benzene by Hydrogenation.

A. D. Petros, E. A. Rozhiltzeba and D. N. Andreyev

The distillation of shale and the further refining of shale tar to motor fuel has been practiced in England and Germany for a long time and recently also in countries which lack petroleum resources of their own (Esthland and Japan) and also in districts which are a long distance away from petroleum deposits. In the Sovjet Union, their is also a research project for the study of shale distillation at Kashpir, where furnaces with an outside heating system are in operation and plans have been made for the erection of furnaces with interior heating (the Fushunsky type) which will process 25 cu. m. per day and of Pamferstonsky retorts for 35 cu. m. In the Leningrad district, one plant is finished and a project for a large combinc in the district of Glov has been started. There are also auspicious prospects of obtaining considerable amounts of raw material from other districts, Kendirli, Barzis, etc.

In Mantchzhuriya (in Fushun) eight 50-ton retorts are in operation. The distillation of raw shale is carried out by introducing a gas which has been heated to 500°. The average output of tar is only 6%, i.e. it is considerably lower than the yields obtained from many types of shales in the Sovjet Union and in particular from the shale deposits in the Leningrad district. The shale semicoke which is still containing a small quantity of carbon, is charged into gas generators, where the nitrogen which is contained in semicoke is entirely removed from it in the form of ammonia under the action of air and water vapor. The gas whichcomes from the gas generators is used for the distillation process, and thus, there is no special heating system needed for the unit. The units process 1,350,000 m^3 of shales per year, with an output of 69,000 m^3 of tar and of 18,000 cu. m. of ammonium sulfate. The tar is exported to Japan, where it is worked up to motor fuel (Chemistry Industry 51, 326,1932).

Under these circumstances there is no doubt that the problem of obtaining a high-grade motor fuel from tar by low-temperature distillation is very important also for the Sovjet Union. It is moreover certain that in the very near future and even before tackling the problem of refining shale tar on a commercial scale by means of cracking and berginization, we shall have to deal with the questions of refining and stabilizing benzene, obtained by straight distillation from the shale. This benzene differs from vapor-phase cracking benzene. It contains a higher proportion of unsaturated and aromatic hydrocarbons and a lower percentage of several other bodies which are present in petroleum. Therefore we must expect that refining with sulfuric acid would result in high losses.

The extent of these losses may be estimated from the data regarding the losses occurring in the refining of primary coal tar obtained by D. Hicks and J. King (Fuel Research, Technical paper, No. 34, London, 1931) who record losses of from 13

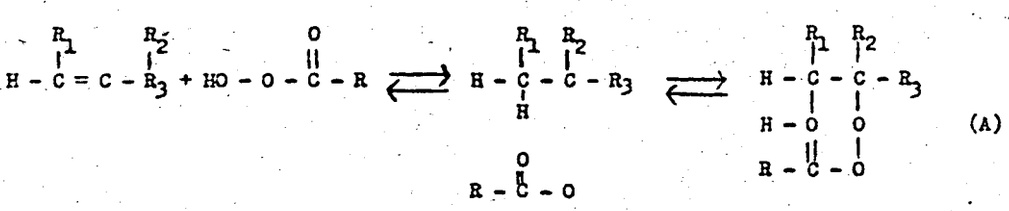
to 16 per cent. On the other hand, by its very composition (its high content of aromatic hydrocarbons and — as we shall see later on, also of saturated and unsaturated hydrocarbon isomers) shale tar benzene ought to be distinguished by a high antiknock capacity, as it follows from the diagram fig. 1, which is taken from an article of Garner's (J. Inst. Petr. Technolog., 18, 751, 1932). Consequently it is of utmost importance to repress resin-formation tendencies since the presence of resins affects the antiknock properties most adversely.

It is a well known fact that we must distinguish so called "active" and "potential" resins in benzines. "Active" resins we call the residue (in mg) which is left over when 100 ml of benzene are evaporated. "Potential" resins are called those which are characteristic for the tendency of a given benzene to form resins when it is stored for a very long time and in an unrational manner (mg per 100 ml of benzene); they are obtained by preheating benzene in an autoclave in contact with hydrogen.

Only the active resins can exercise harmful effect upon the working of the motor, by causing the carbon residue to settle out on the carburetor and the valves, and only the contents of this type of resins are matters of standardization in the requirements for automobile and aviation fuels. W. Hall (J. Inst. Petr. Technolog., 1, 147, 1915) was the first to describe resins formed by the evaporation of benzene which had been manufactured by cracking petroleum in the vapor phase. Brooks and Humphry (J. Amer. Chem. Soc. 40, 852, 1918) established the fact that probably resin formation is caused by diolefins. Later on, Smith and Cook (Bureau of Mines, Reports, 2394, 1922; 2686, 1928) found aldehydes in the resins of cracking benzene, and Brooks developed the theory still further (J. Ind. Eng. Chem. 18, 1198, 1926) by assuming that they were due to the formation of unstable organic peroxides and polymerizates which originate in the course of these processes.

However, long before this time, Engler and Weisberg (Ber. 33, 666, 1900) had studied the autooxidation of certain olefins. They studied and isolated also the peroxides of commercial amylene, trimethyl hexylene and hexylene. When amylene was left standing in dispersed daylight (after removing the non-converted amylene in a vacuum) they obtained a syrup-like residue, which contained about 31.9% of oxygen, about 45% of which was present in the form of peroxides. Trimethyl ethylene gave an analogous product, containing 29-30% of oxygen; and hexylene — 7.2% of oxygen.

Recently Brooks used laurene limonene and myrcene to illustrate his thesis that the resin-formation rate is approx. proportional to the number of double bonds in the molecule, and that the presence of diolefins stimulates the formation of resins also from saturated hydrocarbons. The oxidation and condensation mechanism (for olefinic hydrocarbons) was schematized by Wagner and Ryman is the following manner; they took thereby partly into account the possibility of aldehyde condensation with peroxide compounds and also the role of the hydroperoxides R – O – OH



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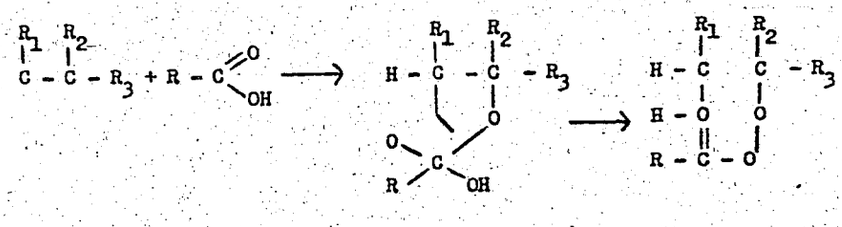

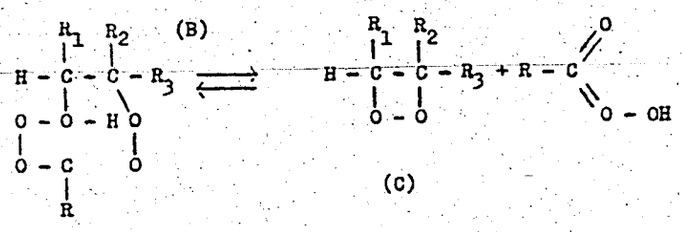

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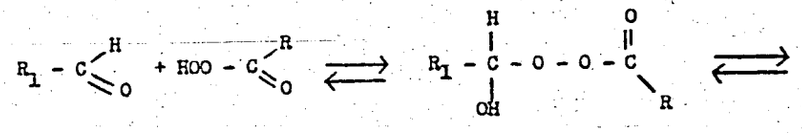
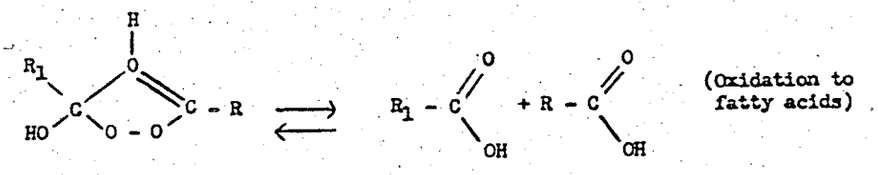
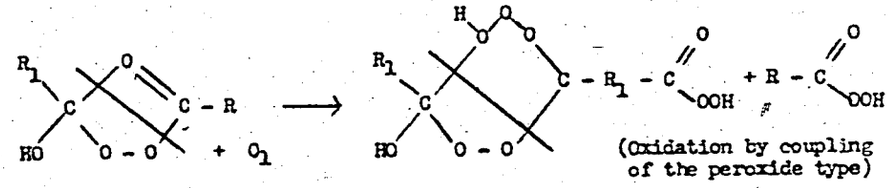




(Oxidation to fatty acids)



(Oxidation by coupling of the peroxide type)

As a final observation concerning the oxidation and resin formation mechanisms, we shall state that in the formation of aldehydes and peroxides there are not only olefins involved but also hydrocarbons of other types.

For instance, the oxidation of methane proceeds in the following steps:

1.) $CH_4 + O_2 \longrightarrow (CH_4O_2) \text{---} CH_3OOH$ (alkyl hydroperoxide)

2.) $CH_3OOH \longrightarrow CH_2O + H_2O$

3.) $CH_2O + O_2 \longrightarrow H - \underset{\underset{O}{\|}}{C} - O - OH$ (acyl hydroperoxide)

4.) $H - \underset{\underset{O}{\|}}{C} - O - O - H \text{------} HCOOH + O$

Thus, also hydrocarbons of the methane series originate aldehydes as well as compounds of the peroxide type. With regard to the comparative stability of the oxidation products of olefins and paraffins, there are a few data available which point to the fact that higher olefins, for instance, are harder to oxidize than normal paraffins. (1) The effect of a double bond and of a methyl side group reflects very strongly upon the stability of the olefins and with a somewhat favorable position of these elements, the stability of the olefins against oxidation is considerably higher than that of the homologous paraffins.

With regard to paraffinic hydrocarbons — e.g. isooctane — it was shown by Pope, Dykstra and Edgar (J. Amer. Chem. Soc. 51, 1875, 1929; 51, 2203, 1929; 51, 2213, 1929) that iso-octane oxidates the less easily, the higher branched its molecule - structure.

When we shall now turn to the problem of the stabilization of shale benzene or cracking benzene by hydrogenation, we may state that these are the fundamental issues:

1.) Removing any already formed resins and improving the respective antiknock properties.

2.) Changing the structure of the cracking-benzene hydrocarbons in such direction that it makes for maximum stability of the adjusted benzene during storage.

The first point of the problem which leads to the removal of ultra-reactive dienes and newly formed oxygen-containing compounds (aldehydes and peroxides) may be answered comparatively easily. There are no difficulties to be met in removing the liquid resins which are present in the benzene, and the formula of which was given by Smith and Cook on the basis of the elementary analytical data as $(C_6H_3O)_x$. The oxygen number of these resins is approximately 65, and the saponification number 250-300, which indicates that the structure of the resins ressembles ether or lactone.

The second problem is very complicated. The method of heating stock under high pressure is a well-known contribution towards its solution, as has been confirmed by experiments made with individual hydrocarbons and some artificial mixtures of hydrocarbons (2).

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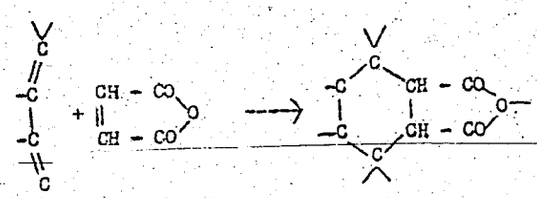
(1) Survey, P.S. Paniyutina, Symposium on Combustion and Detonation, p. 26,. Sbiyotoizdat, 1939.

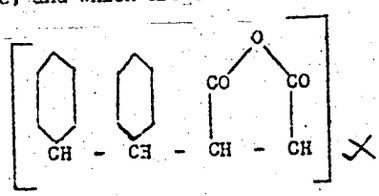
(2) Review of P.S. Panjutin, Symposium on combustion and detonation. p- 128, 1932.

However, without catalysts, the rate of isomerization which takes place thereby, is only very small. Future experiments (with individual hydrocarbons or mixtures of specific hydrocarbons) will have to search for catalysts which will yield a maximum rate of isomerization reactions under otherwise desirable reaction conditions.

When we proceed from the above-mentioned view point which is of a theoretical character, to the concrete problem of stabilizing shale benzene, we are immediately confronted by the fact that in the said crude benzene there are hydrocarbons of the diene type present, which condense with maleic anhydride according to the mechanism:



However, we failed to obtain with shale benzene the crystalline derivatives (butadiene, isoprene, piperylene, cyclopentadiene and cyclohexadiene) which S. Birch and W. Scott (Ind. Eng. Chem. 24, 49, 1943) had found when they refined vapor-phase cracking benzene in a corresponding manner. Invariably, whether we had a wide fraction or different narrow fractions, we found semiliquid resins which were either like a kind of rubber or infusible white amorphous compounds, apparently similar to Wagner-Jauregg's heteropolymers which had been obtained by the condensation of maleic anhydride with toluylene, and which are of a structure of about the following type.



The presence of unsaturated hydrocarbons which give additional products with maleic anhydride, was very noticeable. In the 100-110° b.p. fraction, for instance, the percentage of unsaturated hydrocarbons was 30% before the maleic-acid treatment and 20% after it; the unsaturated hydrocarbons were removed with 84% H_2SO_4 under agitating. By the way, the removal of dienes with maleic acid is an I.G. Farbenindustrie patent (Brit. 332 104, May 17, 1930) entered as a method of refining cracking benzene. Since with the development of commercial oxidizing catalysts possibilities for manufacturing inexpensive maleic anhydride have increased, it is without any doubt also of interest to investigate, whether this refining method might not at the same time yield a valuable raw material for the varnish or plastics industry. We shall see in the experimental part of this work that dienes are easy to remove, and when they are simply heated in an autoclave with 1% of $AlCl_3$ (or even Al_2O_3), thick sticky resins are formed, and when the benzene was distilled off from the resins it possessed still a sufficient quantity of resin forming substances.

The processing of the various fractions of shale benzene with maleic anhydride showed that the output of condensation products is approximately proportionate to the gum formation number of the given fraction; this finding is analogous to the general situation which we discussed above (whereby a connection is established

between the presence of dienes and the rate of gum formation) which had been established by the study of petroleum cracking benzene.

Since the complete removal of the sulfur can be obtained only by a very long-lasting hydrogenation, this procedure does not seem to be necessary in this case. Since shale benzene contains little sulfur anyway, we operated with short heating periods and low pressures, which were not too hard on the apparatus and the metal parts. It turned out that also under these circumstances (initial hydrogen pressure 50 atmos.; maximum temp. 330-350°; duration -- 1 hour; catalyst: 5% MoS_3 + CuO) resins and diene hydrocarbons could very easily be converted. At the same time, aromatics were not attacked by the hydrogenation at all, as the experiments showed, and about 50% only of the olefins were hydrogenated on the average.

Cracking and polymerization of the olefins took place only to an insignificant extent. Isomerization processes occurred in a more noticeable way; they are reflected in a small expansion of the boiling ranges of the hydrogenation products.

For this reason, we tried to establish whether under the conditions prevailing in the catalytic pressure hydrogenation, there takes really place an isomerization of the hydrocarbons. We made a comparative analysis of the benzene and of its individual fractions, both before and after the hydrogenation reaction. We employed the methods of determining the mercury and rhodan numbers and of treating the materials with $SbCl_5$.

There is an isomerization reaction, to be sure. It explains the satisfactory stability of the benzene even if it is kept in storage for a long time. Apparently it can be calculated from the standard number. But in order to make a quantitative appraisal (and mainly for the establishment of the conditions where a maximum amount of olefins as well as of paraffins would be isomerized) further experiments are required to be made with the individual types of hydrocarbons and with other compounds contained in shale benzene.

With respect to the practical problems of refining and stabilizing benzene, we may assume that an entirely satisfactory solution has been found for determining the suitable hydrogenation conditions. It stands to reason that the yields (and losses) found with a laboratory apparatus, may be assumed to be quite orientating (the losses due to spreading in the autoclave and evaporation are greater). The data published in the German literature (Rosenthal, Petroleum XXVIII, No. 3, 13, 1932) give the refining losses suffered in commercial-scale operations -- with benzol produced from coal tar -- for the hydrogenation step as less than 1%. When this type of raw products is refined with sulfuric acid, the losses reach up to 25%.

Experimental Part

We used for our studies unrefined shale-tar benzene made in a large-scale plant in Esthonia from Weimar shales (Province Leningrad). The raw product had been kept for more than a year and was full of tarry impurities; it was distilled with a dephlegmator and the fractions with b.p. up to 230° were taken for the experiments. Test-runs for determining the gumming capacity of freshly distilled benzene were made, and then also with the same benzene after it had been left standing. We used the evaporation method.

The second day after distillation, 96 mg of resin was found, after 12 days 273 mg. When the benzene was left standing for a still longer period, the rate of gum formation did not increase in the course of four months. Thereafter, we rectified with a dephlegmator eight liters of benzene (b.p. up to 230°) which had been

three times fractionated into ranges of 10°. The quantitative distribution of the benzene in the various fractions was plotted in fig. 2.

The gum-forming capacity was determined for the 10-degree wide fractions (they had been determined two to three days after they had been prepared by means of fractional distillation). These data were plotted in fig. 3.

As we see, the gum-formation tendencies vary greatly in the various fractions. Fraction 200-210° is distinguished by a maximum of gum-formation (658mg); but by the way, this fraction forms a very small portion of the benzene. It may be deduced from our investigation results that it is suitable to separate the benzene with boiling points up to 190°.

The sulfur content has been determined as being 0.889% (by the lamp method). A control determination according to the Karius method gave 1.12%. Then, we determined the sulfur content of the individual fractions; it is plotted in fig. 4. The rate of sulfur contents is constantly and regularly going up, without fluctuation, like the gum-formation rate. There is not any connection, however, between the various kinds of sulfur compounds found in a given type of benzene and the gum-formation numbers of the individual fractions.

The total content of unsaturated hydrocarbons of various kinds contained in the individual fractions was estimated by determining the iodine numbers of these fractions, as plotted on fig. 5.

When we compare this curve for the iodine numbers of shale benzene with that curve which had been made by Panyutiny and Milobidova (Works of the Scientific Automobile Institute, No. 21, 37, 1931) for the iodine numbers of benzene manufactured by vapor-phase cracking of petroleum (in a Leningrad factory), we shall see that there is a considerably higher content of unsaturated hydrocarbons in shale benzene. In unrefined petroleum-cracking benzene there are iodine numbers varying from 198.7 up to 163.9 for the fractions which boil in the 60 to 150° range.

Moreover, a series of fractions was treated with maleic anhydride, according to the method of Diels and Adler (Ann. 460, 113-116, 1927), which had been applied to butadiene, dehydrobenzene, and felandrene. But even though we varied the reaction conditions, there was not one fraction which yielded crystalline complex compounds — in all cases we received invariably only rubber-like resins, which failed to crystallize from solvents of all kinds (alcohol, chloroform, ligroin, benzene, etc.). It is of interest only to point out that the amount of resins, separated out by a treatment with anhydride, turned out to be to a remarkable extent proportional to the gum-formation number of these fractions: fr. 40-50° — resins 0.5 cc per 10 cc (gum formation number 40 mg); fr. 70-80° — resins 1.5 cc (gum-formation number — 122 mg); fr. 90-100° — resins 4 cc (gum-formation number 310 mg); fr.100-110° — resins 2 cc (gum-formation number 180 mg); fr. 110-120° — resins 2.5 cc (gum formation number 270 mg); fr. 190-200° -- resins 3 cc (gum formation number 435 mg); fr. 200-210° — resins 4 cc (gum formation number 658 mg).

The fact that there is nearly a direct proportion between the amount of resins which have been settled out by the anhydride and the gum formation capacity — is evident for most of the fractions. But the amount of resins which settled out by condensation withmaleic anhydride is approximately the same in the fraction with gum formation of 658 mg as in the fraction with gum formation of 310 mg. Under these conditions it is obviously impossible to deny the possibility of some influence of compounds of other classes among those present in a given benzene upon the rate of gum formation, even though there is no doubt that the gum formation depends chiefly upon diene-type compounds.

The connection of the rate of gum formation with the presence of easily polymerized compounds of the diene type, was also confirmed by tests in which a broad fraction of benzene was heated in an autoclave together with Al_2O_3 and $AlCl_3$ (confer Table 1).

The gum formation is considerably reduced if the benzene is heated to more than 200° under vapor tension pressure. If a particularly active catalyst is used, such as $AlCl_3$, one-hour's heating is sufficient. But when the heating is carried out without hydrogen, one part of the hydrocarbon is condensed to a large extent to higher-boiling products, the output of which reaches 15-30%. Obviously, the polymerization and condensation reactions are not limited to the dienes, but comprise also other compounds, which are present in the benzene in question.

The hydrogenation tests started by hydrogenating olefinic and aromatic hydrocarbons; then they were extended to narrow fractions of benzene, and finally, to a broad fraction of benzene with a boiling point up to 230°. We tried to find out in these experiments the conditions for a short and in particular low-temperature hydrogenation reaction in which the benzene would be sufficiently stabilized without impairing the aromatics and with a minimum of cracking or polymerizing the olefins.

On the assumption that there is a possibility of carrying out a hydrogenation under gentle conditions, it was in such a case also unnecessary to remove entirely the sulfur compounds, which indeed were present only in very small amounts.

The hydrogenation catalyst was a mixture of molybdenum sulfide and copper oxide. The autoclave had a one-liter capacity.

Test No. 1: Amylene—trimethylethylene, obtained by the dehydration of tertiary amyl alcohol — 40 g; catalyst: MoS_3 5% + CuO 5%. Initial hydrogen pressure — 50 atmos.; maximum temperature 330-350°. Duration: one hour. Absorbed: 15 atmos. hydrogen. The hydrogenation product's boiling range was considerably broader than that of the feed stock and distilled over in two fractions: First fraction 30-50° — 50%; Second fraction: 50-80° — 50%. Iodine number: first fraction = 7.44, second fraction = 49.6, that of the starting amylene = 302.1.

Test No. 2: Fifty grams of diisobutylene Butlerov (b.p. 102-104°), made from trimethylcarbinol; catalyst MoS_3 5% + CuO 5%. Initial hydrogen pressure 50 atmos. Absorbed 15 atmos. hydrogen. Duration and temperature the same as above. The entire hydrogenation product distilled over in a boiling range of 97-104°. Iodine number: starting material, diisobutylene = 204.5, hydrogenation product = 49.2.

Test No. 3: Fifty grams of cryoscopic benzol; catalyst MoS_3 5% + CuO 5%. Initial pressure 45 atmos. Temperature and duration of reaction: the same. Absorbed: 2 atmos. hydrogen. The reaction product distilled over at 80-82°. A control nitration according to Eglof showed the benzol to be absolutely unaffected by the hydrogenation.

Test No. 4: One hundred grams of a fraction of shale oil (b.p. 90-100°); catalyst: MoS_3 5% + CuO 5%. Initial hydrogen pressure: 50 atmos. Temperature and duration of heating — the same. Absorbed: 8 atmos. of hydrogen. The hydrogenation product distilled over in two fractions: first fraction, b.p. 75-120°, 72 g, and second fraction 120° and up, 8 g. Iodine number: 1. fraction 97.7; starting material 178.8 gum formation of the 75-120° fraction — 10 mg.

Test No. 5: Seventy five grams of a shale benzene fraction 110-120°; catalyst MoS_3 5% + CuO 5%. Initial hydrogen pressure 50 atmos. Temperature 350°, duration of heating one hour. Output of hydrogenation product, 61 g. The product

distilled over at a range of from 100-130° in an amount of 54 g. Iodine number of this product = 70°, before the hydrogenation = 169. Gum formation after the run 10 mg, after ten days' storage in the light, 20 mg.

The results obtained in hydrogenating a broad fraction with boiling points up to 230° are given in Table 2.

Before the hydrogenation, this broad fraction had an iodine number of 155.3, after the hydrogenation of 77.25.

The sulfur content in this broad fraction was determined by the lamp test, as already mentioned. Due to the hydrogenation it was lowered from 0.91% to 0.64%, or by approximately 30%. The sulfur content of the 90-100° fraction after the hydrogenation was 0.44%, that of the 110-120° fraction — 0.18%.

Table 1

No.	Stock cc	Temp. °C.	Duration hrs.	Yields fra up to 230° per feed stock %	Gum formation benzene after polymer. mg	feed stock mg
Tests with (1%) $AlCl_3$ in the one-liter autoclave						
1	200	100	3	80	118	273
2	200	200	3	73	28	273
3	200	280-300	1	68	43	273
Test with (1%) Al_2O_3 in the one-liter autoclave						
4	200	200	3	85	43	273
5	200	300-320	3	61	27	273

Table 2

Hydrogenation of a benzene fraction b.p. up to 230° at 300-350° in a one-liter autoclave.

No.	Stock g	Catalist	Initial Pressure atmos.	H_2 absorpt. in press. atmos.	Dur. hrs.	Yields after run	Gum Form. after 1-1/2 mths. 10 days in light
1	50	10% CuO + 10% MoS_3	50	10	1		

No.	Stock	Catalyst	Initial Press. atmos.	H_2 abs. in press. atmos.	Dur. Hrs.	Yield prod. g	Yield fr. -230 g	Gum after run	from
1	50	10% CuO + 10% MoO_3	50	10	1	40	—	8	30
2	50	10% CuO + 10% MoS_3	50	10	1	38	34	20	4
3	100	5% CuO + 5% MoO_3	70	15	1	—	—	16	72
4	100	5% CuO + 5% MoS_3	70	22	1	92	83	16	0
5	100	3% CuO + 3% MoO_3	50	10	1	—	—	40	80
6	100	15% CuO	50	10	2	82	71	20	—

In summarizing the hydrogenation results, we may point out that even a most gentle hydrogenation under a small operating pressure at a temperature of 330-350° and at a total duration of heating at this temperature for one hour, with a catalyst 5% MoS_3 and 5% CuO reaches in an entirely satisfactory fashion our objective of stabilizing the benzene with respect to the rate of gum formation. At the same time, we may omit the preliminary refining process of the shale benzene which entails great losses of material. In particular it is important that this type of hydrogenation does not attack the aromatics. This feature is particularly valuable since otherwise, the antiknock value would be considerably lowered. The olefinic hydrocarbons are not entirely hydrogenated, either.(1)

Large-scale tests in the three-liter Bergius autoclave have shown that the hydrogenating action of the hydrogen extends in the first line upon the most undesirable compounds, and in particular upon the dienes and oxygenous compounds (aldehydes, ketones, peroxides) which appear to be natural intermediary steps on the way to gum formation. At the same time, a considerable amount of water was formed in the hydrogenation, and the hydrogenation product did not yield resins when it was treated with maleic anhydride. Finally we tried to confirm the changes in the structure of the olefinic and paraffinic hydrocarbons which resulted from the hydrogenation reaction under pressure. For this purpose, we treated it with mercury acetate, free rhodane and(for the saturated hydrocarbons) with $SbCl_3$, according to Schaarschmidt's method (Petroleum 28, 12, 1-4, 1932) as well in the form of a broad fraction as in narrow fractions and before as well as after the benzene had been hydrogenated.

Just as Panyutiny and Milobidoba had pointed out, the actions of free rhodane and mercury acetate on olefinic hydrocarbons are very antagonistic. Furthermore, hardly one half of the unsaturated hydrocarbons which enter easily into a reaction with mercury acetate, are capable of an addition reaction with rhodane. At the same time, as Tausch's experiments (Chem. Zeit. 102, 1023, 1913; Tausch, Brennstoff-Chem. 10, 337, 1929, etc.) and those of other scientists had shown, normal olefins will selectively enter into a combination with mercury and only a few of the iso-olefins, with comparatively little branched chains. The highly-branched olefins do not enter into complexes but are oxidized.

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(1) It has been found that the octane number of benzene which was stabilized by hydrogenation (boiling end 180°) was 65. According to the data of P. A. Virobantz, the octane number of Grosnen benzene with a boiling end of 177° was 51. Maykovsky found an octane number of 60 for a benzene with boiling end of 153°; benzene from Baku with a boiling end of 180° has an octane number of 70. That means that benzenes made from the better Baku oils, with respect to its antiknock character. Control measurements carried out when the benzene was stored in the dark that it remained stable for about 4 months; when it was stored in the light, the gum formation number would rise from 2 to 1 127 mg. The increase of the gum formation in the light was reduced by adding diethylamine.

The following data were obtained:

	Rhodane No.	Mercury No.	No complexes with $SbCl_3$
1.) For the wide-range fraction.			
Before hydrogenation	141.75 (1)	18	44% (in the individual fractions varies the content of this type of hydrocarbons from 25 to 75%).
After hydrogenation	65.15	14	40%
2.) For the fraction 80-100°			
Before hydro.	—	48	—
After hydrog.	—	40	—
3.) For the fraction 110-120°			
Before hydrog.	—	50	—
After hydrog.	—	47	—

The decrease in the mercury number after hydrogenation indicates obviously a decrease in the proportion of normal olefins. To judge from the rhodane numbers, we may assume that a large part of the iso-olefins is hydrogenated and converted into the corresponding paraffins. At the same time, a practically identical correlation between saturated normal and iso-olefins (while the over-all content of saturated hydrocarbon is approximately doubled as a consequence of the hydrogenation) points to the probability that in the course of the hydrogenation reaction not only a hydrogenation reaction takes place, but also a considerable isomerization of the olefins and paraffins in the direction of originating hydrocarbons with more highly branched chains.

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(1) For narrow fractions within the boiling range 50-150°, vary the rhodane numbers between 166 and 109, going down step by step.

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January 10, 1949

SR-12

0475

Translation Book 224
API-TOM 255
Chemistry of Solid Fuels
Vol. 4, No. 6, p. 573-577 (1933)

Determination of the Hydrocarbon Groups in Shale Benzene

Chelintsev, V.V. and Sibertsev, A.P.

We learned already a long time ago that shale tar contains a large proportion of unsaturated hydrocarbons; indeed, the percentage may be as high as 70% in the light fractions, according to the works of D. K. Petri and D. P. Stewart (Chemistry of Oil Shales). On the basis of the most recent studies dealing with unsaturated compounds, it may be said that this feature shows shale tars to be a valuable raw material, in particular, for the production of unsaturated hydrocarbons which are used for various chemical purposes. However, up to this time, there has not yet been made a detailed study of the unsaturated shale-oil components, as well as of the other types of hydrocarbons which are contained in the shale tar. And yet, a number of methods have been developed for determining the percentages of unsaturated as well as of aromatic components and also of alicyclic and paraffinic hydrocarbons in the various commercial mixtures.

To be sure, the recently developed methods are not yet one hundred per cent foolproof. Therefore, it can not yet be stated in many cases, what is their degree of accuracy. But on the average, they enable us to establish to a near approximation the real figures for the contents of definite groups of hydrocarbons in petroleum as well as in different kinds of tars and pitches. As a consequence of the appraisal of these methods by certain authors (1), there is still much uncertainty and, for instance, it is still difficult to draw quite a definite demarcation line between unsaturated and aromatic hydrocarbons, but the delimination line between these two groups of hydrocarbons, on the one side, and the alicyclic and paraffinic on the other side -- is already sufficiently clearly drawn. It is also possible, thanks to these methods, which are based on differences in solubility, to speak with greater or smaller exactness about the correlations between paraffinic and alicyclic hydrocarbons.

The method of determining hydrocarbons underwent a constant gradual development, and in 1932, for instance, works like those of S. C. Vlugter, H. I. Waderman, H. A. con Vesten (2), A. B. Manning, F. M. Shepherd (3), N. Popa and A. Velculescu (4), E. V. Kester and Pohls (5) and of others were published.

(1) A. F. Dobranskij, Analysis of Petroleum Products, 1932.
(2) Chem. Weekbl. C. 29, 226 (1932)
(3) Dep. Scient. ind. Res. Tud. Res. No 28.
(4) Bull. Chim. pure applic. Bukarest 33, 3 (1931).
(5) Ind. Eng. Ch. Anal. Ed. 3, 294.

We shall abstain from a detailed review of all the pertinent scientific literature. For our objective, the determination of unsaturated and aromatic hydrocarbons, we used the Katvinkel method and for paraffinic and alicyclic hydrocarbons, the aniline-point method.

Condensations of olefins and aromatics may occur. K. Michel's (Czech. Patent 34,979 and Brit. 1,878,963) latest disclosures show that. Of course, there is no over-all vigure given for unsaturated hydrocarbons plus aromatics, but they described these and other hydrocarbons in comparative quantities. We could not apply in our experiments the ideas on which the works of the Standard Oil Development Co. (Fr. 731,556, 1932) are based, namely, the condensation of olefins and alicyclics with phenols, since the products used in our experiments did not contain any phenols.

Experimental Part

We used benzene manufactured from Weimar shale-kukkersite, which was either distilled or treated in a stationary retort, or in a rotating Fischer retort, at a temperature of 450° and for a heating period of four hours. In order to obtain the benzene fraction, the primary tar was at first freed from water and then distilled at a temperature up to 200°; the entire benzene portion was thereafter more finely rectified in a dephlegmator of half a meter length and fractionated into definite fractions, suitably into the commercially used fractions: benzol, toluol, xylene and mesytilene-cymol.

With this method of operation, the following chief fractions were obtained from the crude benzene (Table 1).

Table 1

Fractional distillation of Weimar shale-benzene.

No.	Boiling range °C.	Absolute quantity in g from 612 g	Results %
1	up to 60	10	1.6
2	60-95	81	13.2
3	96-122	115	18.8
4	122-150	121	20.0
5	150-200	179	29.3
6	above 200	106	17.1
	Total	612	100.0

Table 2

Contents of basic and acidic bodies.

No. of fraction	Boiling range °C	Chief benzene fractions	Separated with HCl & NaOH in %
1	Up to 60	—	—
2	60-95	I	7.3
3	95-122	II	4.2
4	122-150	III	2.1
5	150-200	IV	2.1
6	above 200	—	—

The chief fractions 2-5 were thereafter washed with 10% hydrochloric acid, then with 10% alkali hydroxide, in order to remove the pyridinic, basic and acidic components, i.e., phenols and acids.

Then the product is washed with water and dried with calcium chloride or calcined sodium sulfate and carefully collected. The figures obtained differed from prior ones by quite specific magnitudes; they were characterized in general by the presence of higher percentages of basic and acidic bodies in the chief benzene fractions. (Table 2).

For the purpose of determining unsaturated and aromatic components, they were treated with Katvinkel's reagents.

The first reagent, which served for an overall determination of the unsaturated and aromatic hydrocarbons, was prepared by dissolving phosphorous anhydride sulfuric acid (spec. weight 1.84), at a ratio of 30 g of phosphorous anhydride to 100 cc of sulfuric acid. The second reagent, which served only for absorbing the unsaturated bodies, was made by dissolving sulfuric acid (spec. weight 1.84), (5 g of boric acid per 100 cc of sulfuric acid).

The absorption of unsaturated and aromatic compounds was carried out in sulfonation units, at a 1:3 ratio of the benzene fractions to the reagents. They were shaken for five minutes and carefully cooled, in order to avoid a raise in temperature.

The final figures regarding unsaturated compounds in the fractions, comprises both the quantities present in the sulfuric-acid layer and the quantities contained in the benzene-fraction liquor in the form of condensation products. These figures have been determined not only for the solid fractions but also for their solutions in petroleum benzene, which had been specially prepared for this purpose by means of treating aviation benzene repeatedly (boiling range 75-95°) with sulfuric acid (spec. weight 1.84). The shale-benzene fractions were diluted with this benzene in a 1:1 ratio, but the figures obtained in these tests differ only to a very slight extent from those, obtained without dilution, on the whole, only by 0.4-0.8%.

The total amount of unsaturated and aromatic compounds, which has been determined in experiments referring to four benzene fractions (Table 3) can be expressed in the following figures.

TABLE 3

Total quantity of unsaturated and aromatic hydrocarbons.

Chief fractions °C	Absorb. in 4 $H_2SO_4 + P_2O_5$	Separated in distill. %	Total amount of unsaturated & aromatic
I. 60-95	45	39	84
II. 95-122	38	27	65
III. 122-150	34	40	74
IV. 150-200	56	18	74

In the sulfuric-acid layer there separate out the esters, formed by the reaction of unsaturated hydrocarbons with this acid, i.e., the sulfonic-acid alkyl esters; in the benzene layer are the compounds formed by the autocondensation of unsaturated hydrocarbons and by the combination of the unsaturated hydrocarbons with aromatics. The first group has been determined by augmenting the sulfuric-acid layer; the second, by distilling the fractions after treating them with the Katvinkel reagent. Before processing, boiling ranges of the individual fractions were accurately determined. The entire residue, of higher boiling range than these fractions, was obtained by a final distillation after the experiment, and combined with the condensation products. The quantity of these products varies in quite a unique manner according to the fractions, as the Table indicates, and that means probably a difference in the character of the hydrocarbons which are present in the different fractions.

Table 4 gives the results of the treatment with the other Katvinkel reagent, i.e., sulfuric acid and boric acid.

Table 4

The quantity of unsaturated hydrocarbons.

Main fractions °C	Absorb. in % H_2SO_4 + $B(OH)_3$	Separated in % in distillation	Amount of unsatur. %
I. 60-95	45	36	81
II. 95-122	33	—	—
III. 122-150	—	34	—
IV. 150-200	56	13	69

Due to some accidents which occurred in the course of the experiments, some figures could not be determined; this fact makes it impossible for us to give the final figures for two fractions (II & III). But in certain prior experiments, we had found that these fractions contained the following amounts of aromatics: II-6.7, II-6.4. By deducting these amounts, referring to aromatics, from the sum total obtained for the two types of hydrocarbons together, which had been determined for fractions I and IV from the above given data, we obtained finally the following values for unsaturated and aromatic hydrocarbons (Table 5) which verify the figures given in Tables 3 and 4.

Table 5

Amounts of unsaturated and aromatic hydrocarbons.

Chief fraction	Sum total of amounts of unsatur. and arom. %	Amount of unsatur. %	Amount of arom. %
I. 60-95	84	81.0	3.6
II. 95-122	65	58.3	6.7
III. 122-150	74	67.6	6.4
IV. 150-200	74	69.0	5.0

If we compare the values obtained for aromatic hydrocarbons with those for definite types of hydrocarbons -- benzol, toluol, xylene, and mesytilene-cymol-- the values obtained from the data given by the method applied, indicates the proportion of these hydrocarbons in the benzene fractions of Weimar tars (Table 6).

The percentages of paraffinic and alicyclic hydrocarbons have been moreover determined by means of the aniline point method for separate cuts of the benzene fractions.

In order to determine the benzene fractions in this fashion , a treatment with 98% sulfuric acid was first applied, whereby the benzene was vigorously shaken, each time for a period of 15 minutes. The first time the benzene and the acid were used at a 1:2 ratio, and the second and third time at a 1:1 ratio. Altogether, each fraction was treated three times. The temperature was not permitted to exceed 40°. Each fraction, after being treated in this fashion, was washed with water, dried with calcium chloride and distilled exactly in the corresponding temperature ranges, removing all the polymerized and condensed substances.

Table 6

Amount of the aromatics only

Main fractions	Amount of fractions in commercial benzene %	Predominant hydrocarbon type	Amount of aromatic hydrocarbon %
I. 60-95	13.2	benzol	3.0
II. 95-122	18.8	toluol	6.7
III. 122-150	20.0	xylene	6.4
IV. 150-200	29.3	$C_9 - C_{10}$	5.0

Through determining the aniline points for the individual benzene fractions studied, we found the comparative amounts of alicyclic compounds, and from them (through deducting the above mentioned amounts of unsaturated and aromatic hydrocarbons) the paraffin percentage was calculated.

The aniline points were determined by the universally accepted method and the figures of the groups of hydrocarbons mentioned were calculated from them according to the tables.

The results of these determinations are given in Table 7.

Table 7

Amounts of alicyclic and paraffinic hydrocarbons.

Main fractions	Aniline points	Amount of alicyclics %	Amount of paraffinics %
I. 65-95	63.0	3.8	12.2
II. 95-122	62.0	7.5	27.5
III. 122-150	63.2	8.6	17.4
IV. 150-200	68.8	8.2	17.8

On the basis of the figures obtained for the corresponding hydrocarbons we can draw the conclusion that from the paraffinic series hexane C_6H_{14} corresponding to the fraction I, is not to be found in large quantities in the shale benzene, that heptane, corresponding to fraction II, is present in a 2-1/2 times greater quantity, that octane, corresponding to fraction III, and, decane and undecane (corresponding to fraction IV) are present in a quantity only 1-1/2 times larger than hexane.

Thus by applying the aniline point method to shale benzene, we are obtaining some data, the meaning of which can only be determined after comparing them with those data which had been obtained by other methods. However, it is obvious that when the methods in question are adjusted especially for shale benzene, we shall always have in them convenient and sufficiently rapid methods for the performance of our tasks.

Summary

By using the Katvinkel and aniline-point method for shale benzene, the following results were obtained for the individual fractions of these benzenes made from Weimar shales, and broken down to definite boiling ranges (I — 60-95°, II — 95-122°, III — 122-150°, IV — 150-200°).

Table 8

Amounts of individual hydrocarbonsgroups in individual benzene fractions

No.	Paraffins	Olefins	Arylenes	Alicyclic
I.	12.2	81.0	3.0	3.8
II.	27.5	58.3	6.7	7.5
III.	17.4	67.6	6.4	8.6
IV.	17.8	69.0	5.0	8.2

For other shales however, we do not yet have such a complete picture of the contents of the individual groups of hydrocarbons in the individual benzene fractions and for this reason, we can not compare these data with the data for benzenes of different provenience, and not in a summary way, either with benzenes from Schtch shales for instance; in general, however, comparisons will be admissible in special cases.

For Scotch shales, we have data for groups of hydrocarbons but they are only applicable for fractions which boil at about 110°. When we compare these data with the data obtained for fraction II of Weimar benzene, which boils in a range of 95-122°, then we obtain the following picture (Table 9).

Table 9

Benzene fractions of shale benzene

Paraffins %	Olefins %	Arylenes %	Alicyclics %
	From Weimar benzene (95-122°)		
27.5	58.3	6.7	7.5
	From Scotch shale (110°)		
42.0	40.7	7.3	10.0

This table shows that the values obtained for cyclic hydrocarbons in both benzenes are sufficiently close to one another; this observation is also true for aromatic and alicyclic hydrocarbons, with a slight prevalence of alicyclics in Scotch benzene. With respect to paraffins and olefins, however, (and to the latter, dienes are probably admixed, too,) Weimar benzene has a much higher content of unsaturated hydrocarbons than of paraffins. For Scotch benzene we do not yet have exact figures, but we know that the tar contains 60-70% of unsaturated hydrocarbons.

The data obtained are conformant with our general ideas concerning shales. And while Scotch shales are paraffin-base oils and yield up to 9.1% of solid paraffins, our shales, like the Volga shales and Obshshe-Sirto shale tars, give hardly any solid paraffins and in general much less paraffins.

Finally we may start from our findings, saying that fraction I in the benzene which we studied, had been 13.2%, fraction II 18.8%, fraction III 20.0%, fraction IV 29.3%, and compute the total contents of the individual groups of hydrocarbons with the boiling points 60-200°.

This computation gives the following results (Table 10).—

Table 10

The total amount of the various types of hydrocarbons in Weimar benzene (60-200°)

Paraffin	Olefin	Arylene	Alicyclics
18.8	67.8	5.4	8.0

These are the results obtained with the Katvinkel and aniline point methods. They indicate that shale benzenes are a very rich material, insofar as they contain a large amount of unsaturated hydrocarbons. Therefore, these benzenes may be used for various chemical purposes, in particular for making medium to high-molecular alcohols and low- or medium-molecular aldehydes, ketones and acids which play now such a great role in commercial production. For instance they may be used for softeners, plasticizers, solvents, in the lacquer, tanning, resin, film industry and in making various new artificial materials.

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Translation Book 226
Chemistry of Solid Fuels
p. 598-605, Vol. IV, No. 6 (1933)
API-COM Reel 255

0482

January 3, 1948

SR-13

Destructive Hydrogenation of Kashpir Tar

S. S. Nametkin, F. I. Sanin and E. F. Rudakoba

In a previous publication (Chem. of Solid Fuels, 4, 332, 1933) we discussed the results obtained in a detailed study of the mechanism of the destructive hydrogenation of Kashpir tar, on the laboratory scale. We had found in particular that the use of 8% of molybdenum bisulfide as a catalyst makes it possible to obtain in a one-step hydrogenation 70.4% (by volume) of benzine (up to 225°), practically completely devoid of sulfur (the benzine contained only 0.02% of sulfur), even though an enormous percentage (9.1% of sulfur) had been present in the starting material. The yields of benzine can still be increased by rehydrogenating the stock. Moreover, we found that the use of molybdenum bisulfide permits us also to apply an operative pressure of 100-120 atmos. (50 atmos. initial pressure).

Since our results with the distillation of Kashpir tar under laboratory conditions, were satisfactory regarding the rate of output as well as regarding the properties of the product, we decided to make analogous tests with commercial stocks made in the shale-distillation plant, without subjecting them to any pretreatment.

In carrying out this investigation, two problems were kept in mind:

(1) To ascertain the comparative suitableness of various commercial products (crude tar, light and heavy oil) as hydrogenation feed stock, and

(2) to find out whether the operating (less than 100 atmos.) and initial (less than 50 atmos.) pressures can still be lowered[1].

Apparatus and Operating Method

The hydrogenation tests were carried out in a horizontal rotating autoclave, of 5-liter capacity, which had already been described in a prior article. The method was the same, too, excepting that the analysis was carried out after hydrogenating the oil, which was not fractionated according to Engler, but in a metal round-bottomed flask with a three-bulb glass dephlegmator, whereby we withdrew fractions up to 200° and from 200° to 300°. In all experiments 8% of molybdenum bisulfide were added to the hydrogenation stock.

Comparative Hydrogenation of Kashpir Tar and Light and Heavy Oil

The following commercial products were used as feed stocks for the hydrogenation: crude tar, distilled from Kashpir shale in the Ostashkov plant, and oils which had been manufactured in the Kashpir plant by means of rectifying the tar into two fractions (so-called "light" and "heavy" oils) and a pitchlike

(1) This latter question is of special interest, because there are contradictory data in the scientific literature concerning the possibility of processing foreign shale tar with an initial pressure of 30 atmos. H. G. Shattwell, The Hydrogenation and Desulfurization of Norfolk Shale Oil (J. Inst. Petr. Techn. 11, 550, 1926) and P. N. Kogerman, Desulfurization of Estonian Shale Oil (J. Inst. Fuel, 5, No. 22, 1932).

residue. The chief characteristics of these oils are given in Table 1.

The iodine numbers of the stock have been determined according to Margosches, , and the sulfur content, by burning a weighed portion in a bomb. The distillation was also carried out from a metal round-bottomed flask, like that with a three-bulb glass dephlegmator which had been used for the hydrogenation products . We tested for carboids by diluting the product with benzol and found that there were not any carboids in any of the materials. Previous to the hydrogenation, the feedstock was only subjected to a dehydration by settling and dried with calcinated sodium sulfate dehydrate. We have not carried out any other operations.

Table I.

Properties of the feed stock

Starting material	15 15°	Iodine number	Sulfur content %	Distillation with 3-bulb dephlegmator (weight %) —200°	200-300°	Residue & losses
Crude tar	0.9935	80.65	6.79	12.1	31.5	56.4
Light oil	0.9253	86.63	8.93	61.3	15.0	23.7
Heavy oil	0.9752	81.91	7.13	0.0	59.0	41.0

The first series of experiments which had the objective of elucidating the effect of the starting material upon the nature of the products, was carried out at 425°, 120 minutes, and under an initial hydrogen pressure of 70 atmos., since our previous experiments on the destructive hydrogenation of Kashpir tar had shown that under these conditions the hydrogenation process was sufficiently deep for our purposes. Table 2 gives the data for these experiments.

On comparing experiments Nos. 42, 43, and 44 (confer Table 2), the following phenomena attract our particular attention: the large rate of water output obtained in hydrogenating crude tar, which may probably be explained by the presence of a large amount of hydrogen-containing tar-asphalt bodies in the crude tar; and the large losses (17.8%) sustained in the hydrogenation of light oil. The latter phenomenon appears to be not only a result of a further decomposition of the low-boiling substances which are already present in the light oil, to a gaseous form, but also to the volatility of a large quantity of still lower boiling substances which are formed in this process along with the gas, when the latter is discharged from the autoclave.

This explanation is confirmed also by the lower initial boiling point and the prevalence of lighter fractions in the composition of the benzine, formed by the hydrogenation of light oil, in comparison to the composition of the benzine made by hydrogenating crude tar or heavy oil (Table 4).

In both cases, the specific weights of the liquid products undergo a considerable reduction. The sulfur content in the hydrogenation benzines goes down to 0.17-1.32% (in comparison to a sulfur content of 9.55% in the first-distillation benzine).

In the given case, the examination of the fraction-wise composition of the liquid hydrogenation products in comparison with the fraction-wise composition of the feed-stock is of greatest interest (confer Table 1 and 2). The greatest increase in the proportion of the fractions which boil below 200° was observed when heavy oil was hydrogenated. When light oil is hydrogenated the proportion of benzine fractions in the liquid products, increases 14.2% by weight; with crude tar, the increase is 25.1%; and when heavy oil is hydrogenated, the increase in newly formed benzine fractions ascends to 39.1%. When the second hydrogenation is carried out in a different fashion, more benzene may be obtained, at the expense of the decomposition of the kerosene fractions, which constituted 48.9% of the product in Exp. 42 (feed stock --heavy oil) as well as at the expense of the hydrogenation residue after the distillation of benzine and kerosene. The specific weight of the residue is 0.9372 in Exp. 42, i.e.; the residue is an entirely suitable starting material for rehydrogenation.

Under the point of view of obtaining a maximum output of benzine by a one-step hydrogenation, heavy oil turns out to be the most suitable raw material of the three types examined. The lower fractions of Kashpir shale oil may be used for making thiophene oil, which -- or rather the thiophene it contains -- is the active basis of some thereapeutic preparations, such as ichthyol, and albichthyol (1), or they may be used as motor fuels(2), after being desulfurized. The pitchlike residue which is left after distilling heavy oil made from Kashpir tar, may be used as material for highway-bitumen (3).

By lowering the hydrogenation temperature of crude tar from 425 to 410° (Table 2) the output of liquid products (oils) is increased from 80.6 to 85.1% but the quality of the oil produced under these conditions is slightly inferior. Its specific weight goes down from 0.8493 to 0.8842 and the proportion of the benzine fractions goes down from 37.2% to 21.8% by weight. This benzine has a sulfur content of 1.03%.

The following experiments have been carried out with heavy Kashpir-tar oil.

The Hydrogenation of Heavy Kashpir-Tar-Oil

The hydrogenation of heavy Kashpir-tar oil was carried out with an initial hydrogen pressure of 75 and 30 atmos. Table 3 gives the test data.

Exps. No. 42, 49, and 50 (Table 3) were carried out with an initial pressure of 75 atmos. varying the residence periods. It was found that under the given test conditions (apparatus, speed of rotation, amount of feed stock, agitation, etc.), at a temperature of 425°, the desulfurization of heavy oil was practically completed in 60 minutes (the sulfur content dropped to 0.16% -- confer Exp. 50) whereas the benzination process requires a longer period of time (or a comparatively higher operating temperature). For instance, by extending the hydrogenation period from 60 to 120 minutes, the benzine output from the liquid hydrogenation product goes up from 21.1 to 39.1%, while the sulfur content of the benzene remains unaltered (0.16% and 0.17%) within the limits of analytical error.

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(1) A.M.Berkengeim, H.G.Yartseva, E.F.Polumina and E.I.Chykhna, "Albichthyol, a new ichthyol-like preparation", Oil Shales, 3, 22, 1933.

(2) Confer also S.S.Nametkin, P.I.Sanin, S.V.Makover and A.H.Tsiba, The Catalytic Desulfurization of Kashpir Benzene in a hydrogen atmosphere," Oil Shales, 3, 32, 1933, No. 1; H.A.Orlov and A.S.Brown, "Catalytic decomposition of thiophene in the presence of hydrogen," Chem. of Solid Fuels, 3, No. 11-12, 817, 1932.

(3) M.Paingar, A.Tishina, L.Efremova, L.Urusov, "The Preparation of Bitumen from Shale Tar." Fuel Shales, 2, No. 1, 35, 1932.

By comparing tests No. 42 and No. 45, which were carried out under the same conditions regarding temperature (425°) and residence (120 min) but with an initial hydrogen pressure of 32 atmos. (58-72 atmos. of operating pressure) we elucidated to a certain extent the effect of the rate of pressure upon the hydrogenation mechanism of heavy oil. The lowering of the initial hydrogen pressure from 75 to 32 atmos. has next to no influence upon the output of oil, but a very considerable one upon its qualities. The specific weight of the oil goes up from 0.8269 (Exp. 42) to 0.8708 (Exp. 45). The amount of benzine obtained by distilling the oil drops from 39.1 to 29.6%. At the same time, there is an increase in the sulfur content of the benzine from 0.17 to 0.57%.

Since on the basis of the results of Exp. 45 it can be difinitely said that the final hydrogen pressure was extremely low (13 atmos.) and that the reaction proceeded consequently under comparatively considerably varying conditions regarding the intensity of the hydrogen pressure, the usual method was altered in the following test insofar as the final pressure was not allowed to drop below 20-25 atmos. We achieved this result by discontinuing the heating when one half of the period required for the hydrogenation reaction had passed; then the autoclave was cooled, the gases were discharged from it; then it was refilled with hydrogen up to the rate of the initial pressure, and the test run was continued until the full period of time required for a normal hydrogenation process had been completed.

When Exp. 45 was repeated with this altered method, i.e. by withdrawing the gas and adding hydrogen, but without discharging the product in the midst of the run (Exp. 46) the following results were obtained: the specific weight of the hydrogenation oil dropped to 0.8555; the output of benzine rose to 33.2%, and the sulfur content dropped to 0.16% -- in contradiction to the corresponding values of 0.8708, 29.6%, and 0.57% obtained in Exp. 45.

The Exps. 51 and 52 were also carried out by charging hydrogen after the first half of the test run. In Exp. 51 the product was discharged from the autoclave after withdrawing the gas, weighed, the amount of water in it determined, and after removing the water, it was recharged to the autoclave and the hydrogenation was continued. Exp. 52 was carried out at a lower temperature (400°). The operating pressures in both of these tests did not exceed 83 atmos.

Along with exp. 46, these tests show that when heavy oil is hydrogenated with 8% of molybdenum bisulfide, even an initial hydrogen pressure of 30 atmos. (operating pressure -- about 80 atmos.) is sufficient for achieving a practically complete desulfurization (up to 0.11% S in the benzene) as well as considerable yields (up to 27% by weight, calculated on the basis of the feed stock) of benzine in a one-step hydrogenation. In Exp. 51, the specific weight of the residue left after distilling off the benzine and kerosene fractions of the hydrogenation product, is 0.9548; thus, the benzine output can be increased by a second distillation not only at the expense of the kerosene fraction but also at the expense of the hydrogenation residue. In none of the tests, we found any carboids.

Hydrogenation Benzines.

The distillation of benzene fractions by the Engler method is represented in Table 4. Among the light fractions prevails benzene. When light oil is hydrogenated, 14% of the fraction up to 80% consist of benzene, 29% of the fraction up to 100° and 63% of the fraction up to 140°. The benzenes from a heavy oil hydrogenated at an initial hydrogen pressure of 75 atmos. and 30 atmos. do not show any difference from one another. They average 12% (from 7 to 18%) in the fractions up to 100° and 42% (34-50)% of the fractions up to 140°.

The chemical compositions of the benzines manufactured in the five most characteristic hydrogenation tests were studied. In another context, we have

described our method of determining the various hydrocarbon classes. Table 5 shows the chemical composition of the benzine fractions.

After conversion we obtain an overall picture of the chemical composition of the benzines (Table 6) up to 200°.

From Table 6 we can see that the maximum amount of aromatic hydrocarbons (20.1%) is found in benzines manufactured by hydrogenating heavy oil and that it varies considerably depending upon the hydrogenation conditions. For instance, when the hydrogenation period is extended from 120 min. (Exp. 42) to 240 min. (Exp. 49) the content of aromatics in the benzine drops from 20.1 to 13.7%, while a lowering of the temperature to 400° and that of the initial hydrogen pressure to 30 atmos., at the same length of the hydrogenation run (240 min) increases the aromatics contents in the benzine to 19.3% (Exp. 52), just as in Exp. 49. But these figures must only be regarded as a general orientation, since the benzine-analysis method had been worked out for petroleum benzines, and its applicability to shale benzine has not yet been verified.

The proportion of unsaturated hydrocarbons in both benzine specimens is very small; its maximum rate in a benzine from the hydrogenation of light oil is e.8%.

Summary

(1) Kashpir tar and commercial products manufactured from Kashpir tar (light and heavy oil) were hydrogenated. Molybdenum bisulfide at a ratio of 8% of the feed stock served as the catalyst.

(2) The greatest amount of benzine fractions has been obtained by hydrogenating heavy oil, and in particular, the proportion of the fractions up to 200° in the hydrogenation product goes up to 39.1%, as against 0.0% in the heavy oil stock.

(3) In a one-step hydrogenation of the heavy oil at an initial hydrogen pressure of 30 atmos. and an approximate operating pressure of 80 atmos., a product was obtained which contained 28.2 % by weight of benzine (up to 200°), with a sulfur content of 0.11%.

(4) More benzine can be obtained, by applying a somewhat altered method in the re-hydrogenation of the kerosene fractions as well as of the residue, which is obtained after benzine and kerosene have been distilled over.

(5) The hydrogenation kerosenes are distinguished by a low sulfur content, averaging 0.2 - 0.3%.

(6) The chemical composition of the hydrogenation benzines is distinguished by a considerable content of aromatics (in the fractions up to 200° up to 20.1%) and a minute proportion of unsaturated compounds, which varied in different specimens of unsaturated compounds, which varied in different specimens from zero to 3.8%.

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TABLE 2

Hydrogenation of Kashpir Crude Tar and Heavy and Light Oils Manufactured from Kashpir Tar

No.	Starting Material	Charge g	Temp. °C	Duration min.	Pressure in atmos. Initial	Maximum at oper. temp.	Minimum at oper. temp.	Final	Yield of Hydrog. Products (% per stock) Water	Oil	Gas & Losses	Character of oil obtained by hydrogenation: Distillation in % by weight up to 200°	200-300°	residue & losses	d 15° 15°	S-Content of benzine	S-Content of kerosene
43	Light Oil	400	425	120	70	175	143	39	2.0	80.2	17.8	75.5	16.8	7.7	0.7805	0.19	0.17
42	Heavy Oil	400	425	120	75	180	150	47	1.6	84.5	13.8	39.1	48.9	12.6	0.8269	0.17	0.19
44	Crude Tar	400	425	120	65	147	116	30	4.7	80.6	14.7	37.2	36.5	26.3	0.8493	0.32	0.37
47	Crude Tar	400	410	120	73	162	132	45	4.0	85.1	10.9	21.8	34.1	34.1	0.8842	1.03	-

TABLE 3

Hydrogenation of Heavy Kashpir-Tar Oil

No.	Charge g	Temp. °C.	Duration min.	Pressure in atmos. Initial	Maximum at oper. temp.	Minimum at oper. temp.	Final	Yield of Hydrog. Products (% per stock) Water	Oil	Gas & Losses	Character of oil obtained by hydrogenation: Distillation in % by weight up to 200°	200-300°	residue & losses	15° d 15°	S-Content of benzine	S-Content of kerosene
42	400	425	120	75	180	150	47	1.8	84.5	13.9	39.1	48.3	12.6	0.8269	0.17	0.19
49	400	425	240	75	167	127	40	3.0	84.7	12.3	36.8	52.2	11.0	0.8311	0.16	-
50	400	425	60	73	166	140	44	2.5	83.8	13.7	21.1	56.5	22.4	0.8519	0.16	0.32
45	400	425	120	32	72	58	13	2.8	83.9	13.3	29.6	50.2	20.2	0.8708	0.57	-
46 I	300	425	60	32	71	64	-	-	-	-	-	-	-	-	-	-
46 II	-	425	80	32	101	98	29	0.7	81.6	17.7	33.2	47.9	18.9	0.8555	0.16	0.33
51 I	400	425	120	30	67	52	13	2.5	85.0	12.5	-	-	-	-	-	-
51 II	350	425	120	30	83	80	23	0.0	97.6	2.4	28.2	49.3	22.5	0.8559	0.11	0.27
52 I	040	400	120	30	69	49	-	-	-	-	-	-	-	-	-	-
52 II	-	400	120	30	82	78	24	1.2	88.8	10.0	18.8	49.8	31.4	0.8763	0.26	-

TABLE 4 (?)80

Englor-Distillation of Hydrogenation Benzines

No.	Hydrogenation Stock	Hydrogenation Conditions: Temperature °C.	Initial Pressure atmos.	Duration min.	15° d 15° benzine	Initial boiling point °C	Distilled over in % up to: 60°	80°	100°	120°	140°	160°	180°	200°	Evaporated: °C	cc	Residue	Losses
42	Heavy Oil	425	75	120	0.7746	50	3	9	18	29	46	65	81	91	227	97	2	1
43	Light Oil	425	70	120	0.7493	34	4	14	29	46	69	86	94	97	200	97	2	1
44	Crude Tar	425	65	120	0.7573	36	3	10	19	36	54	71	87	95	220	98	1	1
45	Heavy Oil	425	32	120	0.7579	42	2	7	18	32	50	67	81	89	220	96	2	2
46	Heavy Oil	425	32	120	0.7665	59	-	2	11	25	45	60	77	89	225	98	1	1
47	Crude Tar	425	73	120	0.7564	50	-	3	11	26	45	66	80	92	235	99	-	1
49	Heavy Oil	425	75	240	0.7750	50	1	5	13	26	44	62	80	91	235	98	1	1
50	Heavy Oil	425	73	60	0.7670	61	-	1	7	21	37	60	81	93	227	98	1	1
51	Heavy Oil	425	30	240	0.7745	51	-	3	10	22	39	59	79	90	235	98	1	1
52	Heavy Oil	400	30	240	0.7678	63	-	1	8	16	34	56	76	88	225	98	1	1

TABLE 5

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Chamical Composition of the Benzine Fractions

NO.	Hydrogenation Stock	Hydrogenation Conditions			Boiling range of fractions	Proportion of total distillate up to 200° C % by weight	Contents of the various hydrocarbons % by weight			
		Temperature °C	Initial pressure atmos.	Duration min.			Aromatics	Unsaturated	Naphthenics	Paraffinics
42	Heavy Oil	425	75	120	up to 60°	2.7	-	1.8	-	98.2
					60 - 95	12.2	11.1	1.9	25.6	61.4
					95 -122	17.1	10.4	2.6	36.8	50.2
					122-150	27.9	20.8	2.9	37.6	38.7
					150-200	40.1	27.6	3.4	57.6	11.0
43	Light Oil	425	70	120	up to 60°	3.3	-	3.8	-	96.2
					60 - 95	19.8	5.2	3.8	16.7	74.8
					95 -122	25.6	9.7	3.8	38.4	48.1
					122-150	31.6	21.0	3.8	44.3	30.9
					150-200	19.7	26.8	3.8	69.1	0.3
44	Crude Tar	425-	65	120	up to 60°	2.9	-	2.3	-	97.7
					60 - 95	11.8	4.6	2.3	26.8	66.3
					95 -122	21.2	11.1	2.3	29.2	57.4
					122-150	29.4	9.5	2.3	66.9	21.3
					150-200	34.8	26.4	2.3	57.8	13.5
49	Heavy Oil	425	75	240	up to 60°	0.4	-	0.0	-	100.0
					60 - 95	11.9	6.5	0.0	30.6	62.9
					95 -122	16.6	7.8	0.0	45.8	46.4
					122-150	28.5	10.8	0.0	73.7	15.5
					150-200	42.6	20.1	0.0	61.9	18.0
52	Heavy Oil	425	30	240	up to 60°	0.0	-	-	-	-
					60 - 95	4.7	6.1	2.0	22.8	70.5
					95 -122	18.0	7.4	2.0	25.2	65.4
					122-150	27.6	17.4	2.0	31.0	49.6
					150-200	49.7	25.9	2.0	50.5	21.6

TABLE 6

Chemical Composition of Hydrogenation Benzine

No.	Hydrogenation Stock	Hydrogenation Conditions			Proportion of Various Classes in % by Weight			
		Temperature °C	Initial Pressure atmos.	Duration min.	Aromatics	Unsaturated	Naphthenics	Paraffinics
42	Heavy Oil	425	75	120	20.1	219	43.1	33.9
43	Light Oil	425	70	120	15.4	3.8	40.8	40.0
44	Crude Tar	425	65	120	14.8	2.3	49.1	33.8
49	Heavy Oil	425	75	240	13.7	0.0	58.6	27.7
52	Heavy Oil	400	30	240	19.3	2.0	39.2	39.5

SINCLAIR REFINING COMPANY

RESEARCH & DEVELOPMENT DEPT.

January 27, 1949

SR-14

Translation Book No. 228
Chem. of Solid Fuels
Vol. 5 No. 3 p. 267-273 (1934)
API-TOM Reel 85255

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Catalytic desulfurization of Kashpir tar shale benzines in the presence of hydrogen under atmospheric pressure.

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Since shale tars and benzines are preeminently used as fuels, the removal of sulfur compounds from them is very important. Consequently, many scientists tried to find rational and profitable methods for the desulfurization of shale tars and benzines.

The publications on the desulfurization of the tars by means of chemical reactants and absorbents, show that this problem would be very hard to solve in this fashion. For, shale tars and similar tars contain, along with a great proportion of unsaturated hydrocarbons (40-50%), rather stable compounds such as thiophene and its derivatives, in quite important quantities. In view of the fact that a great many inconveniences are connected with the removal of sulfur by the usual methods, many studies have been devoted to the task of desulfurizing shale by catalytic hydrogenation under atmospheric or elevated pressures.

Among these works we must mention in particular the following ones: Nesse (C.I. 9, 1046 (1931), Terrisse and Dufour (Confer: Symposion on "Oil Shales and their Commercial Use." p. 421, 1932), Tallcheyeva and Seledzhiyeva (ibid. p. 449), Nametkina, Sanina, Makover and Tsiba (J. of Chem. Ind. 6, No. 3, 494, 1933). These authors treated tars and their fractions with hydrogen under pressure in the presence of various catalysts, reducing the sulfur content to the norm of the required standard.

It is particularly important to single out the work of Orlov, Likhacheva and Tishshenko (Chem. of Solid Fuels 3, No. 7-8, 443, 1932), where it was demonstrated that a very complete desulfurization can be accomplished under gentle hydrogenation conditions even if the shale distillates treated are extremely rich in sulfur by using low pressures, of the magnitude of 20-40 atmos., with a molybdenum catalyst, at temperatures of 340-360°.

But even though these investigations had given positive results, commercial production ran into many difficulties in the last years; they were connected with the use of high-pressure equipment in large scale production. For this reason, we tried in this investigation to work out a method of desulfurizing Kashpir shale tar with hydrogen under atmospheric pressure. We started from the premises expounded in a prior publication of Orlov and Broun (Chem. of Solid Fuels, 3, 11-12, 817 (1932), on the catalytic desulfurization of thiophene in the presence of hydrogen under atmospheric pressure.

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Experimental Part

The entire study has been carried out with a benzine fraction up to 200°, which constituted 5.8% of the Kashpir-tar stock.

The distillation of this benzine fraction up to 200° gave the following results:

Boiling beginning 123°	d_{20}^{20}	= 0.897
123-160°		36.35 %
160-180°		25.45 %
180-200°		15.45 %
Residue		14.54 %
Losses		8.21 %
Total		100.00 %

A composite catalyst was used. It consisted preminently of nickel oxide and contained traces of cobalt oxide, aluminum and magnesium. This contact was prepared by precipitating the metal oxides from their corresponding nitrates upon pea-sized pumice lumps. The catalyst, after being charged into the reactor was subjected to a preliminary reduction with hydrogen at the reaction temperature for the length of one hour; thus, it became pyrophoric catalyst.

Into a glass tube -- (the reactor was 50 cm long and equipped with a heating jacket; its diameter was 2 cm; 65 g of contact charged or 8.8g of NiO; 1 g of Al_2O_3; 0.2 g of MgO and 0.8 g CoO) shale benzine and hydrogen were simultaneously fed. The tube was heated by an electric furnace; the temperature inside the tube was measured with a thermocouple. The velocity of the hydrogen stream was registered by means of a rheometer. The reaction products were discharged through a cooling coil into a receiver, which was equipped with a long bulb cooler. An auxiliary oil scrubber had been placed behind the cooler, but turned out to be unnecessary, since all of the liquid products were condensed and separated out in the cooler.

The total amount of sulfur contained in the liquid reaction products was determined by the lamp method. The pyrogenizates obtained in several tests were distilled. Furthermore, the proportion of unsaturated hydrocarbons contained in them was determined as well as the forms of sulfur and their specific weights.

Each run lasted from 1-1/2 to 2 hours. 25 g of benzine were passed through the tube. The hydrogen was passed at a velocity of 8, 12 and 24 liter per hour. The reaction temperature varied between 300 and 400°. We used one and the same catalyst usually for three tests, so that the catalyst would altogether be in service for 4-1/2 and 6 hours. The determination of the sulfur in each specimen, obtained after a six-hour or two-hour test, enabled us to evaluate the desulfurization mechanism and the changes of catalytic activity in the course of time.

By comparing the results of tests 1, 2, 3 and 7, 8, 9 (Table 1) we see that by raising the temperature from 300° to 400° a more vigorous desulfurization effect is achieved. A higher hydrogen flow-rate is said to have also a positive effect on the removal of the sulfur -- that is true for a reaction

temperature of 300° (Exps. 1, 2, 3, 4, 5 and 6). But we can not speak of a positive effect of this factor at a temperature of 400°, regardless of the duration of each test (Test 7, 8, 9 and 13, 14, 15; 10, 11, 12 and 16, 17, 18). It is correct that the activity of the catalyst suffers less when less benzine ispassed over the catalyst, while the flow-rate of the hydrogen is increased at the same time (Exps. 10, 11, 12, 16, 17, and 18). The sulfur content of the benzine is considerably lowered at 400° when the contact time with the catalyst is prolongated, provided, however, that the amount of hydrogen passing through in the course of such a test is equal to that which is passed through when the experiment is carried out at greater speed. This fact is well illustrated by the values obtained in experiments 13, 10 and 19.

It is an interesting observation, by the way, that in experiment 10, where benzine is passed over the catalyst in the course of three hours, the rate of desulfurization shows abrupt increase reaching 42.7%, and thereafter a similarly sudden decrease to 0%. This phenomenon may be with great probability explained by the fact that the excessive lowering of the sulfur content in the benzine caused a complete poisoning of the catalyst. A pretreatment of the catalyst with hydrogen for four hours, instead of for one hour, did not increase the desulfurization rate, as we see from exps. 21, 22, 23, 24. All the tests indicate finally that the activity of the catalyst decreases in proportion to the amount of benzine passed over it.

The pyrogenizates obtained in two test were distilled and their specific weights were determined.

Pyrogenizate Exp. 3

$d_{20}^{20} = 0.874$

Initial boiling point	124°
124-160°	38.88 %
160-180°	33.33 %
180-200°	16.66 %
Residue	5.55 %
Losses	5.58 %
Total	100.00 %

Pyrogenizate Exp. 13

$d_{20}^{20} = 0,881$

Initial boiling point	124°
125-160°	50.0%
160-180°	25.0%
180-200°	12.5%
Residue	5.0%
Losses	7.5%
Total	100.0%

The distillation data and the determinations of the specific weights indicate that in the course of the shale benzine desulfurization, pyrogenizates are formed which are richer in light fractions and of lower specific weight than the feed stock.

In the pyrogenizate of Exp. 23 sulfur compounds were determined which show that the residual sulfur consists of 0.53% of hydrogen sulfide, 0.38% of elementary sulfur, 0.38% of mercaptane 1.23% of disulfide and 2.47% of sulfons.

The difficulties encountered in determining the forms of sulfur in products like shale benzine and its pyrolysis products, does not give us much confidence in the exactitude of the figures obtained. For the same reason, it is not possible, either, to determine the forms in which sulfur is present in the benzine stock.

Under these circumstances there is no sufficient basis for the assertion that the forms in question have been found in the pyrogenizate as a result of the breaking of the thiophene ring.

A great number of investigations show however that hydrogen sulfide, sulfur, mercaptane, disulfide and sulfides can be removed equally easily by means of catalytic hydrogenation. In the previously mentioned work of Orlov and Broun on the Catalytic Desulfurization of Thiopheries by means of Hydrogenation (1), The possibility of a scission of the thiophene ring has been expressly stated. If we start from this basis, the supposition is permissible that when thiophene is found in shale benzine, and if all sulfur compounds with the exception of thiophene had been removed, the thiophene ring was broken in the reaction, along with the formation of hydrocarbon desintegration products and of some sulfur compounds of non-thiophenic character.

When one works with Kashpir shale-tars one must keep in mind that these products do not only contain a large percentage of sulfur compounds but also many unsaturated compounds. Both of these factors are bound to exercise a negative effect upon the activity and the positive character of the catalyst. Unsaturated hydrocarbons will to a certain extent settle out tar derivatives on the catalyst at higher temperature, poisoning it thereby. For this reason, the thought arose as a matter of course of blending the shale benzine with petroleum benzine.

In carrying out these experiments, the Kashpir shale tar fraction up to 200° was passed over the catalyst without hydrogen at 400°. The fraction in question was moreover diluted with rectified petroleum benzine in a 1 : 2 ratio. The resulting mixture contained about 3% of sulfur. Of course, the concentration of unsaturated compounds in the solution was also three times lower. This solution was passed over the catalyst at 400° without hydrogen and with hydrogen.

When the results of experiments 25 and 28 are compared (Table 2) we see that the desulfurization rate rises from 21.42% to 26.84% when shale benzine is diluted with petroleum benzine. This phenomenon can be explained by the fact that the feed stock solution in Exp. 28 had a much lower sulfur concentration. But the possibility is not excluded that the higher rate of desulfurization be caused by the action of hydrogen, which may have been formed by the dehydrogenation of hydroaromatic compounds present in the petroleum. It is possible that both factors contributed to the increase in the rate of desulfurization: the lower rate of sulfur concentration in the solution and the combination with a hydrogenation reaction which, by the way, under our operating conditions ought to be combined with the formation of aromatics at the expense of the dehydrogenation of the hydroaromatic compounds contained in the petroleum benzine.

The data obtained in exps. 31 and 34 are not uninteresting, either. They show that when a solution of shale benzine and petroleum benzine is passed simultaneously with hydrogen the rate of desulfurization reaches 52.63 to 66.77%. In the diluted benzine remain 0.99% of sulfur.

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(1) N. A. Orlov and A. S. Broun, Chem. Solid Fuels, 3, 11-12, 817 (1932).

The analysis of the forms in which sulfur appears showed in one of the experiments that as much as 30-40% of the residual sulfur was represented in the form of easily removable sulfur compounds. Consequently, the possibility is not excluded to produce a fuel oil which contains 15-16% of unsaturated hydrocarbons, some given amount of aromatics and 0.5-0.6% of not readily removable sulfur products.

In order to verify still more carefully the assumption that in the above-mentioned experiments (Table 2) the desulfurization was the result of the hydrogenation which took place at the same time and was accompanied by the formation of aromatics, we planned a series of experiments in which the Kashpir-tar fraction up to 200° and thiophene were dissolved in purified dimethylcyclohexane and also thiophene in xylene and were passed over the catalyst without hydrogen.

Expts. 39 and 40 (Table 3) on the one hand, and 41, on the other hand, showed that the thiophene in the xylene solution does not give up the sulfur, while the thiophene in the dimethylcyclohexane is desulfurized. Moreover, in the hydrogenizates 39 and 40, xylene has been discovered, the presence of which can only be ascribed to a dehydrogenization of the dimethylcyclohexane. Under these circumstances, the results obtained may be said to confirm our hypothesis with respect to the desulfurization mechanism of shale benzine in a petroleum benzine solution. A final judgement in this question, however, will be possible only after obtaining the results of a new special study which the author has devoted to this problem.

SUMMARY

(1) An increase in temperature from 300 to 400° intensifies the desulfurization process of shale benzine under the test conditions.

(2) At the 300° level the desulfurization intensity goes up if the hydrogen flow-rate is accelerated from 12 to 24 liters per hour.

(3) A prolongation of the contact period between benzine and catalyst leads to a better removal of the sulfur.

(4) A longer pretreatment of the catalyst with hydrogen does not result in a greater quantitative desulfurization.

(5) The greater the quantities of sulfurous benzine passed over the catalyst, the greater the poisoning effect.

(6) The dilution of shale benzine with petroleum benzine makes it possible to carry out a more complete desulfurization.

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TABLE 1

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No. of Experiment	Reaction temperature	Weight of benzine passed over catalyst g	Duration of run (hours)	How many times worked catalyst	Hydrogen flow rate hr/hr	Volume of hydrogen passed l	Amount of sulfur, % Benzine Stock	Amount of sulfur, % In pyrogenizate	% of desulfurization	Yields of pyrogenizates
1	300	25	1	1	12	12	9.68	8.13	16.1	16.7
2	300	25	1	2	12	12	9.68	8.37	13.53	20.12
3	300	25	1	3	12	12	9.68	8.87	8.36	20.28
4	300	25	1	1	24	24	9.68	6.66	31.19	8.5
5	300	25	1	2	24	24	9.68	7.29	24.69	22.8
6	300	25	1	3	24	24	9.68	8.05	16.80	20.0
7	400	25	1	1	12	12	9.68	6.22	35.74	15.5
8	400	25	1	2	12	12	9.68	7.21	25.51	20.5
9	400	25	1	3	12	12	9.68	7.82	19.21	19.7
10	400	25	2	1	12	24	9.68	6.45	33.36	12.1
11	400	25	2	2	12	24	9.68	7.17	25.92	19.5
12	400	25	2	3	12	24	9.68	7.17	25.92	22.7
13	400	25	1	1	24	24	9.68	6.60	31.81	15.0
14	400	25	1	2	24	24	9.68	7.38	23.76	17.3
15	400	25	1	3	24	24	9.68	7.59	21.59	23
16	400	25	2	1	24	48	9.68	6.53	31.61	12.87
17	400	25	2	2	24	48	9.68	7.12	26.44	21.7
18	400	25	2	3	24	48	9.68	7.17	25.92	19.7
19	400	25	3	1	8	24	8.37	5.82	42.71	14.7
20	400	25	3	2	8	24	8.37	8.37	-	-
21(1)	400	25	1	3	12	12	8.31	5.72	31.15	15.8
22(1)	400	25	1	1	12	12	8.31	6.05	27.19	21.8
23(1)	400	25	1	2	24	24	8.31	5.66	31.9	17.3
24(1)	400	25	1	3	24	24	8.31	6.44	22.50	22.8

(1) For Expt. 21, 22, 23 and 24, the catalyst have been reduced for four hours in a hydrogen stream (instead of for one hour) at a temperature of 400° C.

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TABLE 2

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Series Number	Test temperature °C	Weight of substances passed over catalyst, g	Duration of run (Hours)	How many times worked catalyst	Hydrogen flow rate l/hr	Volume of hydrogen passed l	Quantity of sulfur, % In feed-stock	Quantity of sulfur, % In pyroge-nizate	% of desulfurization	Weight of pyrogenizate g	Weight of catalyst charge, g
					Fraction up to 200°						
25	400	25	1	1	Without H_2	Without H_2	8.31	6.53	21.42	13.9	65
26	400	25	1	2	"	"	8.31	6.78	18.41	21.4	65
27	400	25	1	3	"	"	8.31	6.88	17.20	23.1	65
					A solution of the fraction up to 200° in petroleum benzine						
28(1)	400	25	1	1	Without H_2	Without H_2	2.98	2.18	26.84	18.1	65
29(1)	400	25	1	2	"	"	2.98	2.50	16.10	22.9	65
30(1)	400	25	1	3	"	"	2.98	2.82	5.36	22.5	65
31(1)	400	25	1	1	12	12	2.98	1.41	52.68	16.8	65
32	400	25	1	2	12	12	2.98	1.99	33.22	18.2	65
33	400	25	1	3	12	12	2.98	2.30	22.81	18.6	65
34	400	25	1	1	24	24	2.98	0.99	66.77	14.6	65
35	400	25	1	2	24	24	2.98	1.66	44.29	17.8	65
36	400	25	1	3	24	24	2.98	2.56	14.09	14.6	65

(1) A determination of the proportion of unsaturated hydrocarbons showed it to have dropped to 10%, after the solution had been passed over the catalyst. In these cases, the catalyst charge failed to evolve H_2S under the action of H Cl

TABLE 3 (1)

Series number	Test temp. °C	Weight of solution fed g	How many times worked catalyst	Amount of S. % In feedstock	Amount of S. % In pyrogen.	Weight of pyrogen. g	Duration of run hr.	
			Solution of a Kashpir-tar fraction up to 200° in dimethylcyclohexane					
37(2)	400	25	1	3.12	2.38	23.71	18.0	1
38	400	25	2	3.12	2.67	8.01	22.0	1
			Solution of thiophene in dimethylcyclohexane					
39	400	25	1	4.07	3.73	8.35	19.9	1
40	400	25	2	4.07	3.73	8.35	28.0	1
			Solution of thiophene in cydene					
41	400	25	1	4.08	4.08	No desulfurization	19.1	1

(1) The catalyst charge weighed 65 g
(2) In Exp. 37, the pyrogenizate consisted of: H_2S - 0.0% S - 6%; mercaptane 13.4%; disulfide 1.2%, sulfide 5.4%

SINCLAIR REFINING COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT

Translation Book No. 229
API-TOM Reel ~~223~~ 255
Chemistry of Solid Fuels
vol. 5, No. 4 (1934), p. 333-357

February 16, 1949

0498

SR-15

Desulfurization of Shale Benzines by Hydrogenation in the Presence of Catalysts.

by

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In a prior publication of ours[1] we summarized the preliminary data obtained in our investigation on the desulfurization of shale benzines in the presence of sulfur-containing catalysts: molybdenum bisulfide (MoS_2), cobalt sulfide (CoS), and a mixed catalyst, consisting of cobalt sulfide plus alumina ($CoS + Al_2O_3$).

The results obtained led to the following conclusion: benzine with a sulfur content of 10.6 % can be completely desulfurized by pressure hydrogenation -- initial hydrogen pressure 50 atmos., operating pressure 80 atmos. -- in the presence of molybdenum bisulfide. The benzine thus obtained was quite colorless and of satisfactory stability; it contained hardly any unsaturated compounds. The specific weight was 0.750 - 0.760; the output was about 85 %, calculated on the basis of the feed stock weight.

Hydrogenation at atmospheric pressure at a temperature of 400-500°, did not yield results like those obtained by pressure hydrogenation. The minimum sulfur content, which could be achieved by this mode of operation, was 7.6 % S.

Following up these data, we continued our studies of the desulfurization reaction under atmospheric and elevated pressure, extending our research project into various directions. Even though a catalyst, suitable for the pressure desulfurization had been found, it was still necessary to study its effect on the process under varying hydrogenation conditions (duration, temperature, pressure, etc.) Moreover, a catalyst which would be suitable for the hydrogenation reaction at atmospheric pressure had to be found.

1. Hydrogenation under Hydrogen Pressure.

All the pressure-hydrogenation tests were carried out in an autoclave, which had been described in our prior publication. The mode of operation and of analyzing the hydrogenation products (benzine and gas) remained also unchanged. We used molybdenum

(1) Journ. of Applied Chem. (U.S.S.R.) 6, 494, 1933) Desulfurization of Shale Benzine by Hydrogenation in the Presence of Sulfur- Containing Catalysts.

bisulfide as a catalyst (MoS_2). Like in the prior experiments, the feed stock consisted of the 150 - 175° Kashpir fraction which contained thiophene. The characteristic data of this fraction are as follows:

$d^{15}_{15}g$ = 0.8908 Sulfur content = 10.6 %

Engler Distillation

Initial boiling point	100°
Up to 150°	0.7 % (by volume)
150 - 175°	84.7 %
175 - 200°	10.7 %
Residue plus losses	3.9 %

In this study we shall investigate the influence of the following factors upon the hydrogenation process and, consequently, upon the rate of desulfurination of the benzine: 1.) intermixing of the substrate, 2.) duration of the process, and 3.) proportion of the catalyst charge. Moreover, a series of tests was made for the purpose of establishing the extent to which molybdenum bisulfide retains its characteristic properties when it is in service for a longer period of time under hydrogenation conditions (duration of the catalytic activity).

Effects of Intermixing the Substrate.

The charge (benzine, catalyst, hydrogen) was mixed in the autoclave with a rotating two-blade agitator (l.c. p. 486, fig. 1). The intermixture intensity varies with the rotation speed of the agitator; the more intense the contact between the solid (catalyst), liquid (benzine) and gaseous (hydrogen, benzine vapor, hydrogenation gases) phases, the more satisfactory will be its effects on the hydrogenation process. In our first experiments, we chose a speed of 120 r.p.m. (Expts. 1-26). The construction of our apparatus did not permit for a further increase in the agitator's speed of rotation, even if it had been desirable to get the substrate more thoroughly mixed. But, there was no absolute necessity for increasing the speed. For, the reaction product was already entirely free from sulfur at the given speed and under the given conditions. Table 1 summarizes the tests made under different mixing conditions: we operated with 120, 50 and zero r.p.m. In the last instance, the agitator was disconnected. A change in the number of rotations per minute from 120 to 50, had no effect whatever on the yields or composition of the reaction products, with a benzine charge of 30 g (the catalyst was MoS_2; 10 % of the weight of the benzine stock), a test period of one hour, at a temperature of 350°, and under an initial hydrogen pressure of 50 atmos. In both cases, the desulfurization proceeds to termination.

It is necessary to point out that by the term "sulfur-free benzine", a benzine of 0.2 % sulfur content is designated, since preliminary experiments had proved that the residual sulfur is easy to remove by re-hydrogenating the benzine; the additional hydrogen consumption is inconsiderable. Even if the first hydrogenation

had been carried out under optimum conditions, a certain amount of sulfur, however small (0.2 %) will be found in the benzine. This phenomenon may be explained by certain peculiar features in the construction of our autoclave, in which the tests were made. An important part of the total capacity of the said autoclave consists of two coolers, which are connected with the reactor. Thus, a certain part of the benzine vapor and of the hydrogen is always at a temperature below reaction temperature, the minimum temperature required for yielding an entirely sulfur-free product.

According to the data found by S. Namstkin, F. Sanin and Rudakova (1), the sulfur content of the end product will also be higher when the hydrogenation is carried out in a rotary autoclave at a temperature of 325°, than when it is conducted at a temperature of 400-425°C.

The hydrogenation proceeds considerably less satisfactorily without stirring (Expts. 48, 49) than with stirring: a greater quantity of hydrogen is consumed; the specific weight of the hydrogenation benzine is increased; the proportion of the fractions up to 150° is lower. At the same time, the benzine is not completely desulfurized; the end product has a sulfur content of 5.7 - 5.8 %.

The control test O_7 was made without using a catalyst, after Expt. 49.

We made sixteen control tests without catalysts, covering the entire range of our studies (l.c. p. 504 - 505). In some cases, the control tests were made before we started the positive test series; at other times, afterwards. They were supposed to show to what extent the catalytic action of the autoclave walls affects the results obtained in the positive tests. In other instances, the control tests were made after the autoclave had been subjected to a special cleaning (the autoclave was washed with a hot, 10-% aqueous alkali solution), which was supposed to lower the catalytic action of the autoclave walls and to remove catalyst residues. The preceding investigation had shown the catalytic action of the autoclave walls to increase with the number of experiments run in the presence of a sulfur-containing catalyst. In studying the various hydrogenation conditions, it is of utmost importance to eliminate any effects emanating from this factor.

In the subsequent experiments, we limited the speed of the stirrer to 120 r.p.m.

Table 1 shows that a one-hour hydrogenation run may yield entirely satisfactory results (complete desulfurization) (Expt. 33). In Table 3 all factors were constant, excepting the duration, which was varied within the range of

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(1) Chem. of Solid Fuels, 4, Bi.4 (1933), "Destructive Hydrogenation of Kashpir Shale", Expt. 35 (Table 8).

zero to four hours. Under the term "duration", we understand the period of time during which a given temperature, the operating temperature, is maintained in the reaction area, i.e., a temperature of 350° in the given series of experiments.

Duration of the Hydrogenation.

When the duration of the experiments was varied from one hour to four hours, the character of the hydrogenation benzine thus produced remained practically unchanged: $d_{15}^{15} = 0.748 - 0.760$; sulfur content 0.10 - 0.25 %; output of fractions up to 150°, 53.3 - 55.0 %. When the duration of the run is reduced to thirty minutes, the specific weight of the benzine increases to 0.782 and the sulfurcontent to 2.67% S; a comparatively smaller amount of light fractions is produced (Expt. 34). Expt. 38 was carried out in the following fashion: at first, the autoclave was filled with hydrogen and kept in the said fashion for thirty minutes; then, like in other tests, the autoclave was heated to 350° (the stirrer starts operating at 250°), and immediately thereafter, the autoclave was cooled (the stirrer was switched off at 250°). The autoclave was not left for any length of time at a temperature of 350° (duration of the test equals zero); the hydrogenation of the benzine could take place only during the heating (20 min.) and cooling (one hour) periods. The character of the benzine produced in Expt. 38 resembles that of the benzine produced in the control test O_4 (without catalyst); the sulfur content of the hydrogenation benzine (8.45 and 9.49 %) approximates that of the feed stock (10.6 %). That goes to show that a one-hour duration is the minimum required for complete hydrogenation and desulfurization.

It is likewise undesirable to prolong the reaction beyond the one-hour range, since it fails to result in an increase in hydrogen consumption or in an improvement in the character of the hydrogenation benzine. The duration of the subsequent experiments was therefore limited to one hour.

Temperature.

Under the above-mentioned conditions, complete hydrogenation was achieved at 350°C. A further increase in temperature, for the purpose of modifying other hydrogenation factors (shortening the duration, or lowering the operating pressure), turned out to be undesirable. On the contrary, from the viewpoint of the commercial application of the pressure-hydrogenation reaction, there exists the greatest interest in operating at a minimum temperature, since a decrease in hydrogenation temperature (and pressure) results in a corresponding simplification of the equipment.

Table 3 gives the data obtained with different hydrogenation temperatures. The temperature was varied within the range of from 100° to 350° C. As was to be expected, hand in hand with a lower hydrogenation temperature went a deterioration in the character of the hydrogenation benzine. When the operating temperature was reduced from 350° to 100°, the specific weight of the hydrogenation benzine went up from 0.759 to 0.877, and the sulfur content in the benzine from 0.25 % to 10.47 % S. Even at a temperature of 300°, the desulfurization is incomplete; the end product has a sulfur content of 1.75 % S. The hydrogenation benzine obtained in Expt. 41 (operating

temperature, 100°) resembles the feed stock in specific weight, sulfur content and Engler distillation. A three-hour hydrogenation of benzine at 250°, failed to give desirable results. Consequently, it may be assumed that under the conditions in question, complete desulfurization in a one-step hydrogenation operation can not be achieved at a temperature of less than 350° C.

Better results are obtained when the benzine is three times hydrogenated (Table 4). The first and second times, the benzine was hydrogenated for a period of one hour; then the apparatus was cooled, and the gases present in it were replaced by pure hydrogen (50 atmos.); but the benzine was discharged and analyzed only after the third hydrogenation. Benzines, hydrogenated twice (Expt. 63) or thrice (Expt. 64) at a temperature of 200°, were of a somewhat lower sulfur content (9.26 and 8.89 % S) than those which had been once hydrogenated in the absence of catalyst (Expt. O_{11}) (11.) %). Benzine, three times hydrogenated at 250° C. (Expt. 61) is nearly completely desulfurized. The end product contains about 0.75 % S. Most probably, a thrice repeated hydrogenation at a temperature of 300°, would result in complete hydrogenation and desulfurization. In continuous operation, when hydrogen is constantly charged, and hydrogenation gases are constantly discharged from the hydrogenation chamber, a hydrogenation temperature of 300°C ought to suffice for all practical purposes. Since our subsequent tests, however, as well as the preceding ones, were conducted in an apparatus designed for discontinuous operation, we kept the initially chosen hydrogenation temperature of 350° C.

Pressure.

As the first series of experiments had shown, complete desulfurization of the benzine can be achieved with a hydrogen charge of 7 % (2.1 g), calculated on the basis of the weight of the feed stock (30 g); under these conditions about one half of the entire hydrogen charge is consumed in operation. Lowering the initial hydrogen pressure without changing the benzine charge, is tantamount to a decrease in the proportion of the hydrogen charge. The latter fact may affect the course of the process, irrespective from the hydrogen pressure. When the pressure drops below 25 atmos., the hydrogen charge is insufficient for complete hydrogenation. This circumstance can be corrected only by decreasing the amount of benzine fed. Since we worked at that time with an autoclave the capacity of which (0.5 l) permitted only for a charge of 30 g of benzine, it was undesirable for technical reasons to reduce the benzine charge — we studied the effect of pressure variations in an autoclave of different construction. Expts. 50 and 51 (Table 5) were carried out in 5-liter rotary autoclave, described in the said publication of S. Nametkin, F. Sanin and Rudkova; Expts. 68-70 and O_{20} were carried out in a 5-liter autoclave with internal stirrer driven by an automatic pump(1).

(1) For details confer: Franz Fischer, Entwicklung der Ueberdruckoxydation und Apparatur. Gesammelte Abhandl. zur Kenntnis der Kohle, 4, 13 (1919) and 5, 166 (1919).

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In the first series of experiments, the hydrogen charge is calculated in relation to the weight of the benzine only and amounts to 7 %. The initial hydrogen pressure only sustained variations. Lowering the pressure from 50 atmos. to 40 atmos. has an adverse effect on the nature of the hydrogenation benzine; the benzine in Expt. 51 is of a sulfur content of 3.48 %. At still lower pressures (30 - 10 atmos.) the hydrogenation nearly fails to proceed at all. In Expts. 68-70 and O_{20} (1) the hydrogenation gases did not contain any hydrogen sulfide. Under these circumstances, the initial hydrogen pressure cannot be lowered below 50 atmos. (and consequently the operating pressure) in an apparatus designed for discontinous operation, without changing also the other operating conditions. The given intensity of hydrogenation and desulfurization can also be obtained at an initial hydrogen pressure of 40 atmos.; but then, there must either be a corresponding prolongation of the hydrogenation period, or a raise in temperature. Because of the said considerations, we did not proceed in our studies of how the process might be affected by initial hydrogen pressures of less than 50 atmos.

Amount of Catalyst.

For those experiments which have the objective of studying the conditions immediately connected with the catalyst -- how the process is affected by variations in the proportion of catalyst to the stock, by the duration of the activity of the catalyst (catalyst poisoning), etc. -- it is of basic importance to calculate and, as far as possible, entirely to eliminate any extraneous factors which may affect the course of the hydrogenation. For instance, in our first series of tests, where the proportion of catalyst was gradually decreased, errors might have occurred since the effect of this phenomenon, the reduction of the catalyst charge, might have been offset by the catalytic action of the walls, which increases with the number of tests run. In order to exclude errors due to this factor, the autoclave was not only cleaned in the usual way before each run (Table 8), but it was also subjected to an extra cleaning and, moreover, control tests without catalysts were made (Expts. O_8-O_{19}). In Expts. 54-57 and 65, where the benzine charge and hydrogen charge remained constant, and temperature and pressure only were varied, the catalyst charge was varied between 0 and 20 % (based on the weight of the benzine). The benzine is completely hydrogenated and desulfurized when the catalyst portion is 10 -20 %. If the proportional charge of catalyst is further reduced, there is an increase in the specific weight of the benzine and in its sulfur content. The interrelationship between the specific weight and the sulfur content is plotted on Fig. 1. When the proportion of catalyst is reduced from 10 to 5 %, the specific weight and the sulfur content of the hydrogenation benzine will go up even though not to a large extent. But when the proportion of catalyst is as low as 5 - 0 %, the said increase is very abrupt, the curves become nearly vertical. The minimum percentage of catalyst, by which complete hydrogenation and desulfurization is effected in a one-hour, one-step reaction, is 10 % of the weight of the feed stock.

How long a catalyst introduced in this fashion will retain its catalytic activity under hydrogenation conditions will be investigated in future tests.

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(1) The tests were made without a corresponding reduction of the benzine charge. The 160-175° fraction of a light shale-tar distillate served as the stock; this fraction contained the distillate fraction of up to 150° (15 %), if it was not washed with acid and alkali; specific weight -- 0.876; it contained 10.0 % S.

The preservation of catalytic activity

In Exp. No. 66/1-66/14 (Table 7) the weight of the catalyst charge was left unchanged; at the beginning of each test run, the benzine charge was introduced by means of a pipette and analyzed as usual; the catalyst which had settled at the bottom of the autoclave was left there for the subsequent test. Fourteen runs were carried out, without changing the catalyst charged at the first run (10% of the weight of the benzine charge); each run lasted for one hour; altogether an amount of 14 x 30 g of benzine was subjected to hydrogenation (420 g). Table 7 shows that the hydrogen consumption amounted to 3% in Expt. 1, to 2.2% in Expt. 9, and to 1% in Expt. 14. When the hydrogen consumption goes down, in connection with the length of time the catalyst was in service, the quality of the benzine is lowered; its specific weight and its sulfur content go up; the proportion of the fraction up to 150° drops from 60 to 30%. The character of the hydrogenation benzine obtained in Expt. 14 ressembles that of Expt. 011, where we operated without a catalyst. The change in the hydrogen consumption and the character of the benzine product is also plotted in fig. 2 for the whole series of experiments. A definite hydrogenation reaction occurred only in the first experiment; in the following runs the activity of the catalyst decreases, and the sulfur content of the final product is constantly increasing. This drop in activity may be explained as being due to one of two causes: (1) the catalyst is poisoned because his surface is covered with tarlike bodies, or because its composition and character are changed under the effect of a prolonged contact with the hydrogenation products; (2) the catalyst is not poisoned and the decrease in catalytic activity is connected with a decrease in the amount of catalytically active components. A supplementary analysis of the catalyst showed that, under our operating conditions, the latter reason is the predominant one. In the series of experiments No. 61/1-61/14, [illegible] grams of catalyst had been charged; after the fourteenth experiment we succeeded only in discharging 1.8 g of catalyst, that is 6% of the weight of the benzine [illegible] hydrogenated. An analysis of the discharged "catalyst" shows it to consist fundamentally of iron (50%) and nickel (10%) in combination with sulfur, chromium (6%) and aluminum (8%) and of only an inconsiderable proportion of molybdenum bisulfide (MoS_2). That means that nearly the total genuine catalyst which consists almost entirely of pure molybdenum bisulfide, had been removed from the reaction area in the course of these fourteen experiments -- when the stirrer is in action, the catalyst clogs up the top interior part of the autoclave in the form of fine dust -- and the mass discharged, a powder mixed with tiny flakes, and thought to be the catalyst, turned out to be the corrosion products from the autoclave walls (iron, chromium, nickel, sulfur) and of the aluminum lining. We wanted to exclude any effects which may be occasioned by a change in the quantity of active catalyst; therefore we carried out the experiments No. 67/1-61/5 under the same conditions as Expts. No. 66/1-14, but we introduced a catalyst charge of 20%, based on the weight of the feed stock (6 g), assuming that a decrease of the catalyst from 20-10% in the course of the experiments according to Table 6, will not be reflected in the hydrogenation results. Nevertheless, in the course of the operating period, the catalytic activity of the catalyst dropped steeply (Expts. 67/1-5. After Expt. 67/3, the catalyst was discharged and washed with benzol before being recharged for Expt. 67/4; this kind of cleansing had hardly any effect on the activity of the catalyst. After Expt. 67/5, there was a considerable iron content (11%) in the catalyst mass (19% of the weight of the feed stock benzine).

The poisoning of the catalyst under pressure hydrogenation conditions -- if there is any -- could be studied only under the conditions of batch-wise operation. When the hydrogenation was conducted in an autoclave, the catalyst did not only sustain losses and pollutions (it is expedient to line the interior walls of the autoclave with aluminum) but there prevailed also the injurous circumstance that after each hour of hydrogenating, the autoclave had to be cooled and the hydrogenation products to be discharged, along with discharging the benzine and the hydrogen; the catalyst operates with long interruptions, under the conditions of a variable gaseous phase (1).

Analysis of the Hydrogenation Gases and the Hydrogen Consumption.

A method of analyzing the gases was discussed in our previous publication. Unsaturated hydrocarbons, carbon dioxide, carbon monoxide, and oxygen were usually present in the hydrogenation gases or were found in insignificant amounts. The porportion of saturated hydrocarbons did not exceed 5% by volume, nitrogen 10%, (the atmospheric nitrogen in the autoclave + the nitrogen content of the commercial electrolytically produced hydrogen). About 80% of the gas consisted of hydrogen and hydrogen sulfide. With complete hydrogenation the hydrogen-sulfide content in the gas rose to 10%.(2)

In Table 8 the hydrogen consumption in the hydrogenation process has been summarized. The amount of hydrogen charged to the autoclave (graph: Hydrogen Charge) has been calculated in the following manner; in order to fill the 0.5 liter autoclave (that of the rotatory autoclave was five liter) to 50 atmos. a charge of 25 l - 0.5 l = 24.5 l of hydrogen is required, which consists of 23.3 liter of pure hydrogen since "hydrogen" obtained by electrolytic hydrogenation consists of 95% of hydrogen and 5% of nitrogen. The output of hydrogenation gas consisted of the amounts registered by the gas meter + 0.5 liter of gas which remains in the autoclave under normal conditions. The calculation of the amount of hydrogen which had been consumed in the autoclave was carried out by two methods:

1.) By analyzing the gas formed during and after hydrogenation and by determining the quantities of gas present, the difference between the amount of hydrogen charged and the total amount of hydrogen found in the hydrogenation gas gives the rate of hydrogen consumption (either in liter or in gram).

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(1) The experiments made by Nametkin, Sanin and Rudakova (l.c.) failed to show any poisoning taking place in the rotatory autoclave, in which there is no decrease in the amount of catalyst charge during the test period and no escaping from the reaction area, phenomena which occur in the stirrer equipped autoclave which we used for our experiments.

(2) Run made without stirring.

2.) On the basis of the drop in pressure in the autoclave in the course of the hydrogenation. As we have already pointed out before, the hydrogenation gas consists of hydrogen, hydrogen sulfide, nitrogen and an inconsiderable amount of unsaturated hydrocarbons, which can be neglected in the calculations. The total amount of nitrogen present in the autoclave does not undergo any change in the course of the hydrogenation. There is no hydrogen sulfide present in the gas at pressures which correspond to the terminal perssure (about 30 atmos.) since hydrogen sulfide is liquified at a pressure of 18 atmos. at 20° (confer the preceding article) and does not participate in the overall gas pressure. Under these conditions, the pressure drop, registered by a manometer, is equal to the difference between the initial and final hydrogen pressure, and is determined exclusively by the consumption of hydrogen. in the hydrogenation. When the pressure drop is 19 atmos. as in Expt. 47, the hydrogen consumption is 0.5 l x 19 = 9.5 l, or 2.7% calculated on the basis of the weight of the benzine stock.

As it was to be expected, the figures for the hydrogen consumption rate obtained by the second method, are somewhat lower than those obtained by the first method. When hydrogen-consumption values are those of the pressure drop during hydrogenation they are bound to be greater than the former value where the partial pressures of the hydrogenation gases have been deducted from the later (confer, for instance, Expt. 49, which has been carried out without mixing). Nevertheless, the figures given in the graph under the heading "Hydrogen consumption, on the basic of the gas analysis" must be deemed less accurate because of errors which will inevitably arise in calculating the gas charge, and of others which are bound to occur in analyzing a mean sample, etc.

When benzine is hydrogenated until all the sulfur is removed, about 3% of hydrogen are consumed under the given conditions, calculated on the basis of the weight of the benzine stock.

Yields

Maximum hydrogenation (full desulfurization) of shale benzine can be carried out in the given apparatus under the following conditions: (a) catalyst -- molybdenum bisulfide, MoS_2 (10% on the basis of the weight of the benzine stock, (b) duration of the hydrogenation run -- 1 hour, (c) initial hydrogen pressure 50 atmos. (operating pressure, 80-90 atmos.), (d) hyerogen charge, 7% on the basis of the weight of the benzine stock; (e) hydrogen consumption -- 3%, on the basis of the weight of the benzine stock, (f) vigorous stirring of the substrate.

Changes in the individual factors in a direction which is favorable to the hydrogenation reaction (higher pressure, temperature, etc.), are yet unsuitable since a maximum benzine hydrogenation takes already place under the conditions in question; and variations in the opposite direction (lowering of pressure, temperature, etc.) make for a poorer quality of the hydrogenation benzine produced.

The study devoted to several questions (the effect of the pressure, the poisoning of the catalyst) was insufficient, due to lack of time. Nevertheless, the preliminary data are a sufficient basis for starting experiments with a continuous mode of operation.

II. Hydrogenation at Atmospheric Pressure

We described already a method of operating at atmospheric pressure and analyzing the end products of this kind of hydrogenation. Fig. 3 shows a schematic representation of the apparatus; it does not seem necessary to explain its individual parts. Like in the experiments which were conducted under hydrogen pressure, the 150-175° fraction of a thiophene-containing oil served as feed-stock; its specific weight was 0.8908, sulfur contents 10.6%.

At the beginning of this article it had been pointed out that hydrogenation without pressure had failed to give satisfactory results. For this reason, we experimented with various metals and their oxides in this study, and also with mixed catalysts. There were in the scientific journals as well as in the patent literature, certain remarks pointing to the use of such catalysts for desulfurization purposes (in the presence and in the absence of hydrogen). They had been used for various oils, among them, shale oils. To be sure, these remarks confirm our opinion that the desulfurization of hydrogenation products rich in sulfur is most wearisome under atmospheric pressure. But they indicate also that by working in this direction, we may expect to succeed to a certain extent.

We investigated the following catalysts: the oxides of molybdenum, tungsten, aluminum, chromium, reduced cobalt and iron ore, and mixed catalysts.

Preparation of the Catalysts

1.) Molybdenum trioxide. MoO_3. Commercial molybdenum-oxide ammonium was purified by recrystallization from an aqueous solution of ethyl alcohol and thereafter was transformed into molybdenum trioxide by calcination in a porcelain bowl (up to red heat). The white trioxide powder thus obtained was formed into pellets of 4-5 mm diameter and dried in a drier at 100°.

2.) Cobalt oxide (Co_2O_2). From powdered cobalt oxide (a Kahlbaum commercial product) a catalyst mass has been prepared in the same manner as Molybdenum trioxide.

3.) Tungsten trioxide WO_3. Metallic tungsten, a Kahlbaum product, calcined in a porcelain bowl at red heat, was oxidized to tungsten trioxide. From the trioxide powder, a contact mass was made in the above mentioned fashion.

4.) Vanadium pentoxide V_2O_5. Vanadium-oxide ammonium (NH_4VO_3) was heated in a porcelain bowl until all the ammonium was driven off. When the heating was continued, the yellow powder thus obtained, V_2O_5, would melt (melting temperature 658°) and then crystallize in rings of about 4 mm diameter, which recalled the form of Raschig rings. The crystallization was carried out in the following fashion: the molten mass of vanadium pentoxide was pumped into a glass tube of suitable diameter by means of a water-jet pump. The crystalline mass thus formed assumes the form of the hollow tubes. The glass tube was then removed and the mass divided into rings (shorter pipes, about 10 mm long).

5.) Aluminum hydroxide, $Al_2O_3 . (1-3)H_2O$. To a 20% solution of commercial alluminum sulfate was added a 20% solution of caustic soda until all the aluminum hydroxide settled out in it was transformed into sodium aluminate. The sodium aluminate was decomposed with a 20% solution of sulfuric acid, and aluminum hydroxide was formed. The settling out of the hydrate from the solution proceeds rapidly and a sufficiently dense precipitate is obtained. The precipitate was washed with hot water in a Buchner funnel, until the sulfuric acid ions were removed. It was dried in a drier at 100°.

6.) Chromium hydroxide, $Cr_2O_3 . x H_2O$. From a 10% solution of chromium nitrate (prepared from commercial chromium hydroxide) a hydrate is precipitated with a 10% solution of an aqueous ammonia solution. The hydroxide precipitate was washed with hot water in a Buchner funnel until the ammonium nitrate was removed and dried at 100°.

7.) Chromium metal Cr. Prepared by the aluminum thermical method (Goldschmidt reaction).

8.) Iron hydroxide $Fe_2O_3 . xH_2O$. From a 20% ferric nitrate solution a Kahlbaum product, iron hydroxide was precipitated by means of a 10% aqueous ammonia solution; the hydrate precipitate was washed with hot water in a Buchner funnel until the ammonium nitrate was removed. Then, it was dried at 100°.

9.) Iron ore No. 2. It was used in pieces of 3 mm diameter.

10.) Chromium hydroxide ($Cr_2O_3 . xH_2O$) + molybdic acid ($MoO_3 . H_2O$. A 10% solution of potassium chromite, prepared from chromium hydroxide, was mixed with a 10% solution of ammonium molybdate, which had been purified by being recrystallised from an aqueous solution of ethyl alcohol. By means of a 10% solution of nitric acid, chromium hydroxide and molybdic acid were simultaneously precipitated from the solution in question. The precipitate was washed on a Buchner funnel until all the nitrate salts of potassium and of ammonium were removed and then it was dried at 100°. Before drying, the salt solutions were mixed in such porportions that the dried product would contain 1 gram molecule of molybdic acid per gram molecule of chromium hydroxide.

11.) Chromium hydroxide ($Cr_2O_3 . xH_2O$) + cobalt oxide (CoO). A 20% solution of chromium nitrate was mixed with a 20% solution of cobalt nitrate. With a 10% solution of caustic soda, both compounds were simultaneously precipitated (like in the preceding paragraph, in equimolecular quantities) and then boiled.

By adding a 10% solution of caustic soda to the solution in question, followed by boiling, both compounds, chromium hydroxide and cobalt oxide, were precipitated simultaneously, in equimolecular amounts, as above. The precipitate was washed until all the caustic soda and sodium nitrate were removed and then dried at 100°.

12.) Chromium hydroxide ($Cr_2O_3 . xH_2O$) + aluminum hydroxide ($Al_2O_3 . (1-3)H_2O$) After mixing a ten-% solution of chromium nitrate with a 10% solution of aluminum nitrate, prepared by dissolving the nitrates in nitric acid, chromium hydroxide and aluminum hydroxide were simultaneously precipitated with a 10% aqueous solution of ammonia. The precipitate was washed with water on a Buchner funnel and dried at 100°.

13.) Chromium hydroxide ($Cr_2O_3 \cdot xH_2O$) + iron hydroxide ($Fe_2O_2 \cdot xH_2O$)

(a) A 10% solution of chromium nitrate was mixed with a 10% solution of iron nitrate. To this solution was added a 10% aqueous ammonia solution, effecting the simultaneous precipitation of the chromium and iron hydroxides in equimolecular quantities. The precipitate was washed with water and dried at 100°.

In this fashion, but at different quantitative proportion of the chromium and iron hydrates, two of the following catalysts were prepared.

(b) A catalyst which contained 1 gram molecule of iron hydroxide per two gram-molecules of chromium hydroxide.

(c) A catalyst which contained two grams molecules of iron hydroxide per one gram-molecule of chromium hydroxide.

14). Chromium hydroxide ($Cr_2O_3 \cdot xH_2O$) + cobalt sulfide (CoS). A 10% solution of chromium nitrate and a 10% solution of cobalt nitrate are mixed. A 10% solution of ammonium sulfide is added. Chromium hydroxide and cobalt sulfide are precipitated at the same time in equimolecular quantities. The precipitate is washed with water and dried at 100°.

Catalists 5, 6, 8 and 10-14 appeared to be solid dry masses after being dried at 100°. But the density of the various catalysts was not uniform. This mass was charged into the reaction tube and separated into disks of 3 mm diateter. The atmospheric-pressure hydrogenation runs were carried out at a temperature of 400° in a hydrogen stream of 10 l/hr. Under such conditions, the composition of nearly all catalysts was bound to sustain certain changes in the course of the experiments: loss of the water of hyuration, reduction of some of the oxides, etc. In order to exclude such phenomena, each catalyst, after being charged into the reaction tube, was maintained for three hours at a temperature of 400°. in a hydrogen stream (velocity--10 l / hr.). Under such a treatment the chromium hydroxide and iron hydroxides and molybdic acid loose their water and are converted into anhydrous oxides. ($Al_2 \cdot 3H_2O$, dried at a temperature of 235-250°, has the composition $Al_2O_3.H_2O$, and looses the last water molecule at a temperature of 800°(1). Some of the oxides undergo farther-reaching transformations. Cobalt and iron are reduced to metals. Molybdenum and tungsten trioxide, vanadium pentoxide, are not reduced to metals under the given conditions (tungsten pentoxide is reduced to metal in hydrogen only at a temperature of 1200°), but they are converted into oxides of a lower order. Iron ores are also redued.

Under these circumstances, the composition of the above mentioned catalysts immediately before they are used in the following way may be rendered with some probability by the following terms: 1.) Mo oxide:- 2.) reduced Co, 3.)tungsten oxide, 4.) vanadium oxide, 5.) Al_2O_3, 6.) Cr_2O_3, 7.) Cr metal, 8.) reduced Fe, 9.) reduced iron ore No 2, 10) Cr_2O_3 + Mo oxide, 11.) Cr_2O_3 + Co, 12.) Cr_2O_3 + Al_2O_3, 13a.) Cr_2O_3 + 2 Fe, 13b). Cr_2O_3 + Fe, 13c.) Cr_2O_3 + 4 Fe, 14.) Cr_2O_3 + CoS.

(1) Ipatiev, "Glinosem, as a Catalyst in Organic Chemistry, p. 7.

Catalyst: Metals and Metal Oxides

All the experiments which are recorded in Table 1, were conducted at a temperature of 400°. A higher temperature occasions an extensive formation of gas, and impairs the uniform proceeding of the reaction. Moreover, the output of benzine goes down to a large extent. The amount of benzine passed over the catalyst (1) was 20 cc in some of the experiments (flow rate 10 cc/hr), in others — 100 cc (flow rate 50 cc/hr), the amount of hydrogen was 10% of the weight of the benzine stock (1.78 l of hydrogen per 17.8 l of benzine) and 2%.

Tungsten, vanadium and aluminum oxide exhibit next to no catalytic activity in the hydrogenation and desulfurization process under the given conditions. The specific weights (d_{15}^{15} = 0.888-0.879) and the sulfur contents (10.51 - 9.60% S) of the end products were nearly the same as the specific weight (d_{15}^{15} = 0.891) and the sulfur content (10.6% S) of the feed-stock benzine. Reduced iron (Expt. 54) has a more satisfactory activity; reduced cobalt (Expt. 35) and molybdenum oxide (Expt. 21) remove about one half of the sulfur contained in the feed stock benzine and lower its specific weight to 0.821. The most active catalysts are : chromium oxide and reduced iron ore No. 2. Hydrogenation in the presence of reduced iron ore gives a slightly fluorescent product which smells like pure benzine, with a content of 0.95% of S.

When the velocity of the flow of the benzine vapors which pass over the catalyst, goes up (and the amount of hydrogen goes down in proportion), up to 50 cc/hr., the products sustain an abrupt deterioration. Chromium oxide, for instance, does not exhibit under these conditions any effect upon the desulfurization process (confer the character of the benzine in Expt. 43). Under such circumstances, when the flow rate of benzine is increased above 10 cc/hr. and that of hydrogen to over 10 l/hr., unsatisfactory results are obtained. Nevertheless, even at these flow rates, a satisfactory degree of desulfurization is only obtainable when the amount of benzine passed over the catalyst is very small.

From Table 10 follows that the activity of the catalyst quickly goes down in inverse proportion to the amounts of benzine vapors passed over it. In the presence of a chromium oxide catalyst (Expt. 41), a product which contains 1.61% S is obtained from the first 20 cc of benzine. The second benzine batch contains already 4.33%. When 100 cc of benzine have been continuously passed over the same catalyst, the product will contain 5.84% S. The same picture appears also for other catalysts, only with that difference that the activities of the other catalysts go down still faster (Expt. 51, 54, 33). Incomplete desulfurization is of course independent of differences in the composition of sulfur-containing compounds contained in shale benzine, but must be explained by the poisoning of the catalyst, since the re-introduction of the benzine over a fresh catalyst leads to a more complete removal of the sulfur from the benzine. The sulfur content of the benzine prepared in Expt. 41 (5.84%) was reduced to 2.31% by re-hydrogenating it (Expt. 43). When the capacity is small and the length of the contact mass is small, too, the incompleteness of the desulfurization might also be explained by the assumption that the content of the benzine vapors with the catalyst is not of sufficient duration. This period

(1) The number of cu cm of benzine which entered into the superheater, was measured. (Fig. 3)

of time may be computed on the basis of the mean molecular weight of the benzine, the cross-section area of the reaction tube (2 cm) and the length of the contact mass (30 cm); in our tests it was 2.5 minutes (the linear velocity of the benzine vapors was 12 cm/min.

In Fig. 4 the data obtained in Expt. 44 are plotted (catalyst: chromium oxide) in which the length of the contact mass was increased to 90 cm (weight 93 g), the length of the reaction tube (two combined tubes with a common superheater) was increased to 198 cm. Expt. 44 was conducted under conditions analogous to those prevailing in Expt. 41 (confer Table 10). A total amount of 340 cc of benzine was passed over the catalyst. From Fig. 4 and from the data for Expt. 41 it may be deduced that the (threefold) prolongation of contact time between the benzine vapors and the catalyst, does not have a striking effect on the intensity of desulfurization. The sulfur content in the end product increases in Expt. 44 nearly as rapidly with an increase in the amount of benzine passed over the catalyst as in Expt. No. 41. When as much as 140 cc of benzine have been passed, the sulfur-content curve becomes nearly horizontal — the activity of the catalyst is constant. (1)

Catalyst: Reduced Iron Ore No. 2

In the previous discussion (Table 9, Expt. 90), it had been pointed out that under the given conditions, about 90% of the sulfur is removed from benzine passed over iron ore. The initial sulfur content is 10.6%, the final 0.95 %. Table 1, gives the results of our further studies regarding the hydrogenation process in the presence of iron ore.

The first series of tests was carried out with the objective of getting a general understanding of the effect of temperature and residence of benzine vapors and hydrogen over the catalyst. At 200° and with varying flow velocities of the benzine vapors, there is next to no desulfurization effect to be observed (Expts. 76, 86, 88); raising the operating temperature from 200° to 500° does not occasion a remarkable deterioration of the hydrogenation products, if the flow rate of benzine is 50 - 100 cc/hr. and the total benzine stock 100 cc. The nature of the product shows an abrupt improvement when a smaller quantity of benzine is passed over the identical catalyst. In Expt. 83, for instance, 100 cc of benzine was passed through the reactor at a rate of 50 cc/hr. and the sulfur content of the benzine dropped from 10.6 to 8.13% S. But the end product in Expt. 78, which was conducted under less favorable conditions (great velocity of the benzine vapors) but with a smaller amount of benzine stock (25 cc), contains 1.46% S. In the subsequent experiments, 20 cc of benzine was the maximum amount passed over pure (untreated) iron ore. For such amounts, a slower flow of the benzine vapors amounting to up to 10 cc/hr. (while at the same time the volume of hydrogen is raised ten liters per 10 cc benzine without any change in velocity), lowers the sulfur content in the benzine from 10.6 to 1.46 % S (Expts. 80, 82, 87).

While we kept unchanged the optimum velocities of benzine vapors and hydrogen, we varied the temperature in Expts. 83-91. At 200°, the sulfur contents

(1) Elgin, Bilder and Taylo obtained analogous results when the operated with petroleum of 0.4% sulfur content under similar conditions in the presence of nickel and iron catalysts. Ind. Eng. Chem. No. 12, 1291 (1930).

of the starting material and of the end product were one and the same. At 300° the end product contains 0.95% S, at 500° 0.40% S. At 500°, the benzine output is very insignificant. This phenomenon is obviously due to the great quantity of gases formed. At high temperatures the proportion of gases is higher. Under these circumstances, with an iron-ore catalyst (and, to a certain extent, also with other catalysts), the optimum conditions for an atmospheric-pressure hydrogenation are as follows: velocity of benzine vapors 10 cc/hr., hydrogen 10/hr., operating temperature 400°. The output of benzine of a sulfur content of 1% or less will be as high as about 70% (by volume) of the feed stock.

Since with nearly all of the catalysts, the desulfurization proceeded only when small quantities of benzine were passed over the catalyst (Table 10, 11, and 12), as thus, catalytic activity must soon have stopped in the course of operation, we made a special experiment with the objective of determining the length of time during which iron ore retains its activity. Expt. 92, which was run under optimum conditions, a sample being drawn after each 20 cc batch of benzine passed, gave a result very much at variance with that of other catalysts. The activity of iron ore remains nearly constant up to a period of ten hours (100 cc of benzine). But we can not exclude the possibility that this result is due to the large amount of catalyst charged (165 g).

Hydrogenation Gases

The cooled gas which issues from the apparatus (Cig. 3) was recovered in the gas meter and analyzed. The gas, whenever its sulfur content only was to be determined, was immediately passed through a bottle with a solution of copper sulfate. By changing the concentration of the copper-sulfate solution (titration) the amount of hydrogen sulfide was computed which was consumed in the formation of copper sulfide. The average composition of the gases obtained in several experiments made at a temperature of 400°, with different catalysts, is as follows:

CO_2	0.0% (by vol.)	CO	0.0%
H_2S	0.0-2.5%	Saturated hydrocarbons	1.0-1.5%
Unsaturated hydrocarbons	1.0-2.0%	H_2	90.0-80.0%
O_2	1.0-2.0%	N_2	7.0-12.0%

When the operating temperature is raised to 500°, the total content of saturated and unsaturated hydrocarbons in the gas will become as high as 8%. When the operating temperature is lower than 400°, none of these compounds will be recovered but hydrogen stock (95% of hydrogen and 5% of nitrogen) which passed the reactor in a hardly changed form will be present. The hydrogenation of benzine at a temperature of 400° goes hand in hand with a reduction in the proportion of hydrogen in the gas to 10-15%. If the volume of the gas would remain unchanged (gas volume before operation equal to gas volume after operation) that would be tantamount to a hydrogen consumption of 0.6-1.7%, on the basis of the weight of the feed stock. But on the other hand, if the volume of the gas is larger than the volume of hydrogen gas which had been fed, then next to no hydrogen has been consumed.

We must, therefore, assume that in an atmospheric pressure hydrogenation, hydrogen will rather more quickly dilute the gases formed (and the formation of hydrogen) than that it participates immediately in the hydrogenation of benzine.

Our chief interest is connected with the presence of hydrogen sulfide in gas. All the catalysts mentioned may be divided into two groups; in the first group are those catalysts which do not form sulfur compounds after the catalytic splitting of the thiophene compounds contained in the shale benzine, whereby hydrogen sulfide is formed (Al_2O_3, Cr_2O_3); to the second group belong those catalysts which enter into a linkage with hydrogen sulfide, forming sulfides (reduced Co, Fe, iron ore). The hydrogen gases formed in the presence of catalysts of the second group will not contain any hydrogen sulfide. Table 14 gives the hydrogen balance for several experiments, confirming what we just said.

The hydrogenation gases produced in Expt. 52 (catalyst: Cr_2O_3 + Co) and Expt. 54 (catalyst: reduced Fe) contain practically no hydrogen sulfide and the difference between the sulfur contained in the feed stock and the sulfur contained in the hydrogenation products consists mainly of that quantity which is bound by the catalyst (and the losses). We analyzed iron ore before and after Expt. 94, which had been conducted under conditions analogous to those under which Expt. 90 had been conducted (Table 13):

Total amount of catalyst	181.00 g
Sulfur in feed stock	1.88 g
Sulfur in finished benzine	0.10 g
Sulfur removed from benzine	1.78 g
Sulfur on catalyst after operation	1.88 g

Since the poisoning of catalysts of this kind is an entirely regular phenomenon, they must be subjected in service to a corresponding regeneration. The regeneration may consist of a simple burning off at the operating temperature. The hydrogenation gases of Expt. 40 (catalyst: Vanadium oxides) and Expt. 41 (catalyst: Cr_2O_3) contain considerable amounts of hydrogen sulfide. The circumstance that the amount of hydrogen sulfide in the hydrogenation products is smaller in the hydrogenation products than in the feed stock, may be obviously determined by means of the losses of sulfur-containing benzine (a certain percentage of benzine is adsorbed by the catalyst, the volatilization of benzine vapors with the gas).

Benzine

The benzine obtained by atmospheric-pressure hydrogenation, is distinguished by its comparatively high specific weight. When benzine has been hydrogenated under pressure to full desulfurization (0.0 - 0.25%) its specific weight is 0.748 - 0.761 (catalyst: MoS_2). But the specific weight of the benzine produced in Expt. 60 (catalyst: Cr_2O_3) is 0.816, while its sulfur content is 0.18% S. Fig. 5 shows that, the sulfur contents being equal, the specific weights of pressure-hydrogenation benzines are always lower than those of atmospheric-pressure

hydrogenation products. This circumstance is a direct function of the hydrogen consumption rate. The composition of the fractions of the two benzines is nearly equal. The chemical composition of the benzine has not been examined.

Summary

Atmospheric-pressure hydrogenation in the presence of metals or metal oxides gives better results than the hydrogenation with metal sulfides.

Optimum catalytic activity (considerable desulfurization effect) showed: chromium oxide and iron ore #2. The activity of chromium oxide is promoted by an addition of iron; there are foundations for the conjecture that additions of some metal sulfides may also be suitable.

When iron ore is used as a catalyst, it must be regenerated, the two catalyst will be studied at greater detail, and the results will be published at a later date.(1)

M. Both

(The graphs mentioned in the text may be reproduced upon request).

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(1) When this work was terminated, we saw the communication of N. Rease and V. Relython (Ind. and Eng. Chem. Sept. No. 9, 1-12 (1933) on the desulfurization of thiophene-containing benzine by means of hydrogenation. The authors tested a number of catalysts, some which were analogous to those which we used; among them were molybdenum and cobalt in the form of oxides and sulfides, chromium oxide and mixed catalysts, $CoS + MoO_3$ and $CoS + Cr_2O_3$. When the operating temperature was 325 and 400°, they succeeded in completely decomposing the thiophene. We may conclude therefrom that the thiophene, benzol, and hydrogen are (C_4H_4S : C_6H_6 : H_2 = 0.005 : 1.0 : 4.0), and 50 times less than that of thiophene-containing oil. The output of the authors on the operating effects of temperature, flow rate of the vapors upon the catalyst, of the sulfur concentration in the feed stock, etc., have been fundamentally confirmed.

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Mr. H. L. Pelzer
All Division Chiefs
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Table 1

Mixing Effect

Test Temperature 350°; duration - one hour; benzine charge - 30 g; catalyst - MoS_2 (10% of wt. of benzine)

Exp. No.	RPM of Stirrer	Hydrogenation Conditions: Pressure in Atmos. Initial	Maximum	Minimum	Final	H_2 Consumption in % by wt of Benzine Stock	Hydrogenation Benzine: Yield % by Wt.	d^{15}_{15}	Sulfur Content % by Wt.	Engler Distillation: Up to 150°	150-175°	175-200°	Residue & Losses
-		Starting Material					-	0.891	10.60	0.7	84.7	10.7	3.9
38	120	50	87	78	30	3.0	73.3	0.759	0.25	56.7	26.7	10.4	6.2
52	50	50	89	78	28	3.3	73.6	0.761	0.28	56.7	26.6	10.0	6.7
48	0	50	105	99	37	1.9	69.6	0.838	5.85	46.7	30.0	10.0	13.3
49	0	50	99	90	36	2.1	73.0	0.812	5.72	46.7	36.6	10.0	6.7
07	120	50	95	91	37	1.9	83.1	0.860	9.44	23.3	60.0	10.0	6.7

Table 2

Effect of the Duration of the Test

Test Temperature 350°; Benzine Charge - 30 g; Catalyst MoS_2 (10% of the Weight of Benzine)

Exp. No.	Duration Hours	Hydrogenation Conditions: Pressure in Atmos. Initial	Maximum	Minimum	Final	Yields % by Wt.	d^{15}_{15}	Sulfur Content % by Wt.	Hydrogenation Benzine: Engler Distillation: Up to 150°	150-175°	175-200°	Residue and Losses
-		Starting Material					0.891	10.60	0.7	84.7	10.7	3.9
27	4	50	79	73	30	70.2	0.857	0.25	65.0	26.3	5.7	3.0
35	4	50	84	75	26	66.7	0.759	0.15	56.6	23.4	13.3	6.7
29	3	50	90	72	24	65.0	0.759	0.22	60.0	26.7	6.6	6.7
24	3	50	81	75	30	78.0	0.755	0.17	65.0	25.0	7.5	2.5
30	2.5	50	81	71	28	62.7	0.798	0.10	64.3	25.0	7.1	3.6
31	2	50	91	72	30	73.3	0.759	0.20	60.0	23.3	9.7	7.0
32	1.5	50	91	78	30	68.4	0.760	-	53.3	26.7	13.0	7.0
45	1.5	50	81	75	30	75.7	0.757	0.25	60.0	23.3	10.0	6.7
33	1	50	87	78	30	73.3	0.759	0.25	56.7	26.7	10.4	6.2
34	0.5	50	90	85	34	67.7	0.782	2.67	50.0	30.0	13.3	6.7
36	0	50	85	-	33	68.5	0.838	8.45	50.0	30.0	13.3	6.7
04	1	50	105	103	37	68.2	0.850	8.49	36.6	40.0	13.4	10.0

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Table 3

Effect of Test Temperature

Exp. No.	Hydrogenation Conditions: Duration Hrs.	Temp.	Pressure in Atmos. Initial	Maximum	Minimum	Final	Yields % by Wt.	Hydrogenation Benzine: d_{15}^{15}	Sulfur Content % by Wt.	Engler Distillation: Up to 150°	150-175°	175-200°	Residue and Losses
33	1	350	50	87	79	39	73.3	0.759	0.25	65.7	26.7	10.4	6.2
37	1	300	50	81	74	30	74.0	0.765	1.73	56.6	26.7	10.0	6.7
39	1	250	50	75	65	30	69.8	0.776	1.84	56.6	23.3	10.0	10.0
42	1	250	50	80	65	30	72.7	0.779	2.37	40.0	33.3	16.7	10.0
43	1	200	50	67	60	33	80.2	0.829	7.82	30.0	50.0	13.3	6.7
41	1	100	50	63	58	35	80.5	0.877	10.47	6.7	73.3	13.3	6.7
59	3	250	50	81	65	30	73.3	0.786	3.04	50.0	33.3	6.7	10.0

Table 4

Repetition of the Hydrogenation Process

Duration - 1 hour; benzine charge - 30 g; catalyst MoS_4 (10% of benzine weight)

Exp. No.	Series No. of Hydrogenation	Hydrogenation Conditions: °C Temp.	Pressure in Atmos. Initial	Maximum	Minimum	Final	Yields % by Wt.	Hydrogenation Benzine: d_{15}^{15}	Sulfur Content % by Wt.	Up to 150°	150-175°	175-200°	Residue & Losses
014	First Hydrogn.	200	50	80	80	44	94.7	0.897	11.00	13.3	73.4	6.6	6.7
62	First "	200	50	80	71	41	81.0	0.853	9.58	26.7	50.0	13.3	10.0
63	First "	200	50	76	70	41							
	Second "	200	50	80	76	44	81.7	0.845	9.26	30.0	50.0	10.0	10.0
64	First "	200	50	79	75	43							
	Second "	200	50	82	77	44							
	Third "	200	50	80	80	44	83.7	0.839	8.89	33.3	46.7	13.3	6.7
42	First "	250	50	80	65	30	72.7	0.779	2.37	40.0	33.3	16.7	10.0
60	First "	250	50	82	69	33							
	Second "	250	50	95	90	45	75.9	-	-	53.3	33.4	9.9	3.4
61	First "	250	50	83	68	33							
	Second "	250	50	91	89	46							
	Third "	250	50	93	93	48	63.8	0.766	0.75	53.3	33.4	9.9	3.4

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Table 5

Effect of Pressure

0517

Exper. No.	Duration Hrs	Temp. °C	Amount of Catalyst g	Amount of Catalyst % by wt. on feed stock	Pressure in Atmos. Initial	Maximum	Minimum	Final	Benzine Charge g	Hydrogenation Benzine Yields % by Wt	d_{15}^{15}
											0.758
50	1	350	30	10	50	101	97	29	300		
51	1	"	24	10	40	81	67	23	240	80.0	0.752
68	1	"	30	10	30	69	61	27	300	89.7	0.863
69	1	"	30	10	20	51	39	-	300	93.6	0.864
70	1	"	30	10	10	36	26	8	300	91.1	0.868
O_{20}	1	"	30	10	10	27	23	9	300	99.0	0.878

(Table 5 Cont'd)

Exper. No.	Hydrogenation Benzine Sulfur content % by Weight	Engler Distillation up to 150	150 - 175°	175-200°	Residue and Losses
50	0.24	60.0	23.0	11.0	6.0
51	3.48	48.0	37.0	10.0	5.0
68	9.32	26.0	59.0	10.0	5.0
69	9.55	25.0	59.0	11.0	5.0
70	9.53	23.0	62.0	9.0	6.0
O_{20}	10.20	14.0	74.0	9.0	3.0

Table 6

0518

Effect of the Amount of Catalyst

Exp. No.	Hydrogenation Conditions: Duration Hrs.	Temp °C	Amt. of Cat. in % by wt on Benzine Stock	Pressure in Atmos.: Initial	Maximum	Minimum	Final	Hydrogenation Benzine: Yield in % by wt	d_{15}^{15}	Sulfur Content % by wt	Engler Distillations: Up to 150°	150-175°	175-200°	Residue and Losses
0_8	1	350	0	50	100	100	39	92.0	0.863	9.63	23.3	56.7	13.3	6.7
54	1	350	20	50	83	81	30	68.2	0.758	0.19	63.3	23.4	9.9	3.4
0_9	1	350	0	50	102	102	41	86.3	0.863	9.62	20.0	56.7	13.3	10.0
55	1	350	10	50	80	77	26	75.9	0.759	0.19	56.7	23.3	10.0	10.0
0_{15}	1	350	0	50	105	105	43	83.5	0.864	9.47	33.3	53.4	6.6	6.7
65	1	350	7.5	50	88	80	26	76.7	0.763	0.53	63.3	23.4	6.6	6.7
0_{10}	1	350	0	50	102	102	41	79.8	0.855	8.77	36.7	50.0	9.9	3.4
56	1	350	5	50	75	66	22	71.2	0.763	0.79	56.7	26.6	10.0	6.7
0_{12}	1	350	0	50	100	100	40	90.5	0.862	9.13	26.7	49.8	10.2	13.3
58	1	350	5	50	89	81	29	80.4	0.751	0.85	63.3	23.4	6.6	6.7
0_{17}	1	350	0	50	106	104	41	82.8	0.828	7.14	40.0	43.3	6.7	10.0
57	1	350	1	50	100	95	38	84.1	0.814	5.95	50.0	30.0	10.0	10.0

Table 7

Duration of the Catalyst's Activity

Catalyst - MoS_2 Test Temperature - 350°

Hydrogenation Benzine

Exp. No.	Pressure in Atmos. Initial	Maximum	Minimum	Final	Yield % by wt.	d_{15}^{15}	Sulfur Content % by wt.	Engler Distillation Up to 150°	150-175°	175-200°	Residue and Losses	H_2 Consumpt. % by wt. on Benzine Charge
015	50	105	105	43	83.5	0.864	9.47	33.8	53.4	6.6	6.7	1.0
66/1	50	88	82	30	73.2	0.757	0.28	60.0	30.0	6.4	3.4	3.0
2	50	97	91	31	79.3	0.772	1.21	60.0	20.0	10.0	10.0	2.0
3	50	95	88	30	80.8	0.758	1.05	60.0	26.7	3.3	10.0	3.0
4	50	94	86	30	76.2	0.762	1.06	60.0	23.3	6.7	10.0	3.0
5	50	105	98	33	78.9	0.789	2.91	60.0	23.3	6.7	10.0	2.5
6	50	102	95	36	77.9	0.807	5.35	53.3	30.0	6.7	10.0	2.1
7	50	110	99	36	77.6	0.803	5.25	53.3	36.7	3.3	6.7	2.1
8	50	103	-	-	-	0.797	4.50	53.3	33.4	3.3	10.0	-
9	50	101	-	-	-	0.805	4.59	50.0	36.7	3.3	10.0	-
10	50	100	91	35	-	0.804	6.73	47.5	35.0	10.0	7.5	1.2
11	50	90	87	36	82.7	0.855	9.32	26.7	53.3	3.3	6.7	2.1
12	50	103	102	44	85.6	0.860	9.31	30.0	60.0	3.3	6.7	0.9
13	50	103	103	42	80.2	0.860	9.55	30.0	53.3	6.7	10.0	1.3
14	50	102	100	43	-	0.860	9.51	30.0	53.3	6.7	10.0	1.0
016	50	100	100	43	87.1	0.871	10.17	30.0	56.7	3.3	6.7	1.0
67/1	50	84	80	29	70.0	0.864	0.45	53.3	33.4	6.6	6.7	3.3
2	50	100	87	32	77.4	0.774	1.56	56.7	26.6	10.0	6.7	2.7
3	50	93	88	30	70.0	0.777	2.28	56.6	30.1	10.0	3.3	3.0
4	50	96	80	30	67.0	0.766	2.41	43.3	36.7	13.3	6.7	3.0
5	50	92	81	32	76.0	0.785	3.58	46.7	36.6	10.0	6.7	2.7

Table 9

Desulfurization of Shale Benzine by Hydrogenation at Atmospheric Pressure in the Presence of Metals and Metal Oxides

Temperature - 400°C

Exp. No.	Hydrogenation Conditions: Catalyst Designation	Catalyst Quantity g	Duration Hrs.	Benzine Quantity cc	Benzine Flow Rate cc/Hr.	Hydrogen Quantity l	Hydrogen Flow Rate cc/Hr.	End Product (Benzine): Yield % by Vol	d_{15}^{15}	Sulfur Content % by Wt
38	W oxide	84	2	20	10	20	10	67.5	0.885	10.51
40	V oxide	59	2	20	10	20	10	67.5	0.888	9.64
51	Al_2O_3	12	2	20	10	20	10	87.5	0.879	9.60
54	Reduced Fe	40	2	20	10	20	10	80.0	0.854	7.83
35	Reduced Co	-	2	20	10	20	10	50.0	0.830	5.48
31	Mo oxide	-	2	20	10	20	10	55.0	0.821	4.46
41	Cr_2O_3	30	2	20	10	20	10	62.5	0.852	1.61
90	Reduced Iron Ore No. 2	165	2	20	10	20	10	67.5	-	0.95
37	W oxide	80	2	100	50	20	10	95.0	0.881	10.56
36	Reduced Co	-	2	100	50	20	10	90.0	0.872	9.59
32	Mo oxide	-	2	100	50	20	10	88.5	0.874	9.60
43	Cr_2O_3	28	2	100	50	20	10	88.0	-	10.64

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Table 10

Desulfurization of Benzine by Hydrogenation under the Prolonged Action of catalysts. Temperature 400°; Flow Rate of Benzine 10 cc/hr; Flow Rate of Hydrogen 10 l/hr. A Benzine Sample for Analysis was Drawn Each Time after Passing 20 cc of Stock

Exp. No.	Catalyst	Duration Hrs	Benzine Charge cc.	Yields % by Vol.	d_{15}^{15}	Sulfur Content % by Wt.
38	W oxides	2	20	67.5	0.885	10.51
		2	20	95.0	0.883	10.26
		2	20	87.5	0.883	10.45
		2	20	90.0	0.883	10.03
		8	80	85.0	0.884	10.31
40	V oxides	2	20	67.5	0.888	9.64
		2	20	88.5	0.878	9.57
		2	20	95.0	0.880	9.29
		2	20	92.0	0.881	9.70
		2	20	86.0	0.881	9.68
	Total	10	100	85.8	0.882	9.58
51	Al_2O_3	2	20	87.5	0.879	9.60
		2	20	82.5	0.880	10.07
	Total	4	40	85.0	0.879	9.84
54	Reduced Fe	2	20	80.0	0.854	7.88
		2	20	86.0	0.869	9.68
		2	20	92.5	0.873	9.77
		2	20	96.0	0.874	9.43
	Total	8	80	88.4	0.868	9.18
33	Mo oxide	2	20	67.5	0.838	5.34
		2	20	92.5	0.845	8.19
		2	20	95.0	0.848	8.02
		2	20	82.5	0.852	8.68
		2	20	85.0	0.855	8.56
	Total	10	100	84.0	0.850	7.76
41	Cr_2O_3	2	20	62.5	0.852	1.61
		2	20	68.0	0.856	4.33
		2	20	90.0	0.866	7.88
		2	20	87.5	0.862	7.69
		2	20	82.5	0.865	7.73
		10	100	78.1	0.860	5.84
42	Cr_2O_3	2	20	71.5	0.836	2.31

Table 11

Desulfurization of Benzene by Hydrogenation in the Presence of Mixed Catalysts (Cr_2O_3 + additives)

Operating Conditions same as Table 10

Exp. No.	Catalyst Designation	Catalyst Quantity	Duration Hrs	Benzine Charge cc	End Product (Benzine) Yield % by Vol.	d_{15}^{15}	Sulfur Content % by Wt.
45	Cr_2O_3	6	2	20	75.0	-	10.44
47	Cr metal	100	2	20	95.0	0.881	10.52
			2	20	95.0	0.883	10.64
			4	40	95.0	0.882	10.58
46	Cr_2O_3 + Mo Oxide	66	2	20	92.5	0.0	9.48
			2	20	90.0	0.868	9.90
			4	40	91.8	-	9.69
52	Cr_2O_3 + Co	33	2	20	75.0	0.833	4.52
			2	20	85.0	0.843	5.85
			4	40	80.0	0.838	5.18
63	Cr_2O_3 + CoS	36	2	20	62.5	0.842	2.88
			2	20	66.0	0.852	-
			4	40	64.3	0.847	-
56	Cr_2O_3 + Al_2O_3	20	2	20	69.0	0.834	4.81
			2	20	67.0	0.842	6.40
			2	20	80.0	0.851	7.18
			2	20	85.0	0.856	7.98
			2	20	90.0	0.861	8.55
			10	100	78.2	0.849	6.98

Table 12

Desulfurization of Benzine by Hydrogenation in the Presence of a Mixed Catalyst (Cr_2O_3 + iron)
Operating Conditions Same as Table 10

Exp. No.	Catalyst Designation	Catalyst Amount	Duration Hrs	Benzine Charge in cc.	End Product (Benzine) Yield % by Vol.	End Product (Benzine) d_{15}^{15}	End Product (Benzine) Sulfur Content % by Wt.
50	Cr_2O_3 + Fe	51	2	20	70.0	0.817	1.44
			2	20	85.0	0.847	6.81
			4	40	80.0	0.832	4.13
55	Cr_2O_3 + 2 Fe	42	2	20	67.5	0.755	0.85
			2	20	73.5	0.817	3.99
			2	20	76.5	0.837	6.65
			2	20	85.0	0.854	8.64
			2	20	97.5	0.860	9.30
			10	100	85.0	0.832	5.88
60	Cr_2O_3 + 4 Fe	61	2	20	71.0	0.816	0.18
			2	20	72.5	0.822	2.27
			4	40	71.8	0.819	1.23

Table 13

Hydrogenation Benzine Desulfurization in the Presence of Iron Ore No. 2

Weight of Catalyst: 165g

Exp. No.	Hydrogenation Conditions: Temp. °C	Duration Min.	Benzine: Amount, cc	Benzine: Velocity cc/hr	Hydrogen: Amount, l	Hydrogen: Velocity cc/hr	Amount of Product: Yield % by Vol.	Amount of Product: Sulfur Content % by Wt.
76	200	60	100	100	10	10	93	10.29
74	300	60	100	100	10	10	93	9.56
73	400	60	100	100	10	10	85	9.48
75	500	60	100	100	10	10	74	8.27
86	200	120	100	50	10	5	84	10.85
85	300	120	100	50	10	5	87	8.75
83	400	120	100	50	10	5	84	8.13
84	500	120	100	50	10	5	67	8.48
78	400	20	25	75	2	6	60	4.46
77	500	20	25	75	2	6	40	3.80
80	400	36	30	50	5	10	82	6.67
82	400	60	20	20	10	10	60	2.21
87	400	120	20	10	20	10	58	1.46
88	200	120	20	10	20	10	75	10.56
89	300	120	20	10	20	10	78	6.39
90	400	120	20	10	20	10	68	0.95
91	500	120	20	10	20	10	35	0.40
92	400	2	20	10	20	10	70	1.21
		2	20	10	20	10	65	0.51
		2	20	10	20	10	80	2.08
		2	20	10	20	10	75	2.51
		2	20	10	20	10	70	2.75
		10	100	-	100	-	72	1.82

Table 14

Sulfur Balance

Expt No.	Catalyst	In Benzene Feed Stock % by Wt.	In Benzene Feed Stock %	Wt. Sulfur In Hydrogenation Products: Benzine % by Wt.	Benzine %	Gas %	Total %	Difference: S in Feed Stock - S in Hydrogenation Products %
40	V Oxides	10.60	1.88	9.64	1.15	0.35	1.50	0.38
		10.60	1.88	9.57	1.50	0.32	1.82	0.06
		10.60	1.88	9.29	1.57	-	-	-
41	Cr_2O_3	10.60	1.88	1.61	0.17	0.09	0.26	1.62
		10.60	1.88	4.33	0.49	0.70	1.19	0.69
		10.60	1.88	7.88	1.23	0.65	1.88	0.00
		10.60	1.88	7.69	1.06	0.44	1.60	0.28
		10.60	1.88	7.73	1.09	0.55	1.64	0.24
52	Cr_2O_3 + Co	10.60	1.88	4.52	0.54	0.00	0.54	1.34
		10.60	1.88	5.85	0.83	0.00	0.83	1.05
54	Reduced Fe	10.60	1.88	7.88	1.06	0.00	1.06	0.82
		10.60	1.88	9.68	1.45	0.00	1.45	0.43
		10.60	1.88	9.77	1.57	0.00	1.57	0.31
		10.60	1.88	9.43	1.57	0.00	1.57	0.31

SINCLAIR REFINING COMPANY

Research & Development Dept.

March 8, 1949

Translation Book 241
TOM API 255
Chemistry of Solid Fuels
Vol. 6, No. 4, p. 340-347 (1935)

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SR-16

Hydrogenation of the Neutral Kerosene Fraction of Gdov Shale Tar

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According to the statistics compiled by the Committee for Fuel Economics, the province of Leningrad will require a fuel supply in 1937, as follows:(1)

1937	benzine	kerosene	tar oil	Total
t	480	390	73	943

Disregarding the fact that the hauling of 943 t of liquid fuel costs about 450 million rubel, such transport would be very difficult, and moreover, a heavy burden on the railroad system. It is possible to lower the volume of liquid fuel to be freighted by using local low-calory mineral products, in particular, fuel shales. Two billions of tons of fuel shale presences are located in the Leningrad district.

The hydrogenation of low-temperature carbonization shale tar seems to be one of the most promising methods of producing high-grade motor fuel from shales.

A series of laboratory investigations indicate the possibilities inherent in this method. Terris (2) and Duffur hydrogenated high-boiling shale oils at a temperature of 500° and at an initial hydrogen pressure of 40 atmos. over iron chloride, and obtained completely stable desulfurized benzine. Kogerman and Konvilem hydrogenated the shale oils, which had been obtained by the distillation of shales in the presence of ferric oxide. Under temperature conditions of: 400-10°, an initial hydrogen pressure of 100 atmos., and a duration of the reaction of 1-2 hours, they found that along with the formation of light oil, about 17% of heavy oils are produced. Khjusse (3) and Keri and Shotell (4) have also established the fact that these catalysts have a desulfurizing effect in the course of the dehydrogenation and promote the formation of stable light products.

Among the publications dealing with the hydrogenation of our native shales (at Kashpir and Gdov) we shall mention the following works: Klukvum and Ephremov (5), Tilichejev and Seledzhijev (6) (also over nickel oxide), S. S. Hamitkin (7) over a MoS_2 catalyst, and under agitation.

Recently, Nemtzov [8] and his coworkers carried out a series of investigations, checking on the behavior of a series of catalysts such as MoS_3 and investigating also that of mixtures in autoclaves and in continuously operating apparatus.

The problem of producing commercial products from shale tars, however, is still far from being solved, and the results which we obtained up to date must be deemed to be most unsatisfactory. At the present time, experiments carried out in a large laboratory scale in batchwise operating and in continuous operating autoclaves showed, even though they are by no means terminated, two methods of processing shale tar to be possible: (1) the hydrogenation of the residuum from which the benzine was removed, (2) the hydrogenation of individual fractions.

The berginization of the tars from which benzine was removed, is bound up with the complicated problems of a commercial scale production, since this type of hydrogenation must be carried out in two or three steps; in view of the particular, complex nature of the charging stock, the reaction is very prone to result in polymerization and coke formation. At the same time, it is also impossible to expose the charging stock at once to a temperature range of 480-500°; it must be given for thirty to sixty minutes low temperature pretreatment over a highly active catalyst.

The benzine-kerosene fraction which is obtained in this process may then be used for the vapor-phase step.

Since we must operate under unsatisfactory conditions (at low temperatures) and with comparatively light fractions, the liquid-phase equipment, which is charged with a low temperature catalyst of very low activity, must be of large capacity. The inconveniences inherent in this process are partly compensated for by advantageous features: there is no need of a preliminary distillation, and the tar can be worked up without difficulty.

The second variant is preferable because the working-up scheme is technologically simpler and because the different fractions can be immediately introduced into a vapor-phase zone for hydrogenation with a high rate of productivity. When we now assume that also the problem of the separate low-temperature hydrogenation of tar to lubricant oils will be successfully solved, the second variant turns out to be more profitable. Under the present operating conditions, however, both variants must be deemed of equal value.

In conclusion, it must be stated that the berginization of the entire tar must be studied in order to learn to understand more accurately the chief hydrogenization mechanisms, and that it is necessary to work, at the same time, with narrower fractions of shale tar and even with fractions from which some types of compounds were removed: e.g., acidic oils and bases. This simplification of the composition of the fractions, permits us to determine with greater accuracy the relation of output and composition of the hydrogenation benzine to the starting material.

Because of these considerations, we used as charging stock a shale-tar kerosene fraction which had been produced from Gdov shale, with a boiling point of 200-300°; acid oils and bases had been removed from it by means of a preliminary washing with 5% NaOH and 20% H_2SO_4. It was treated under liquid-phase conditions i.e., at temperatures of 360-420°. We intended to elucidate in the present study

the behavior of neutral oil under the action of an outstanding catalyst (MoS_2 + ZnO).

The determination of the temperature coefficient of the splitting and hydrogenation reactions, both of which were carried out by us, was intended to determine the relative velocities of these reactions and their acceleration; on this basis, it is also possible to make inferences on the inter-relationship of these reactions.

Apparatus, Operating Method, and Starting Material

The experiments were carried out in a vertical high-pressure autoclave, equipped with a stirrer.

The autoclave was heated by means of a specially-constructed electric furnace, which permitted to minimize the losses of heat, by using a flanged assembly. We succeeded in minimizing the said losses, thanks to a special shell for the furnace and an arrangement for insulating the flanges of the autoclave. The temperature was measured by means of a thermocouple, inserted in the interior pocket of the autoclave. The starting material — a neutral kerosene fraction (200 g), was introduced into the autoclave; five grams of a powdered catalyst was thereafter introduced; it consisted of molybdenum bisulfide and zinc oxide in a 1 : 1 ratio.

The autoclave was closed, blown out with hydrogen, in order to remove the air, and then filled with hydrogen to a pressure of 100 atmos. Then it was put into the heated furnace. The furnace was preheated, in order to reduce the length of time needed for heating the autoclave to the reaction temperature. In order to get products thoroughly mixed, the mixer was adjusted to 240 r.p.m. After the termination of the experiment, the autoclave was removed from the furnace, so that it would cool quickly; thanks to this device, the temperature dropped rapidly, and thus it was possible to stick exactly to the experimental conditions in question. During the runs the temperature was recorded every five minutes.

After the termination of a run and the cooling of the autoclave, the final pressure was measured and the hydrogen was introduced into a gas meter. The autoclave was opened, and the product which had been formed, was discharged into a graduated vacuum funnel in order to avoid the considerable losses caused by grinding, when the products are poured out over the rim of the autoclave. Thereafter, the autoclave was washed with ether. In order to calculate the material balance, the ether was distilled in a water bath and the distillation residue was weighed.

Before being analyzed, the product was dried over calcium chloride. The bromine number according to Agostini [9], and the specific weight of the dried product were determined; thereafter it was fractionated into the following fractions: up to 200°, 200-250°, 250-300°. In all of these fractions the bromine number and the specific weight were determined, and furthermore, the content of aromatics according to Katwinkel.

Table 1 gives a summary of the analytical data of the initial kerosene fractions:

Table 1

Fraction	up to 200°	200-250°	250-300°	residue	Total Products
Weight %	1.5	53.0	36.0	9.0	100
Spec. gr.	—	0.8760	0.8760	0.9101	0.8685
Bromine No.	—	41.1	26.1	—	30.7

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This goes to show that we deal with an unsaturated product, which contains moreover oxygen-containing compounds, the quantity of which was determined by the volumetric method as being 20%.

The experiments with the neutral kerosene fraction of shale oil were made with the purpose of studying the connection between the data obtained and the following varibles: (1) the operating pressure, (2) the residence period, and (3) the temperature.

In the first series, the hydrogen partial pressure was kept unchanged by adding some more hydrogen in the course of the experiment; this device permits us to talk not only about its effect, but enables us also to determine the order of the reactions on the basis of this reagent, proceed (Table 2, Fig. 1 and 2).

By comparing the data given on Table 2, and on Figures 1 and 2, we see that the pressure hardly affects the yields of benzine (the increase observed in an interval of 130 atmos. is less than 4%). The proportion of unsaturated compounds and the specific weight, decrease sensibly. The velocity of the hydrogenation was calculated by the bromine number:

$$\frac{dx}{dt} = kP_{H_2}$$

and when we assume $dx = k'P_{H2}$, we find the clearly expressed direct function:

K - velocity, from lg P_{H_2} (confer: fig. 3).

The first kinetic order of reactions, in which unsaturated compounds are hydrogenated may be computed on the basis of the hydrogen consumption according to certain standards. The decrease in specific gravity of the products, caused by the hydrogenation of the aromatic compounds, and the unusually small yields of benzine show the futility of any attempts of treating the given material under a high hydrogen pressure at a low-temperature range. An unimportant decrease in the yield of the light fraction in connection with the pressure, may be ascribed to the reduction in oxygen-containing compounds; but this phenomenon points out also the prevalence of heavy fraction in the composition of the benzine.

The series of experiments concerning the effect of the residence time is represented in Table 3 and Fig. 4 and 5. The experiments were carried out at a temperature of 420°, under an initial pressure of 100 atmos, without adding hydrogen during the reaction period. The change in the concentration of the two reagents, hydrogen and unsaturated compounds, in the course of time, should be a more complex function of the velocity of their reactions.

However, the computation of the velocity constant K on the basis of the monomolecular law showed a satisfactory convergence of the values obtained. It can be asserted that the velocity of hydrogenation of unsaturated compounds is not a function of their concentration in volume, as determined by the adsorptive capacity of the catalyst. It was not possible to find any selectiveness in the hydrogenation of one or the other fraction.

With a residence period of 100 minutes, the total output of benzine is about 20%. The low temperature of the process does not permit for reducing the length of time to any sensible extent, another indication for the senselessness of

investigating a material of this type under liquid-phase conditions. It is clear that results like these could be obtained at a temperature of 480° already in the course of three to five minutes.

When we scan again the benzine-fraction yields in terms of the length of time, we observe that, for instance, up to 40 minutes, (and with a decrease in the residual pressure to 70 atmos.) the rate of splitting does not exceed 9-10%, and starts to grow considerably only when the residence period is further prolongated. Such a fashion of forming benzine must be explained by referring to a parallelism in the proceeding of the two reactions; the decomposition of the oxygen-containing compounds and the thermal splitting of hydrocarbons. Both of these reactions yield light fractions in the last instance, and besides, they are particularly distinguished by the correlation with the hydrogen partial pressure; while the first reaction is a straight function of P_{H_2}, the second reaction is inhibited by it.(10)

In the tests for the determination of the temperature coefficient (confer Tables 5 and 4, and Fig. 6) in the splitting up and hydrogenation reactions, the comparison of these two phenomena, and also the comparison of E-- the activation, gives us insight into the chemical mechanism of the formation of light fractions.

The series of experiments in which the temperature was the variable, was carried out at a temperature range of 360-420°, without any addition of fresh hydrogen, whereby the residence time was selected in such a fashion that the rate of hydrogenation and splitting up were kept constant, not exceeding 35% for the hydrogenation and 10% for the splitting up. Since within these limits, both of these reactions are of the first kinetical order regarding the given experimental conditions, the calculation is carried out by the formula

$$K = \frac{2.3}{v} \lg \frac{100}{100 - X}$$

The graphical term: lg K - 1/T gave straight, nearly-parellel lines, with apparent E of 27,000 - 30,000 calories. The agreement, within the limits of experimental error, of the apparent E-activation of the splitting up in the hydrogenation, indicates clearly that the light fraction formed is not a product of the thermal splitting. In fact, the homogeneous fission reactions are distinguished by abrupt differences in the magnitude of the E-activation of an order of 60,000 to 70,000 calories. For this reason, the calculation of the temperature coefficient was expressed by the following magnitudes:

q^{10} — hydrogenation — 1.33 $\qquad$ q^{10} — splitting-up -- 1.4

Several of these data, however, are not sufficient for solving the question concerning the chemical mechanism. With respect to the splitting of oxygen-containing compounds, as well as to the adiabatic hydrogenation of unsaturated compounds, we received a similar apparent E value and order of reaction. Only an investigation of the chemical composition of the benzine can answer this question.

When we scan once more Table 6 and Fig. 5, we see that the boiling point curves go up steeply, those for the specific weight are particularly high, with a considerable proportion of unsaturated compounds. The latter fact indicates that unsaturated oxygen-containing compounds were in the starting material, whereby the action of hydrogen was directed in the first line towards the splitting off of the oxygen, a surface reaction with the high-activity catalyst. The firmly held molecule is thereafter desorbed, goes over into the vapor phase and is replaced by new

molecules from the liquid. The benzine was not stable and was quickly resinified; this goes to show that it was not completely hydrogenated under the experimental conditions.

Summary

On the basis of our experiments we may draw the following conclusions:

(1) The hydrogenation velocity of the double bonds is directly proportional to the partial hydrogen pressure, and does not depend on the hydrocarbon concentration.

(2) The benzine fraction is formed at the expense of the reduction of the neutral oxygen-containing compounds.

(3) In the hydrogenation of oxygen-containing compounds with double bonds the reduction reaction goes preferentially via the addition of hydrogen to the double bonds.

(4) The E-activation of the reduction and hydrogenation is under the given conditions limited to 27,000 - 30,000 cal.

(5) The neutral kerosene fraction of shale tar can not be profitably processed in the liquid phase.

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Table 2

Temperature 380°; catalyst 5 g of $Mo S_2$; series where the pressure is the variable

No. of runs	Experimental Conditions: Time min.	Experimental Conditions: Pressure Atmos.	Material Balance (%): Discharge	Material Balance (%): Water	Material Balance (%): Losses	Fractions (in wt. %): Up to 200°	Fractions (in wt. %): 200-250°	Fractions (in wt. %): 250-300°	Fractions (in wt. %): Residue	Specific gravity of fractions D_{20}^{20}: Total Product	Up to 200°	200-250°	250-300°	Residue	Bromine numbers: Up to 200°	200-250°	250-300°	Total Product	K.10^3
12	72.0	120/72	97.5	2.0	0.5	11.8	44.8	30.1	illegible	0.8420	0.791	0.835	0.859	0.928	25.3	17.4	10.9	12.1	12.8
10	75.0	180/75	97.5	2.0	0.6	12.0	44.7	30.2	12.1	0.8410	0.789	0.832	0.859	0.9214	21.0	14.6	6.8	9.0	17.6
9	73.5	200/73	96.5	2.5	1.0	12.4	44.5	30.6	11.8	0.8376	0.786	0.830	0.853	0.9169	20.5	7.9	4.1	7.0	19.8
11	74.2	250/74	96.0	2.5	1.5	13.9	43.9	30.8	10.1	0.8331	0.771	0.821	0.851	0.910	18.9	7.1	3.9	5.8	22.2

Table 3

Series where the residence time is the variable, temperature 420°; catalyst - 5 g of $Mo S_2$; pressure $_{initial}$ = 100 atmos.

No. of runs	Experimental Conditions: Time min.	Experimental Conditions: Pressure Atmos. initial	Material Balance (%): Discharge	Material Balance (%): Water	Material Balance (%): Losses	Fractions (in wt. %): Up to 200°	Fractions (in wt. %): 200-250°	Fractions (in wt. %): 250-300°	Fractions (in wt. %): Residue	Specific gravity of fractions D_{20}^{20}: Total Product	Up to 200°	200-250°	250-300°	Residue	Bromine numbers: Up to 200°	200-250°	250-300°	Total Product	K.10^3
5	26.5	70	97.0	2.2	0.8	8.6	49.7	30.9	10.2	0.8601	0.7910	0.8405	0.8580	0.9234	19.5	43.0	23.6	-	17.2
13	39.2	50	97.2	2.2	0.6	10.8	44.2	34.0	10.3	0.8680	0.7970	0.8436	0.8693	0.9310	12.6	28.4	16.3	9.1	22.3
3	41.6	73	-	-	-	9.1	46.3	34.7	8.9	0.8690	0.7900	0.8370	0.8640	0.9290	12.2(?)	32.0	20.0	11.0	18.2
7	61.5	45	97.0	2.2	0.8	18.4	43.5	28.0	9.2	0.8400	0.7836	-	-	0.9345	9.0	20.0	5.8	4.3	19.7
14	100.5	38	-	-	-	23.7	41.9	23.0	10.3	0.8915	0.7766	0.8407	0.8661	0.9111	4.8	12.1	3.9	3.2	18.4

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Table 4

Determination - Gl^{10} - Hydrogenation

No. of Run	Experimental conditions: Temp.	Correct Time min.	Pressure final atmos.	Bromine numbers: Up to 200°	200-250°	250-300°	Total Product	Spec.grav. Total Product	K - hydrog. $K.10^3$	log K hydrog.
6	360	140	73	34.0	21.6	14.0	19.9	0.8570	30.9	1.489
1	380	85	75	35.0	21.0	14.1	19.8	0.8546	51.9	1.715
2	380	70	78	33.0	21.2	15.0	19.9	0.8566	61.7	1.790
4	400	32.5	79	32.0	21.6	14.3	19.0	-	146.0	2.164
5	420	26.5	70	43.0	23.6	-	19.5	0.8601	172.0	2.235
3	420	41.6	73	32.0	20.0	11.0	14.2	0.8694	182.0	2.260

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Table 5

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Determination - Gl^{10} - Splitting

No. of Run	Experimental Conditions			Fractions (in weight %)				Determination - Gl^{10} - Splitting Spetific gravity D_{20}^{20}					
	Temp.	Correct Time min.	Pressure atmos.	Up to 200°	200-250°	250-300°	Residue	Up to 200°	200-250°	250-300°	Residue	K Splitting X 10^4	log K.10^4
6	360	140	73	8.0	44.8	34.0	11.5	0.8089	0.851	0.869	0.9102	4.81	0.682
1	380	85	75	9.9	42.7	35.5	10.8	0.799	0.847	0.868	0.9201	10.2	1.008
2	380	70	78	9.5	42.9	-	10.9	0.798	0.8461	0.869	0.9248	11.9	1.075
4	400	32.5	79	6.7	46.8	35.5	9.9	0.795	0.840	0.8688	0.9238	16.4	1.214
5	420	26.8	70	8.0	49.7	30.9	10.2	0.791	0.8405	0.858	0.9234	27.3	1.436
3	420	41.0	73	9.1	46.3	34.7	8.9	0.790	0.837	0.864	0.9290	18.9	1.275

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Table 6

The Benzine Fraction

No. of Run	Yield	Bromine number	Aromatics %	Spec. Grav.	Boiling Start	Engler distillation (%)			
						Up to 100°	Up to 150°	Up to 170°	Up to 200°
9	12.4	21.0	7.8	0.7860	70°	3.1	5.6	22.2	76.6
7	18.4	20.0	8.1	0.7836	60°	10.0	30.5	50.0	90.5
14	23.7	12.1	9.8	0.7766	50°	13.0	34.8	54.3	91.0

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Sinclair Refining Company
Research and Development Department

Translation Book 242
API TOM Reel 255
Journal of Applied Chemistry (USSR)
Vol. XII, No. 6, p. 875-877 (1939)

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March 14, 1949
SR-17

Phenols from Primary Tars and Their Stabilizing Influence upon Shale Benzines in Comparison with Synthetic Inhibitors

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Benzine, produced by the distillation of Gdov cuckersite, is a fuel with a high content of unsaturated hydrocarbons, readily oxidizing in storage, produced by cracking petroleum benzine. Oxidation goes hand in hand with an agglomeration of tarlike bodies and with a drop in the octane number. One of the disadvantages of shale benzine is its high content of sulfur and the presence of oxygen-containing compounds which cause its specific disagreeable odor. Experiments showed that purification with bleaching earths, zinc chloride, doctor solution and other familiar agents, does not remedy these unfavorable conditions. Treatment with phosphoric acid yields a high-grade benzine, but this method is still in the experimental stage. Purification with sulfuric acid lowers the sulfur content to 0.1% but fails to improve the stability of benzine. A combination of the sulfuric acid treatment with the addition of inhibitors appears to be the most effective method of obtaining a stable benzine.

The stabilization of benzine produced by cracking petroleum with inhibitors is carried out on a commercial scale. Among the best known inhibitors are: alpha-naphthol and para-aminophenol; monobensyl-para-aminophenol (BAPh), dibenzyl-para-aminophenol (DAPh) phenyl-para-aminophenol (PhAPh) and phenols produced from various primary tars. The ligneous phenols have been employed to a large extent. In the United States they are used as all-purpose inhibitors. According to Wolf and Vasiljev[1], ligneous phenols are distinguished by their excellent stabilizing properties at elevated storage temperatures (35-38°), surpassing alpha-naphthol and DAPh in the presence of iron. Resinous inhibitors possess still a number of positive properties. They appear to be products nearly unsoluble in water and readily soluble in benzine. Tar phenols are further characterized by the feature that they do not yield sludges in contact with metals and metal oxides, and do not cause benzine to go off color. In comparison to the activity of solid synthetic inhibitors in small dosages, tar phenols may be employed in higher concentrations without depositing a sediment on the intake parts of the motor, by virtue of their high rate of volatility.

In order to establish the relative activity of various inhibitors, phenols produced from shale tars, peat tar and ligneous tars were tested and also several of the usual inhibitors, such as alpha-naphthol, BAPh, DAPh, and PhAPh. The experiments were carried out with shale benzine, but it is not impossible that the data obtained might be applicable to benzines of different origins.

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Experimental Part

The para-aminophenol derivatives were synthetized according to the method recommended by Seleznevij. Alpha-naphthol was purchased from Kahlbaum's.

As phenolic raw-materials served: two ligneous tars (one made from conifers, the other from a mixed tar: 75% conifers and 25% greenwood); two fractions of shale tar (a ligroin fraction, 130-250°, and a Diesel fraction of 250-350°) and peat tar. The ligneous tars were obtained from the Institute for Wood Pulp Chemistry, the peat tar from the peat-coke plant at Redkin, and the shale tar from the pilot plant of the All-Union Institute for gases and synthetic liquid fuels.

The phenols were diluted with benzol one to two times, then they were treated with a 5-% salt solution in order to remove the organic acids; finally, they were extracted with a 10-% solution of caustic sodium. The phenols were separated from the phenol solution by means of a treatment with sulfuric acid, extracted with benzol and dehydrated; after distilling off the benzol, they were distilled in a vacuum.

The experiments were carried out with benzine which had been purified with sulfuric acid and redistilled with steam. The characteristic features of the benzine have been described in the article "Chemical Composition and Detonating Properties of Shale Benzine" (confer below).

The stability of the benzine to which inhibitors have been added was rated in relation to the formation of resins in storage and in relation to the length of induction period for fresh samples in the Ramsay bomb at a temperature of 100° and under a pressure of 7 atmos. initial hydrogen pressure. The benzine was stored in welded iron containers of three liters capacity. The relation between the area of the walls and the bottoms of the containers corresponded to the relation which prevails in the usual tanks. In order to render the storage conditions as similar as possible to those normally prevailing, some water was added in two of the containers. The walls of the containers were covered with rust. The benzine was stored at 10-15°, freely exposed to atmospheric circulation. Twelve samples to which inhibitors had been added and one control sample without inhibitor were put in storage. The synthetic inhibitors were added to the benzine in concentrations of 1 mg per 100 ml of benzine, and of 10 mg per 100 ml of benzine; the tar products in a 10 mg concentration only.

In Table I, the induction periods in the bomb and the storage data registered during a 220 day period are summarized.

When we look at these results, we find that alpha-naphthol gives the optimum value for resin formation. However, it is not readily available, and consumption is rather high (10 mg per 100 ml), therefore, the phenols which had been produced from shale ligroin or peat or wood tars are more suitable, since at the same concentration, they do not differ hardly from alpha-naphthol in activity. TAPh and PhAPh yield sufficiently satisfactory results in a concentration of 1 mg per 100 ml. The phenols produced from mixed ligneous tars and from the Diesel fractions of shale tars are less satisfactory in a concentration of 10 mg per 100ml; the same holds of BAPh in a concentration of para-aminophenols results in less satisfactory values with respect to resin formation. These inhibitors are of poor volatility, increasing the weight of the resins. At the same time it is very probable the iron containers produce a harmful effect, like that which has been recorded in the experiments of Wolf and

Vasiljev. Thus, it can be stated that benzine which was stabilized with synthetic inhibitors underwent a change in coloration after a comparatively short storage period. With alpha-naphthol, the benzine turned yellow; with BAPh, pink; with PhAPh and TaPh it turned orange. We must also pay attention to the fact that the induction period in the Ramsay bomb does not agree with the data which are obtained in storage. As a rule, the induction period is longer for synthetic inhibitors than for tar products. Since the storage conditions in the presence of water and iron, reflect more completely the activity of an inhibitor, the data obtained in bomb experiments are of secondary importance. Finally, we must state that the benzine which had been stabilized with shale tar, was subjected to motor tests after a six-month storage period. The test, carried out on the highway Moscow-Leningrad, showed that a thin resinous layer was deposited on the intake parts of the motor consisting chiefly of phenols. The thickness of this layer remains constant during the entire duration of the test and does not exceed the normal thickness. All the other parameters for the evaluation of the work of the motors, among them also the scale formation, give entirely satisfactory values for stabilized benzine.

Results

1.) The comparative activity of synthetic inhibitors in shale benzine (alph-naphthol, monobenzyl-para-aminophenol, para-tolyl-para-aminophenol, phenyl-para-aminophenol) and of inhibitors consisting of tar-products (phenols produced from shales, peat and wood tar has been tested.

2.) Shale phenols in a concentration of about 0.01% turned out to be the most efficient inhibitors; good results were obtained with them in motor tests as well as in storage.

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TABLE 1

The Efficaciousness of Primary-Tar Phenols and of Synthetic Inhibitors

No. of Experiment	Inhibitor	Concentration of Inhibitor (in mg) per 100 ml	Induction Period in The Ramsay Bomb - min.	The resin content (in mg) per 100 ml Benzine in relation to the number of days in storage				
				4	10	25	100	220
1	Alphanaphthol	10	975	0	1	1	3	3
2	Phenols from the shale ligroin fraction	10	205	1	2	2	2	5
3	Phenols from peat tar	10	180	0	1	1	1	5
4	Phenols from conifer tar	10	170	0	2	2	2	7
5	Para-tolyl-para-amino-phenol	1	200	1	1	1	1	8
6	Phenyl-para-amino-phenol	1	175	0	1	1	2	9
7	Phenols from conifer and green wood tars	10	140	1	2	2	2	10
8	Phenols from the shale Diesel oil fraction	10	230	2	2	2	2	12
9	Mono-benzyl-para-amino-phenols	1	235	1	2	2	2	14
10	Para-tolyl-para-amino-phenol	10	555	4	6	8	9	16
11	Mono-benzyl-para-amino-phenol	10	810	5	5	5	7	19
12	Phenyl-para-amino-phenol	10	565	2	4	-	7	23
13	Without Inhibitor	-	120	0	1	1	1	16

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0540

Detailed Discussion of Meiler Operation
on Oil Shale at Balingen
(Building Project)

I. Open-cut Mining

Open-cut mining of shale is economically profitable whenever the shale beds are 2 meters thick, provided that the overburden is not substantially thicker than 1 m.

The lower layers are richer in oil .....

Main Methods of Operation

The overburden over the shale which is to be mined during the subsequent period of time, is removed and transported to a dump. Some of it is necessary for leveling the pile-field.

The shale is at first drilled with electrical drilling machines, using rotary boxers, and then blasted. The blasted material is scooped into dumping box cars and transported to the degradation unit.

II. Crusher and Separating Unit

(a) Delivery Bins

The mined shale is transported to the delivery bins.

The bunkers are burned over, to the right and to the left, over two grates, which are supposed to keep back pieces of more than ca. 600 mm. The shale pieces which are thus left lying upon the grates are broken up by hand. Two service scaffolds are provided for this purpose along the grates. Between the scaffolds and the grates lies a sufficiently wide gap, through which major pieces, which have been recognized to be limestone, can be directly dropped. They fall on discharge chutes arranged below this gap and slide directly into box cars.

Below the grates lies an "intermediate" bunker. Through these grates the shale falls upon a discharge plate conveyer, which is strong enough for shaking off the largest pieces which are placed upon it. Velocity: 0.1 m/sec; 1/2 H.P.-motor. The intermediate bunker is lined with 12 mm steel plates, which are fixed with piercing Anker-screws.

The trucks which lie above the "delivery bunkers" are 600 mm or 900 mm wide. There is sufficient track lengths provided for behind the bunkers for moving the cars around.

(b) Picking Conveyor

From the above mentioned "discharge conveyor" the shale falls upon a picking conveyor which is ca. 9 m long by 1400 mm wide and of a 13° inclination. The velocity of the conveyor is 0.2 m/sec.; 15 H.P. motor. At both sides of the picking conveyor stairlike scaffolds for eight pickers each have been provided (and also a discharge chute on each side). These workers pick, with hooks or hands, all the lumps which they recognize to be limestone, and throw them into the discharge chutes. Boxcars for carrying off the limestone, are placed below the chutes.

The picking conveyor has a coating of steel plates.

The tracks on which the cars for the limestone are placed, along the delivery bins as well as below the chutes, form a part of the network of tracks, so that the limestone can be directly brought to the dumps.

(Note: The chutes are arranged for 4 m ^{3} box cars.)

The "picking conveyor" throws its charge over the tops upon a crank "swinging sieve" which allows to pass pieces having a size of less than 120 mm. The pieces which are larger than 120 mm are thrown into the funnel of the crusher; the crushed material issues upon a discharge conveyor. The material which goes through the sieve drops directly upon the said conveyor via a chute which is placed next to the crusher.

The crank "swinging sieve" is equipped with a 10.5 H.P. motor; 145 rotations per minute.

The above-mentioned parts are dimensioned for a maximum throughput of 180 to 200 tons. Depending upon the thickness of the layers, mined at any specific time, 5 - 10% of the charge may be limestone.

In the course of operation it will be found out whether a roof must be put over the picking conveyor.

(c) Crusher

Esch-spinning crushers, Type KBV, are used.

The Esch crushers have an inlet of 2000 mm diameter and a performance of 220-250 ton/hr. The maximum size of the lumps charged to them ought not to exceed 600 x 900 mm. Initially, the crushers will be equipped with cones breaking the material into pieces of 130 mm. By mounting different cones, the material may be broken into larger lumps, or by adjusting the crusher, sizes of 0-80 mm may be achieved. The crushers are equipped with ball bearings; ca 80 H.P. are necessary; 130 H.P. motors have been installed. The power transmission is by wedge belt gear.

The material which issues from the crusher comes upon a rubber conveyor 800 mm wide and about 35 meters long, measured from axis to axis, ascending at an inclination of about 17 to 20°. The driving power of the conveyor is ca 10 H.P.

(d) Sieve House I

The equipment in Sieve House I serves for separating out the fine shale of less than 10 mm mesh size, since it is not suitable for carbonization. The

conveyor which transports the material from the crusher throws it over top via a conveyor upon a distributor plate conveyor 1400 mm wide and about 34 m long from axis to axis. Below the conveyor are three identical rotary swinging sieves (vibration sieves) 1400 mm wide and 3500 mm long. The machine contains exchangeable bottom, the meshes being 10 mm squares. The sieves are arranged in such a manner that about one third of the coating may be replaced by so-called slate-removing grates which serve the purpose of passing the laminar and scaled off material up to a size of about 40 to 5 mm Ø. These slate-removing grates may be mounted in a very short time. The performance of one sieve is ca 90 tons/hr., so that two sieves must be always in operation, the third sieve is in reserve. Upon the distributor conveyor are two adjustable and removable separators which serve for exchanging the sieves. They are operated by hand-driven cranks via a worm and a worm segment.

The fine material which has passed the sieve is currently discharged via a horizontal rubber conveyor and transported to the shale-fines bin via another ascending rubber conveyor.

The sieve-overflow, that is the material of more than 10 mm mesh size, is recovered by means of two countercurrent rubber conveyors and brought upon a rubber conveyor which transports it to Sieve House II.

The underground part of Sieve House I is constructed of cement, the aboveground part, masonry.

(e) Shale-fines Storage

The shale-fines separated in Sieve House I are transported off by the above mentioned rubber conveyor and dropped in the shale-fines shaft, but on a distributor. This distributor dumps the material all over the entire length of a subterranean bunker. The shale-fines bunker is provided with a continuous discharge slot which is shut by bent racks. A rubber conveyor is installed below these racks. The flow of material is regulated by an adjustment of the racks. The above-mentioned horizontal rubber conveyor is annexed to an ascending rubber conveyor, which ascends to such a height that it can dump the material directly into the box cars via a chute.

Only the subterranean part of the shale-fines bunker is made of cement; the above-ground part is protected by a wood casing and a roof.

The bunker has a capacity of 65 m ^{3}, that is, it holds the fines produced in one half-day's operation.

(f) Sieve House II

The rubber conveyor mentioned in section D transports the utilizable coarse shale into Sieve House II, throwing it upon a chute, from which it is distributed upon the sieves. The sieves are coated with a round-wire mesh, the size of mesh being 35 mm square. The material which falls through the mesh(10-35 mm) is recovered in a subjacent bin of 75 m^3 capacity. The material remaining upon the sieve is transferred at first upon a rubber conveyor and then into a storage bunker of 100 m^3 capacity. The above-mentioned conveyor is operated by hand. The bunkers are emptied by means of continuous slots having hand-operated choking-rack traps. The material issues from the bunkers upon horizontal rubber conveyors of 800 mm width , which are joined to two ascending rubber conveyors which are also 800 mm wide. These ascending conveyors rise to such a height that the material can be dropped into boxcars via a chute.

(g) Shack for Ignition Material

The ignition shale of 35 mm maximum grain size is dumped in such a manner that it may fall through the chute either into a boxcar or upon another belt, which brings the shale into the ignition material shack. In this shack, dumping lorries run upon wooden bridges, are distributing the shale uniformly all over the floor area of the shack. In this manner, a 450 ton capacity may be achieved. The stored ignition shale is brought to the dumping boxcars which run on tracks, built parallel to the longitudinal axis of the shack.

General Observations

Owing to local conditions the various buildings (Sieve Houses I and II, shale-fines bunker, ignition-shale shack) may have to be arranged in different manners and may lie at different levels. Thus, it may happen that the connecting conveyors may reach some of the houses at the front side, or may reach or leave them vertically. Therefore, the description which has been given above must be suitably adjusted to local conditions, but the interior installations will remain unchanged.

In arranging and selecting the individual conveyor elements, attention must be paid in particular to the effects of the weather. The sieves, being particularly sensitive, must always be installed in roofed rooms. All the conveyors which connect the individual buildings are made of rubber. The lower half of them lies nearly everywhere in an indentation, sufficiently protected against wind and storm. The parts of the conveyor which lie above the level ground are placed either upon an earth embankment or upon a simple bridge provided with a sideway. In order to prevent storms from dislocating the upper conveyor part from the supporting rolls protective sheets of metal are placed at both sides of the conveyors at the upper parts. But, at present, we did not yet plan to build roofs over the conveyors which run in the open.

At very low temperatures, the grease in the bearings may thicken and the rubber bands may freeze to the supporting rolls, causing difficulties in starting. For this reason, particular attention must be paid whenever the conveyors are started up in wintertime.

The capacity of the bins in Sieve House I has been determined taking into consideration the rail traffic. In this house, more ignition shale may be stored than is required for one day. Larger quantities must not be stored because of the warlike conditions .....

III. Pile Fields

General Observations Concerning Carbonization in Piles

Heaps of the sufficiently broken and graded shale are charged; they are burnt from the entire surface area inwards. This can only be done when the evolving gases are sucked off at the bottom. This is being done by blowers which suck off the gas by means of grate pipes lying below the pile.

The hot combustion gases evolving during the process pass the pile, traveling from the outside to the center and to the bottom, and heating up the layers in the interior, so that the volatile and liquid oil fractions separate out and are carried off with the gas stream. The residual solid carbon is burnt in the traveling combustion zone and provides the heat required for the advancing carbonization zone.

The carbonization zone travels in the direction towards the grate. When the carbonization is terminated, if possible, before the combustion zone has reached the grate, the operation of the pile is discontinued, that is, the suction blower is stopped.

For this type of pile operation, shale lumps of 10 to 20 cm are most suitable. The surface of the pile must be covered with finer shale granules of 1-3.5 cm size and with peat mixed with sawdust. This ignition material ought to be as dry as possible. The peat is supplied by the central reduction unit, in pieces of about 6-8 cm. The wooden ignition material is supplied by the central wood reduction unit in the form of compressed excelsior bales, the fibres being 5-10 mm wide and 0.3-0.5 mm thick. Twice, namely, when half of the pile has been charged, and again when the construction of the pile is terminated, the corresponding quantities of ignition shale, peat and wood are brought to the pile and distributed by hand tools all over its surface.

The temperatures in the interior of the pile reach 1000 to 1100°C. Two or three days after terminating the carbonization process the surface has cooled down sufficiently so that one may step on it or lay tracks on it.

Travelling Pile

In order to avoid removing the carbonized shale, a process has been developed where the burnt out piles are left "in situ" and the location of the carbonization is moved from place to place. Instead of fixed suction ditches, perforated tubes are installed and the pile is heaped above them. These pipes are connected with the suction line which is supposed to convey the gas to the blowers.

When the ignition has been sucessful, the carbonization is carried out as described, until the combustion zone is only at a short distance from the grate. This moment may be deduced from the temperaturesof the gas which reaches ca 150 to 200 degrees when the carbonization is terminated.

When the carbonization process is terminated, the perforated gas pipes may be pulled out from under the pile and used for erecting another grate over which a new pile may be heaped. The pipes may be used many times.

Whenever the pipes are shifted, alterations become necessary in the pipe line, which connects them with the blowers.

For transporting the shale to the piles, ~~cranes~~ conveyor belts or narrow gauge railways may be used. This plant actually uses only narrow-gauge railways.

The trains bring the charge to the piles, dumping it, whilst the cars are standing either upon an embankment (the slope must be as high as the pile) or upon a slope cut out from a natural hillside. That means that the tracks follow the traveling pile field. The second half of one pile and the first half of the next one are constructed every day. The pile which is finished one day is ignited the next day.

The charging starts at the terminal of the tracks. The length of the road to be traveled becomes thus shorter by one pile length, whenever a new pile is ignited. When a series of pileshas been charged, that is, when the eighth pile has been built, the ninth pile will be erected, the charging train cars standing upon the first pile, shale for the tenth will be dumped from the top of the second, for the seventeenth from the ninth. When a new set of piles is

started, the trains run past the actually burning piles, either upon the embankment or upon the cold piles of a prior set. Three piles are always simultaneously in operation.

How much time it takes to build a pile, depends upon the volume of the pile and upon the shale supply available. The Wuste Plant decided that the volume of shale required for one pile should be the same as the diurnal production capacity. That means that every day one pile must be built. That takes 12 to 15 hours. With a carbonization velocity as chosen, the carbonization period is 72 hours. These lengths of time, in connection with the rates of performance, result in given conditions which determine the nature of the layout of the entire pile field. The carbonization periods can not be altered at will; otherwise the load on the blowers would become non-homogeneous. Without disrupting the operation of the blowers, the carbonization period can be shortened or lengthened only by one or several units of 24 hours. From this period and from the number of piles in operation we may infer the cooling periods available, until tracks can be laid again.

"Cooling Period" is the length of time which will pass from the moment when the carbonization of a pile is terminated until a train can run over this pile, dumping from its top shale for a fresh pile of the next set.

Since a given "cooling period" must be available (it must be possible to step upon a burnt out pile and to run trains over it) 8-pile sets have been decided upon at the Wüste Plant.

Work is started by laying the tracks along the longitudinal part of the field, up to the very far end of the row of piles and by dumping shale in a width of 41 mm from the cars. Each of the trains contains eleven 4 m^3 box cars, transporting 50 tons of shale. Whenever three train-loads have been dumped, the dumping spot is shifted about 30 cm. In order to handle the diurnal output, one train load must be dumped every 24 to 30 minutes. Under these conditions 22 train-loads of graded coarse shale, 1 train load of ignition shale, and 2 one-half trainloads of peat are necessary. When the construction of the pile is terminated, a layer of igniting shale and peat and sawdust must be distributed all over its surface. This can also be done in two parts, facilitating the distribution of the igniting material.

Before the erection of a new pile is started, the set of pipes consisting of the suction pipes and the main pipes must be moved ahead (confer below).

A main pipe has been installed at the new place in the meantime. The suction tubes have been pulled out from under a burnt out pile by means of a special apparatus and the building of the new pile can now be started from the slope, by dumping the shale and pressing it into shape.

The second set of piles is built in the same manner as the first one.

An earth or rubbish embankment must be built at the end of the field to accommodate the tracks which run at first obliquely and then in the form of a curve. Thus, in the course of time, an embankment 75 cm wide on which the tracks run in a curve 70 mm/m, is formed at the edge of the field.

When the entire field is filled with piles in this manner, another layer of piles is built on top of the first piles; all the connecting pipe lines between the main pipe and the chief recovery circuit must be brought ahead again, with that difference only that now they lie at a level which is 3 miles higher than the original one.

A new initial embankment, three meters higher than the first pile, must be erected in due time. From upon this higher embankment the dumping operation is started all over again, in the same manner, as for the same layer.

When the available area is nearly covered for the second time, a given width of area must be left free for the pulling out of the suction pipes and taking them away.

On top of the second layer a third and fourth one may be built; how many of them there may be, will depend upon the fact, how many layers can be supported by the underlying burnt out piles.

The "chief recovery circuit" ought to be always left where it is, under all circumstances. Only the connecting lines undergo changes; with every new layer, a new length of pipe is added, directed upwards in a slant.

Wherever the oblique line meets the horizontal line, a knee joint is installed.

Dimensions of the Pile, Piping

Volume of the pile: 1500 tons; height: 3 inches; length depends upon the length of (?) limited 41 meters by the length of the actual piles. This corresponds to a width of 11 meter. The manner of dumping the shale causes the longitudinal and transversal cross section of the pile to be of the shape of an oblique-angled parallelogram.

There are 17 - 18 suction pipes. They lie across the entire width of the pile about a.35 meters apart. These pipes are 12 meters long, thus they protrude 2 meters from the wide side of the pile. Each of suction pipes has a 0.35 m diameter and weighs about 1000 kg.

The main pipe lies exactly parallel to the length of the pile. It's diameter is 1.6 meter. It is constructed in three parts. Each of the one third pieces weighs 4 tons. Since the form of pipe lines is given and likewise the angle of the charge, the form and dimensions of the piles are given, too.

Since with this method, there are always 8 piles in operation at the same time, it is necessary to have a supply of suction pipes, main pipes and connecting pipes for eight pipes and the entire chief recovery circuit available at any given time. From each of the main pipes which lie under the piles, leads a connecting pipe line to the chief recovery pipe line. This connecting line consists mainly of the same number of 11-meter pipes as thenumber of rows of piles, which can be placed, side by side, on the width of the field. One of these 11-meter pipes is removed whenever a new row (or set) of piles is started when the pile field is gradually filled with rows of piles, the connecting lines become shorter and shorter.

The main pipe is placed at the bottom of the pile, the hind end being 1 m off the edge of the old slope. There are slits in the suction pipes at their end parts (for three meters). The number and size of these slits has been determined in such a manner as to prevent a measurable pressure drop from occurring in this part of the pipe.

Most of the suction pipes are provided with compensation shafts (Kompensations wellen) which facilitate a sidewise motion of the pipes when the main pipe expands.

The pipes with shafts are to be used mainly at the outer sides, those without shafts at the inside (center of pile), where the load is not so heavy.

The pipes connecting the suction pipes with the main pipe are equipped with simple throttle valves, which serve for adjusting the suction performance of each of the pipes according to the temperature of the gas. The temperature is measured with thermomenters placed into strongly fortified cases mounted in screw sockets which are to be welded to the suction pipes at the spot. Four sets of thermometers have been provided for, three of which will be in service, whilst the fourth will be used at the pile at any given time, is fixed up to start operation next.

Initially, it had not been planned that connecting elbow pieces would be used for connecting the outermost suction pipes with the main pipe. Connecting pipes with fixed throttling valves have been supplied. They must be installed at the building place, in accordance with the blue print.

The main pipe is fitted for the mounting of connecting elbow pieces on both sides. All the pipes used at the pile field and for the connecting pipe line leading from the pile field to the condenser unit — excepting the suction pipes-- are provided with loose flanges to facilitate the installation work. At the end of each connecting pipe line, that is, ahead of the "chief collecting circuit," the following instruments are installed: 1 gas meter, instruments for measuring negative pressure and temperature, an oxygen meter and a compensator registering the longitudinal expansion in the connecting pipe line.

The registering measuring instruments are mounted in portable cabinets which are placed upon sonsoles soldered to the "chief collecting circuit." The measuring lines are heated. The condensation-water drain must be watched, so that its regular operation is not upset.

Four measuring cabinets will be supplied. Three of them will be simultaneously in service, whilst the fourth will be connected with the fourth pile which will be under construction at any given time, whilst the instruments used at the first pile will not yet be available for further use. Below the measuring diaphragm is a detour-circuit with an opening for cleaning purposes which makes it possible to transfer the raw products which are recovered in the connecting line from one side of the measuring dial to the other.

These lines must be filled with water before operation is started.

The cabinets are made portable, in order to protect them from shocks. In cold weather, the heating system of the cabinets must be in good working condition; otherwise, the valuable measuring instruments would be imperilled.

At the end of each of the connecting lines, moreover, a junction for a movable blower which may be shut off by means of a slide valve, has been mounted. During the first two to three hours of a carbonization period, the non-combustible gas is sucked off through these blowers.

At the end of the connecting line, immediately ahead of the chief collecting circuit, moreover, there are shut-off slide valves, controlling the sucking-off rate of the pile gases.

The "Chief collecting circuit" is heated by an interior steam pipe. Devices for draining off the evolving water are provided for at suitable intervals. The chief collecting circuit leads directly to the condenser unit (electrical gas purification). Most of the pipe lines are provided with movable flanges which facilitate the installing of connections. Asbestos lined steel rings are used for sealing leaks. If they are carefully handled in mounting and dismounting, they may be used four times. The connecting pipe lines and the chief collecting circuit are provided with manhole sockets at suitable intervals, so that the pipes are accessible and may be freed from sludge.

The connecting pipe lines and the chief collecting circuit are laid upon cement ties armed with angles. At those spots where a backward drop of the pipe line, countercurrent to the gas stream, could not be avoided, drains have been built at the lowest spots of the chief collecting circuit (Building 52). At these drains, the gas circuit is equipped with sockets, which open downward and are immersed into the liquid to a depth sufficient for sealing them against the air. The products recovered at this place are transported via a special product pipe 1,006 to the condenser, if necessary, by means of two pumps. In all cases, such a drain is provided for at the end of the chief collecting circuit, namely, at the electrical gas purifications (Building 90).

Outside of the pile field proper, parallel to the chief collecting circuit, lie the tracks for the cars carrying the movable blowers. The blower together with its drive is mounted upon a car of 900 mm track gauge. This blower is connected by means of a movable connecting circuit to a special socket of the connecting pipe line, provided for this purpose. The socket in question is closed by a slide valve. When the blowers are shifted from one line to the next, both slide valves are used.

Along the tracks stands a row of poles carrying the wires which convey the electrical energy to the movable blowers and to the measuring instruments in the cabinets, and also the wires for the direct current used for charging the electro magnetic cranes.

The movable blowers are connected by means of clamps, the instruments and batteries with plugs. These tracks serve also for transporting the pipes which become available on the pile field, to their new destinations.

Arrangement of the Piles

Piles may be arranged in blocks or rows. This plant has them arranged in rows. The carbonization fields may be built on level ground at units 2, 4, 5, 6, 7, 8 and 10. Terraces are foreseen at units 1, 3 and 9. When we start with a level-ground field, terraces will evolve when the second and third layers of piles are constructed.

Level Field

A level ground may be available or the ground will be leveled. At the longitudinal side of the area, an embankment is constructed or a step is cut into a natural slope for the first tracks. The length of the track bed corresponds to the sum total of the lengths of eight piles plus their slopes. That means, it is 8 x (41+ 2 + 4) = 336 m (sic!)

The width of the total field depends upon the available area.

Along with the area required for the piles a strip of ground must be left free between the piles and the chief collecting circuit. On this strip of ground the pipes are drawn from the last row of piles. Outside of the chief collecting circuit a strip of ground must be leveled for the tracks upon which the moveable blowers are transported. This strip may be on a somewhat higher or lower plane. In the course of time, step by step, a terrace stair-like configuration will evolve, starting with the chief collecting circuit, which will form the base-line.

We must take into account that the piles will settle, more or less, in accordance with the quality and size of the shale. In this case the surfaces must be levelled.

Terrace Arrangement

This is a special case of the level ground arrangement.

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IV. Condensor Unit and Subsidiary Units

The carbonination gas issues from the piles and comes, via the chief collecting circuit into

The Electrical Gas Purification Unit

This unit consists of 5 (and later on 6) filters with a rectangular cross section and the corresponding high tension unit in which the incoming rectary current is transformed into direct current of 60 - 80,000 revolutions. The gas enters the filter at the bottom and leaves it at the top. The drive goes through two connecting pipes equipped with a slide valve NW 600; the connecting discharge pipe has NW 800. Thus, it is suitable to use the discharge slide valve for regulating the gas stream.

The separated tar and the condensed water (if any) accumulates in the bottom part of the filter and issues from it through immersion pipes into the ditches which are located below the fileters. The immersion pipes are immersed to such a depth that one can operate with a negative pressure of 1500 mm water column or with a 500 m water column gauge pressure in the filter, without risking a break-through.

This ditch is constructed of masonry or cement, and it is lined at the inside with hard-burned bricks. Attention must be paid to sealing the seams, in order to prevent the structure from being corroded by the acid constituents of the oil.

In this ditch is installed an overflow tube with a siever which retains any asphalt particles which may float upon the raw product which issues from the filter. The raw product which passes the sieve flows under the power of gravity through a heated pipe line to the raw product ditch near Building 11. These ditches must be cleaned from time to time, using scrapers. A masonry border of the ditch makes it possible to shovel off the raised sludge or drained asphalt. The ditches are steam-heated. The heating tubes are simply suspended; there are no iron clamps or clips which would penetrate the masonry lining. The heating tubes must be checked at regular intervals, since they are subjected to corrosion.

When operation is started for the first time it is necessary to fill the receivers below the filters with water.

From here streams the gas to the

Building 10, Blower Unit

Each unit is equipped with three blowers, which are constructed for a performance of 20,000 $Nm^3/hr.$ with a total rise in pressure of 1400 mm water column, at a temperature of the gas of 65°C. and a density of the gas of 1.37 kg/Nm^3.

One of these blowers is held in reserve. But it is possible to use occasionally also a third blower, when there is a perceptible peak load. Attention ought to be paid to the fact that the load must not exceed 40,000 m^3/hr, since otherwise the yields go down.

The blowers are installed upon fundaments in the open air; they are separated by protective walls(*).....

(*) The text goes on discussing the servicing of the blowers, the construction of the raw-produt receiver, the pumping of the raw product into the settling vat or the phenol water receiver, respectively.. The duplex tar-oil container is steamheated; any residual water separates out.

The gas flows from the blowers to the

Combustion Furnaces

After having passed the blowers, the gas contains hardly any oil. It is saturated with moisture. Therefore, the interior of the gas line leading to the blowers and the furnace must be corrosion-proof (H_2S - content).

If possible, the water condensing in this part of the furnace ought to flow with gas stream into the furnace. Where the gradient can not be arranged in this way, a device for removing the water from the pipe line must be installed directly behind the blowers. Never must condensate be allowed to return into the blower.

All of the three furnaces are equipped for the atomizing of phenol water. Attention must be paid that the temperature of the gas stream at the end of the phenol evaporation must not drop below 800°C. For, otherwise, we may not expect the phenol to be totally consumed.

Boiler House

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Dams Built for the Industrial Water

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Storage Unit

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M Beth

M. Beth

MB:dj

dc: Mr. E. C. Herthel
Mr. H. L. Pelzer
All Division Chiefs

Mr. A. E. Miller (25)

SINCLAIR REFINING CO.

July 30, 1948

Translation Book #174
Reel 113
Document 10, Item I

Dewaxing of Crude Oil with Solvents in the Liquid Phase for the Production of Cold Resistant Oils

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Report by
Dr. J. Moos

General Part

Petroleum is a complex mixture of hydrocarbons of very different chemical compositions, different structures and different molecular gravities (when we disregard in this content the unimportant fractions of O-, N-, and S- compounds). The liquid constituents keep the solid ones in a solution at the normal temperature.

The multimolecular hydrocarbons which on cooling settle out of the oil in a solid state, are called paraffins. This fraction amounts to 0- 45% by weight, depending on the fields from which the oils come (Baker oil has hardly 0.5%; Burma and Rangoon oil more than 45%).

One of the basic operations used by the petroleum technicians is the fractionating of paraffin-containing mineral oils and the separating out of solid paraffinic components. For this purpose, the crude oil is normally subjected to a distillation - - the paraffin becomes thus a part of the higher boiling oil distillates and of the residual oil - - and the products obtained are refined. Three different aims are intended to be attained thereby.

(a) The recovery of the solid paraffinic hydrocarbons of the "paraffin", in the technical meaning of the word, and the optimum separation of the liquid hydrocarbons.

(b) The separation of paraffinic constituents having a higher solidification point from the liquid hydrocarbons for the purpose of obtaining cold-resistant oils.

(c) The isolation of paraffinic constituents in the widest meaning (the liquid paraffinic hydrocarbons as well as those which are solid at normal temperature) by removing the non-paraffinic constituents.

Operation (a) has been familiar for the longest period of time. It is briefly called "dewaxing," and used in laboratory and commercial-scale processes for many decades. This process is so interesting because the paraffin is used in many technical operations. Lately even valuable lubricants are prepared by cracking and polymerizing paraffins; fatty acids are prepared; paraffin is an auxiliary in the preparation of explosives. The modern motor industry needs lubricants of a higher order of refinement, in particular, regarding their viscosity and solidification point; it became imperative to manufacture oils which at extremely cold temperatures are still sufficiently liquid and do not separate out any solid constituents, which would hamper the circulation of the oil in tube lines. Indeed, the suggestion has been made to inhibit the settling out of paraffin by the use of highly polymeric additives (paraflow); but dewaxing is yet unavoidable, since these substances are ineffective when the oils have a higher paraffin content.

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Principles of Dewaxing

The basic principles of the dewaxing process have remained substantially unchanged in the course of time. By lowering the temperature, the hydrocarbons having higher solidification points become of lower solubility; they separate as solid bodies from the liquid hydrocarbon solution in which they had been dissolved. At first, this new phase is confronted with certain evolutional difficulties. When these impediments are overcome, nuclei are formed which grow to form larger individuals. How many nuclei are formed and when saturation is reached (these factors are essentially controlled by the speed of cooling and the temperature to which the oils are cooled and by the concentration and the nature of the solvent) determine the numbers, sizes and forms of the settled-out paraffin particles. Impurities which are present in colloidal solution (e.g. asphalt, resins) can seriously interfere with the settling-out process by altering the interface tensions between the solid and the liquid phase. In those methods which aim at producing paraffin crystals they will have to be removed before the dewaxing phase starts. If they would not be removed, they would also disturb the filter processes by obstructing the pores of the filter.

However, there are difficulties in the dewaxing of crude oil not only because of the presence of inhibitors* but also because the paraffin which has been separated out by cooling permeates the entire body of viscous oil, so that the oil will gel. In order to avoid this difficulty, oil distillates are prepared usually converting the material into a crystalliferous state**; and the dewaxing process will take place only after a treatment with sulfuric acid and/or bleaching earth.

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* Isoparaffin mixtures containing molecules of various sizes will not readily crystallize; the crystallizing properties of narrow cuts are better. Long heterogeneous molecules with side chains do not readily combine to a space lattice; thus there is a tendency towards forming amorphous material.

** In infrequent cases refining methods are used which are not so economically profitable, e.g. with sulfuric acid or by adsorption.

In order to facilitate the separation of paraffin and oil, the viscosity of the oil distillate is reduced by diluting it with benzine (naphtha); the paraffin will settle out by the effect of gravity, if the solution is cooled and allowed to stand.

This "cold-settling process" is nowadays hardly any more applied. The sedimentation of paraffin will be accelerated, if the more effective centrifugal force replaces gravity.

In the Charples-process, for instance, the oil which has been diluted with benzine, is conducted to fast-moving separators (17,000 rotations/minute); the paraffin settles out at the mantle of the centrifuge and removed by means of a scraper. In contrast to the filter methods, amorphous paraffin (1) is used in the centrifuge method. It is indispensable to cool it slowly, the difference in temperature between the cooling medium and material to be cooled must be considerable.(2)

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(1) In the filter method, paraffin settling out in a micro-crystalline state as "amorphous" material, would form a soaplike coating on the filter cloth impeding the filter process. In the centrifuge process, the average density of the paraffinic material must be greater than that of crystalline paraffin. Moreover, the paraffin must be of sufficient plasticity so as to bend around the centrifuge

insertion and to issue from the centrifuge. Moreover, now and then the paraffin will settle at the wall of the centrifuge, thus disrupting its operation. By choosing a solvent of suitable density we can make sure that the paraffin will settle at (.2.2) and not at the walls. In this case it is not important in which state the paraffin will settle out.

(2) Shock cooling is generated by changing pressures and temperature in the cooling zone.

If the distillates are of high viscossity, the paraffin is frequently separated by means of pressure filters, if necessary, at higher temperatures, yielding hard and soft paraffins. This type of paraffin contains still some oil, part of which at least is removed by a subsequent thermal treatment, the so-called sweating process. It is not yet usual to use selective solvents for the removal of this oil fraction. This paraffin fails to settle out quantitatively from an oil solution diluted with benzine. Therefore, the oil which is thus obtained, is of a rather high solidification point. That is why we are looking for substances which are poor solvents for paraffin in the cold. Many of such solvents have been patented; but in many cases, they do not live up to expectations.

For this reaseon, combinations of solvents have been used. One of the components is supposed to dissolve and to dilute the oil, the other one shall "precipitate" the paraffin.

Commercial Dewaxing Methods

As an instance of a dewaxing process using one solvent only, along with the Charples process, we may mention the En-Tri-process (Separator Nobel) which uses tri-chloro-ethylene. Since the solvent is of high density, centrifuges of lower velocity (2,000 to 3,000 rotations/minute) may be used. The paraffin separates out in the interior of the centrifuge. Since tri-chloro-ethylene dissolves asphalt, also residual oils which contain asphalt may be dewaxed by this process.

In the propane process, which enjoys increasing popularity, propane is used which has been liquefied under pressure. Its dissolving power for paraffin and asphalt is surprisingly low; it is of a very low viscosity.

A mixture of solvents is used in the benzol-acetone-process. Toluene lowers the melting point; dilute benzol dissolves the oil; acetone precipitates the paraffin. The paraffin may be removed by means of roller rotary filters, which are suitable also for other dewaxing processes.

In the Barisol-process, benzol is used for dissolving the oil and 1, 2 - dichloro-ethane for precipitating the paraffin.

In the Edeleanu-process benzol is combined with sulphurous acid, liquefied under pressure.

The disadvantages inherent in all the ordinary dewaxing processes are obvious. The costs for cooling agents and equipment (filters — suction and pressure filters — or centrifuges) are high; the cooling process is hard to control; the separated paraffin has a corroding effect upon parts of the equipment; the solid phase is hard to separate from the liquid phase, in particular, so whenever amorphous paraffin appears in the filter process or crystallized paraffin in the centrifuge process. In treating oils rich in paraffin it is necessary to use considerable amounts

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of solvents, in order to attain an economically profitable rate of throughput. If the separated paraffin is of an unsuitable structure, it may mechanically occlude considerable amounts of oil, or it may adsorb it; this property results in losses of oil and a lower-grade paraffin. For certain purposes, paraffin must be as free from oil as possible.

Dewaxing in the liquid phase

These difficulties would disappear if we could succeed in finding a solvent which displays, at temperatures above the melting range of paraffin, a selective behavior with regard to oily substances of a paraffinic and non-paraffinic nature, on the one hand, and with regard to paraffinic hydrocarbons of a higher or lower solidification point on the other hand. In the first stage, we should have to carry out an extraction at a high temperature, using a solvent or a mixture of solvents, separating two liquid phases; one layer would contain an inconsiderable amount of solvent and all of the paraffinic substances, and another layer would contain most of the solvent and the non-paraffinic constituents.

In the second stage, the mixture of paraffinic substances thus obtained, would be further separated into hydrocarbons of lower and of higher solidification points, using another solvent or another mixture of solvents at a high temperature.

Whereas the first-stage solvent is supposed to effect a separation based on chemical properties, the second-stage solvent would have to effect a separation based on differences of a physical nature.

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(1) By the concept of "lower and higher solidification point," we want to contrast those hydrocarbons which are liquid at the operating temperature and those which are solid. The boundary line between both groups is variable, depending upon external circumstances.

Specifications for the solvent

Ideal solvents for the dewaxing in the liquid phase ought to meet the following specifications:

1. They ought to enter into a quantitative solution with the substance to be removed (1) at the operating temperature (above the melting range of paraffin); but they ought not to dissolve the other constituents (2).

2. At a temperature which is higher than the operating temperature, all the paraffinic hydrocarbons, even those of higher solidification points, ought to be dissolved, so that any asphalt that may be present can be separated out before the extraction begins.

3. The solvent ought to be easy to recover from the raffinate and extract solution and easy to separate from water (distillation, washing).

4. The paraffin and the hydrocarbon oil obtained at the extraction ought to be of high quality.

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(1) In the first stage that would be the non-paraffinic constituents, in the second stage, the liquid hydrocarbons.

(2) In the first stage, paraffinic hydrocarbons; in the second stage, paraffinic hydrocarbons of higher melting point.

5. Its gravity should be as different as possible from that of the paraffinic substances.

6. The solvent ought not to react chemically with paraffin and oil.

7. It ought to be non-corrosive, neither poisonous nor inflammable nor harmful to the skin; pressure equipment ought to be unnecessary.

8. The solvent ought to have thermal stability and

9. faborable thermodynamic properties.

The price of the solvents is of secondary importance, in the dewaxing process, because it can be recovered. The price of a chemical will drop, whenever it is used on a commercial scale, for ways and means of manufacturing at lower cost will be found.

We do not know of any solvent which would conform to specification 1. Scientific literature fails to offer useful suggestions.

Only Poole (1) and his co-workers made solubility studies, measuring at the the same time the solubility of dewaxed oil and paraffin in one and the same solvent; and so has Heinze-Goebel (2). But Poole's measurements of oil and paraffin, and Heinze-Goebel's measurements of paraffin, comprise only a small range of concentrations. Heinze-Goebel's measurements do not warrant a comparison of the values (3) obtained for oil and paraffin. Therefore, their findings are not of interest in this study.

(1) Poole and Co-workers: Ind. Eng. Chem. 21, 1098 (1929)
23, 170 (1931)
24, 1215 (1932)

(2) Heinze-Goebel; Oel and Kohle, 38, 470 (1942).

(3) Since the data for these are missing, it is impossible to make an exact conversion.

Aim of Project

We planned to make a quantitative and qualitative study of the dissolving power of organic solvents of all kinds for a definite oil and paraffin; and we shall, at the same time, try to find a solvent which can be mixed with oil, without dissolving paraffin at the same temperature. Moreover, we shall investigate, within this framework, whether the selective property in separating the two components can be changed and if so in how far. Attention had to be paid to the problem, whether there is any interrelationship between the chemical composition of the solvent and its dissolving power with respect to the liquid or solid hydrocarbons. If it would turn out that there is such an interrelationship, it might be possible to manufacture "tailor-made" synthetic solvents having definite properties.

The Problem of Solubility

Several attempts have been made to clarify the basic problem of solubility. Some attempts have been made to interrelate the order of magnitude of solubility with properties which would permit of inferences regarding nature and dimensions of the partners in the dissolving process, such as vapor pressure, boiling point, melting point, dielectric constant, total dipole moment, internal stress, hydrogen bridges, etc. But it has been found out that there does not exist such an unequivocal interrelationship. We must not even try to draw general conclusions with regard to solubility from the presence of certain active groups in the molecule.

The mixing process is a molecular phenomenon, an interation between the molecules of the solvent and those of the substance to be dissolved. The result of this process depends upon the effective intermolecular forces which originate in the atoms and molecules which consist of electrical elementary units, and which are in general formed by three overlepping forces, the directive, inductive and dispersive forces. The molecules being very tightly packed in liquids, the volumes and forms of the molecules exercise important effects. If the dipole is free and easily accessible in a polar molecule, the interaction will be of a different order of energy than when the dipole is located in the interior of the molecule. If an individual molecule consists of two groups different in kind, a change in the size of one group effects a substantial change in the nature of the other group, particularly, if it is a polar group. The magnitude of the interaction energy is a decisive factor in the rate at which intermediary supermolecules are formed in the solute. At present, we can understand only in the case of simply structured substances, how a change in the chemical nature of the molecules of a solvent will effect the intermolecular forces acting upon the molecules of the substance to be dissolved, thus changing the rate of solubility. Therefore, the solubility of oil and paraffin in diverse solvents must be studied experimentally.

The solubility problem "per se" is only of secondary importance for the following question. It is of decisive importance that the difference in the solubility of the paraffin and oil which are to be separated be as great as possible in the solvent in question. The difference in temperature between both solubilities is a gauge for the separative power of the solvent, for its selectivity. This property is also of interest when paraffin is to be freed from oil by means of solvents; the absolute values of the solubility of oil and paraffin are of particular interest when it is a matter of removing paraffin settled in plummets and pipe lines by dissolving it; since, in laboratory operations, e.g., analyses, extraction tests with oily porous rocks, etc.

Special Part

Experiments.

Oil which contains paraffin may be considered to be a two-component system, consisting of oil and paraffin. If a uniform solution is supposed to evolve when we mix the paraffin-containing oil with a solvent, we must choose a temperature above the solubility threshold of each of the components at the given temperature. On the other hand, cooling results in a separation whereby, at first, the least soluble component, paraffin, settles out in solid form, or in liquid form if the temperature is still of sufficient height. This drop in temperature must not be so great that the system oil-solvent would separate, too; this would be an undesirable effect. The solubility curves of paraffin in the oil-solvent mixture and of the oil in the solvent, mirror this phenomenon. For this reason, this feature had to be studied in our experimental investigation. For simplification's sake, the solubility of paraffin

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in the pure solvent was determined in contrast thereto. The true solubility of paraffin in the oil-solvent mixture corresponds then to values within the limiting range of the solubility curve in pure solvent and the corresponding curve for the solubility of paraffin in oil.

The solubility analysis has been made by the synthetic method. Different amounts of both components which were to be tested regarding their mixibility with the solvent, are introduced into small well-dried test tubes, which are thereafter stoppered, avoiding the admission of mixture; with more volatile substances, the tube is melted right above the level of the liquid, without leaving too much space for a vapor area. By immersing the tubes into baths of various temperatures, the temperatures were determined (1) at which separation starts (the appearance of small crystals or droplets) (2).

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(1) When a heating tube explodes, the spattering of the heating liquid may cause accidents. The experimentor ought to protect his face with a kind of welder's mask with an unbreakable sight glass.

(2) When the liquid phase separates, the substance becomes opaque; the temperature which prevails at the moment when the scale of a thermometer adjacent to the test tube, becomes invisible, has been recorded.

The separation temperature temperature could be determined to ±0.1°C. In this manner we found a great number of new values for mixtures.

The substance had to be of high purity; water-soluble compounds had to be free of water, for even slight impurities may falsify results.

For the solubility analyses we used a highly dewaxed

spindle oil . . . . solidification point - 62°C.
flash point 172°C.
and
hard paraffin melting point 51.5°C. (1)
boiling range 200-220°C. at
1-2 mm Torr.

Commercial solvents were brought to the necessary degree of purity, but most of the solvents used were prepared synthetically.

In selecting the solvents, we kept in mind the specification that the melting point of the solvent must not hinder the measuring (2) of the rate of solubility and that the height of the vapor pressure of the solvent must not prevent us from using glass vessels. Circumstances made it frequently impossible to make systematic investigations of interesting groups of substances.

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(1) Measurements made with a synthetic paraffin, the Dotriakontan (melting point 70.5°C.) indicate that, for a paraffin of a higher melting point, the paraffin solubility curves are shifted into a higher temperature range, somehow corresponding to the difference in melting points.

(2) If the solvent is of a higher melting point than paraffin, at first, solvent crystals separate out when the homogenous solution is cooled. A determination of the temperature would in this case indicate the lowering of the freezing point of the solvent. We should succeed in measuring the separation temperature, if the solvent can be cooled sufficiently deep below condensation temperature. But a high melting point of the solvent does not prohibit its commercial use.

Results

A. Organic Solvents

I. Solubility of Paraffin in Oil

The paraffin used for measurements is soluble in spindle oil at the following rates:

Table I

Paraffin in Spindle Oil % by Weight	Separation Temperature °C.
0.6	-20
0.8	-10
1.1	0
2.7	10
7.0	20
21.3	30
50.0	45
93.0	50

For comparison's sake, we have also investigated the solubility of paraffin in a heavier cut of oil, a dewaxed motor oil (8° Engler at 50°C, solidification point -36°C). Paraffin turned out to be less soluble in this oil than in the spindle oil used for the measurements. Since conditions would be more favorable for the measurements in question on using motor oil, because of its reduced solvent power, we have conciously chosen the less favorable spindle oil.

II. Hydrocarbons

On measuring the solvent power of straight-chained synthetic paraffinic hydrocarbons with respect to paraffin, we found the solubility to go down if the C-atom number in the homologous series goes up. Teh selectivity will likewise be lower with an increase in the number of C-atoms; but it is still rather satisfactory even with octane. We measured butane and heptane, made from petroleum, which had been subjected to a careful fractionation (1), and found these products to behave in a manner different from that of the synthetic products.

Table II

Solvent		Paraffin % by weight	Separation temperature °C.
Propane	C_3H_8	32	20
n - Butane	C_4H_{10}	27.5	20
n - hexane	C_6H_{14}	20.9	20
n - heptane	C_7H_{16}	18.5	20
n - octane	C_8H_{18}	16.6	20
n - hexadecane	$C_{16}H_{34}$	9.2	20

(1) Adiabatic rectification head-piece with glass spiral packing.

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On converting the solubility values for paraffin (1) per mol of the various hydrocarbons of the methane series, we found there is a nearly constant value for the same temperature within the homologous series. Our measurements did not show any of those deviations which had been observed by Weber-Dunlap (2). On plotting the results of our measurements, log g paraffin/mol of solvent being the abscissa and 1/t the ordinate, it was found that all the paraffin solubilities measured, up to a mol ratio of 1:1, were lying on a straight line. If we assume on this basis that the gas laws apply to n-paraffinic hydrocarbons (as has been experimentally confirmed by Hildebrand-Swany (3) for a mixture of n-hexane and n-hexadecane) we can, on the other hand, compute the solubilities of other members of the methane series from this straight-line graph.

On comparing the solubility curves th s obtained with those of Weber-Dunlap, which were obtained with a paraffin of 55°C. M.P., it can be seen that, as foreseen, the higher the melting point of a paraffin the lower its solubility. We carried out a measurement with a uniform synthetic paraffin, the Dotriakontan, 70.5°C. m.p.; its results confirmed this assumption.

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(1) We did not plot log mol paraffin, because the mean mol weight of paraffin changes if different solvents and concentrations are used.

(2) Ind. Eng. Chem. 20, 383 (1928)

(3) Journ. Physik. Chem. 43, 297 (1939)

Table 3

Solvent	Paraffin m.p. 51.5°C % by weight	Dotriakontan m.p. 70.5°C % by weight	Separation Temperature °C.
n-octane	17	4	25
	26.5	9	35
	32.5	28	45

With respect to the solubility of paraffin in aromatic hydrocarbons, at concentrations up to 55% by weight, it is less soluble in benzol than in n-hexane. If alkyl groups are introduced into benzol, the solubility increases with the concentration, to a somewhat greater extent for the o-compound than for the n-compound. Both xylenes are of a higher selectivity than n-hexane.

We could not verify the observation (1) that benzol and toluene are of a negative temperature coefficient with regard to spindle oil, that is, that they separate out oil when they are warmed up.

Cyclohexane dissolved more paraffin than n-hexane, whereas the solvent power of benzol is comparatively lower.

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(1) Oel und Kohle 38, 470 (1942) Fig. 9.

Table 4

Solvent	Paraffin % by weight	Separation temperature °C.
n-Hexane C_6H_{14}	45.5	30
cyclohexane C_6H_{12}	51.5	30
benzene C_6H_6	42.5	30

The double bonds are responsible for the lower solubility rate of benzol, as we shall show later on for other compounds.

The solvent power of dekaline is very similar to that of hexane, its selectivity is better; tetraline's solvent power is comparable to that of hexadecane.

Effect of hydrocarbon formation

The following table shows that the double bonds of the benzol are responsible for its poor selectivity:

Table 4b

Solvent	Paraffin % by weight	Separation temperature °C.
Cyclohexane	45.0	25
Cyclohexene	44.0	25
Benzole	27.5	25

Mertens (1) advanced the concept that the solvent power goes up if the hydrocarbon contains double bonds, the sequence being: cyclohexane, cyclohexene, benzol; Table 4b shows that this theory was not verified by our tests.

It was found that the solvent power goes down if the number of double bonds goes up, not only in hydrocarbons but in other types of compounds, too.

(1) Chemie-Arbeit i..o.L. 1944, p.224.

III. Halogen - hydrocarbons

(a) Aliphatic halogen hydrocarbons

Halogen hydrocarbons are the most popular type of compounds in the dewaxing technique. They are used as sole solvents or in combination with other solvents; as paraffin precipitators, in combination with solvents of better solvent power for

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oil than halogen hydrocarbons; as solvents for oils, when they are mixed with solvents of considerably lower solvent power for paraffin than that of halogen hydrocarbons.

Of the substances examined in the course of this investigation, excepting 1, 1, 2, 2 - tetrabromoethane and 1, 2, 3 - tribromopropropane, there is none where the solubility curve for paraffin exceeds the temperature range of the melting points of the solid hydrocarbons in question.

The graphs show that the paraffin-solubility curves are of a similar course, excepting the above mentioned hydrocarbon derivatives, covering a comparatively narrow temperature range (propylchloride and 1, 1, 2 - tribromo - 2 - fluoroethane being the boundary curves). The situation is different in the case of the oil-solubility curves. They cover a large range of temperatures and undergo important changes in form and direction. Different solvents are of different selectivity regarding the oil-paraffin system in question; the selectivity of one and the same solvent will change with the concentration. In comparing the suitabilities of various solvents regarding their suitability as oil solvents or paraffin precipitators, this fact has not always been given sufficient attention.

Substitution of a halogen to hydrogen

If a halogen atom (F, Cl, Br, J) is substituted to a hydrogen atom in an aliphatic, paraffin is less soluble in the evolving halogen hydrocarbon than in the initial hydrocarbon. By comparing the solubility curves of oil and paraffin in hexane and its mono-halogen-substitution products we find n-hexane to be of higher selectivity than n-hexyl-fluoride, but of lower selectivity than Br or J-derivatives hexyl cloride being of equal selectivity.

Table 5

Solvent		Paraffin % by weight	Separation Temperature °C.
Propane	C_3H_8	1	-12
n-propyl-chloride	C_3H_7Cl	1	-0.5
n-propyl-bromide	C_3H_7Br	1	+1.7
n-hexane	C_6H_{14}	21.3	20
n-hexyl fluoride	$C_6H_{13}F$	5.5	20
n-hexyl chloride	$C_6H_{13}Cl$	8.5	20
n-hexyl bromide	$C_6H_{13}Br$	8.0	20
n-hexyl iodide	$C_6H_{13}I$	5.5	20

Effects of various halogens

A comparison of the paraffin-dissolving powers of various halogens shows that in the halogen series fluorine does not hold that place which one would expect it to have corresponding to its atomic volume. For instance, the maximum solubility is found in the chlorine derivate of n-hexane, a lesser one in the bromine body and a still lower one in the fluorine compound. The paraffin-solubility curve of the fluorine compound crosses the bromine and iodine curves, because of the differences in the steepness of the curves. For this reason, the order of sequence may change if concentrations of various hexyl halogenides which differ from those illustrated

in the table, are compared. The selectivity of the fluorine compound is poorer than that of the chlorine, bromine, or iodine compounds.

Our measurements did not confirm the assumptions advanced in the German Patent 699,959 that

(1) the selectivity would be reduced by the substitution of chlorine or bromine in a hydrocarbon, whereas it would be increased by the substitution of fluorine

(2) mixed halogen hydrocarbons, a molecule of which contains more chlorine or bromine than fluorine constituents, would dissolve all oily constituents,

(3) the effect of fluorine introduced into oxygen-free aliphatic compounds is the opposite one of other halogens.

Effects of multiple halogenation

If additional halogen atoms are introduced into a hydrocarbon molecule, the solubility will go down once more, owing to the new substituents, until a minimum of solubility has been reached. If the content of halogen is further increased, the solubility will go up too. Teh selectivity drops with the solubility and rises again after the minimum has been reached.

Table 6.

Solvent		Paraffin % by weight	Separation Temperature °C.
Methyl bromide	CH_3Br	41	30
Methylene bromide	CH_2Br_2	2.5	30
Bromoform	$CHBr_3$	18.5	30
1,1,2 - tribromo -2- fluorethane	$C_2H_2Br_3F$	7	40
1,1,2 - tribromo -1,2- difluorethane	$C_2HBr_3F_2$	25	40
ethylbromide	C_2H_5Br	64.5	40
1,2 - dibromoethane	$C_2H_4Br_2$	37	40
1,1,2 - tribromoethane	$C_2H_3Br_3$	2.6	40
1,1,2,2 - tetrabromoethane	$C_2H_2Br_4$	0.5	40
1,2 - dichloroethane	$C_2H_4Cl_2$	15.5	40
1,1,2,2 - tetrachloroethane	$C_2H_2Cl_4$	42.5	40
n - propyl-bromide	C_3H_7Br	62	40
propylene-bromide	$C_3H_6Br_2$	52	40
1,2,3 - tribromopropane	$C_3H_5Br_3$	2	40
1,1,2,3 - tetrabromopropane	$C_3H_4Br_4$	8	40

With 1, 1, 2, 2 - tetra-bromo-ethane (Table 6) the solubility minimum is probably reached only at a high content of bromine. In this case, measurements are not feasible, because the melting point of the pentabromoethane is too high.

Engel (1) reported that the solubility of homologous hydrocarbons in paraffin increases with an increase in the paraffin substitution; but this statement must be qualified: this increase in solubility will occur only with a high chlorine content after passing through a minimum.

Merten's (2) statement that carbon tetrachloride has a unique position among the halogen hydrocarbons and that its solubility is only like that of paraffinic hydrocarbons, must be qualified for paraffin in that respect that carbon tetrachloride belongs into the halogen hydrocarbon series regarding its solvent power; its solvent power is lower than that of the low hydrocarbons of the methane series and about equal to that of the higher members of this series.

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(1) Petroleum 34. 5 (1935)

(2) Chemie-Arbeiti ..u.L., 1944, p. 225

Mixed halogens

Table 7

Solvent		Paraffin % by weight	Separation Temperature °C.
Carbon tetrachloride	$C Cl_4$	27	25
Tri-chloro-monofluoromethane	$C Cl_3F$	25	25
Di-chloro-difluoromethane	$C Cl_2F_2$	5	25
1,1,2,2 - tetrabromoethane	C_2H_2Br	0.5	40
1,1,2 - tribromo -2- fluoroethane	$C_2H_2Br_3F$	7	40

When bromine or fluorine is substituted for part of the chlorine, the solvent power of the mixed halogen hydrocarbon is determined by the ratio of the different halogens among one another. When fluorine enters the molecule, the temperature coefficient of the oil curve may suffer a "change in sign" (1). When bromine or fluorine are substituted for part of the chlorine, the selectivity will go up, in general.

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(1) Indeed, there is not a real temperature coefficient involved which would originate a second phase.

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Effects of lengthening the carbon chain

It has been observed that a lengthening of the carbon chain results in a decrease in solubility and in an increase in selectivity in the homologous series of alkyl bromides. The decrease in solubility is effected by the preponderance of the hydrocarbon chain, the basic substances of which become also less able to solve paraffin with increasing carbon number (tested up to C_{16}).

On plotting the measured data in a system of coordinates, log g paraffin/mol solvent being the abscissa and V/T being the ordinate, it was found that all the paraffin solubilities measured, up to a 1:1 ratio of mols, were placed on a straight line.

Table 8

Solvent		Paraffin % by weight	Separation Temperature °C.
Methyl bromide	CH_3 Br	41	30
n - propyl bromide	CH_3 $(CH_2)_2$ Br	32	30
n - butyl bromide	$CH_3(CH_2)_3$ Br	29	30
n - heryl bromide	$CH_3(Ch_2)_5$ Br	26	30
n - octyl bromide	$CH_3(CH_2)_7$ Br	23	30

Effect of the hydrocarbon linkage

The solvent power of a paraffin solvent is particularly affected by the prevailing type of carbon linkage. With the transition from the simple bond to the double and finally triple bond, the solvent power of the halogen compound for paraffin, as well as its selectivity go down.

We were unable to verify Engel's rule that the content in halogen being constant, the paraffin solubility increases with the amount of hydrogen.

Table 9

Solvent		Paraffin % by weight	Separation Temperature °C.
n - propyl bromide	CH_3-CH_2-CH_2-Br	32	30
allyl bromide	CH_2=Ch-Ch_2 Br	23.5	30
Propargyl bromide	CH ≡C-CH_2 Br	1	30

(b) Isocyclic halogen hydrocarbons

If a nuclear hydrogen atom in benzol is replaced by a halogen atom, its solvent power for paraffin goes down. The same is true of aliphatic hydrocarbons.

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Table 10

Solvent		Paraffin % by weight	Separation Temperature °C
Benzol	C_6H_6	42	30
fluorobenzol	C_6H_5F	31	30
chlorobenzol (1)	C_6H_5 Cl	30	30
bromobenzol	C_6H_5 Br	21.5	30

(1) In contrast to fluorobenzol or bromobenzol, chlorobenzol has a negative temperature coefficient for oil solubility.

The solvent power suffers a still more important drop, if several halogen atoms are introduced. The selectivity of a compound containing several chlorine atoms is poorer than that of chlorobenzol.

Table 11

Solvent		Paraffin % by weight	Separation temperature °C.
Benzol	C_6H_6	42	30
Chlorobenzol	C_6H_5 Cl	30	30
o - dichlorobenzol	C_6H_4 Cl_2	17.5	30
1,2,4 - trichlorobenzol	C_6H_3 Cl_3	15	30

None of the solubility curves of the compounds in question lies in a range above the melting temperature of paraffin.

It is of interest to observe the changes in solvent power occuring if hydrogen in the side chain of toluene is replaced by a halogen.

Table 12

Solvent		Paraffin % by weight	Separation temperature °C.
Toluene	$C_6H_5CH_3$	58	35
Benzotrichloride	C_6H_5C Cl_3	13	35
Benzodichlorofluoride	C_6H_5C Cl_2 F	14.5	35
Benzochlorodifluoride	C_6H_5C Cl F_2	60	35
Benzotrifluoride	C_6H_5C F_3	20.8	35

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The introduction of halogens will in most cases reduce the solvent power for paraffin. But the instance of benzochlorodifluoride shows how cautious we must be in making such generalizations. The solvent power for paraffin is increased by virtue of the antagonistic effect of chlorine and fluorine to such an extent that it exceeds that of toluene.

The selectivity of the halogen compounds, in particular that of the fluorine substitution products is poorer than that of the original hydrocarbon. The selectivity of benzotrifluoride is poorer than that of benzotrichloride.

In the German Patents Nos. 699,959 and 703,974, it has been claimed that aromatic fluorine-compounds and oil do not separate into layers. The study of benzol fluoride shows that this statement can not be established in a general form. Moreover, the statement that the selectivity of an aromatic chlorine compound is poorer than that of the corresponding aromatic fluorine compound, does not hold, either, in this case. The assertion that the effect of fluorine in aromatic compounds is the opposite one of that exercised by other halogens, has not been proved correct, either.

(c) Heterocyclic halogen compounds

If we replace one hydrogen atom in pyridine by a chlorine atom, the solvent power for paraffin remains unchanged and the selectivity is improved. Fluorine, bromine and iodine reduce the solvent power in the given order, the selectivity goes down, too (the order is different: Cl, Br, F, I).

Table 13

Solvent		Paraffin % by weight	Separation Temperature °C.
Pyridine	C_5H_5N	15	45
2-chloropyridine	$C_5H_4N\,Cl$	15	45
2-fluoropyridine	C_5H_4NF	11	45
2-bromopyridine	$C_5H_4N\,Br$	4.5	45
2-iodopyridine	C_5H_4NI	1	45

The position of the substituent plays an important role with respect to solvent power and selectivity.

Table 14

Solvent		Paraffin % by weight	Separation Temperature °C.
2-fluoropyridine	C_5H_4NF	11	45
3-fluoropyridine	C_5H_4NF	57	45
2-bromopyridine	$C_5H_4N\,Br$	4.5	45
3-bromopyridine	$C_5H_4N\,Br$	65	45

The selectivity of the 3-halopyridines is considerably better than that of the 2-halopyridines.

These results furnish the proof that the statement made in the German Patent 707,710 saying that the fluorination of pyridine improves its selectivity is not correct in this general formulation. For instance, the selectivity of 2-fluoropyridine is poorer than that of pyridine, but that of 3-fluoropyridine is better.

A part of the paraffin-solubility curve of 2-bromopyridine and all of the curve of 2-iodopyridine lies above the melting temperature of paraffin.

The selectivity of fluor compounds is not poorer than that of chlorine, bromine and iodine compounds. But fluorine compounds may excel other halogen compounds insofar as their melting points are considerably lower. Sometimes, their boiling points are lower, too.

IV. Rhodane Compounds

(a) Aliphatic rhodane compounds

Many of the reactions obtained with the radical SCN are similar to those of haloid acids and of hydrocyanic acid. It was therefore of interest to study its effect upon the solubility. Our measuring data show that in the homologous series of rhodane alkyls, the solvent power for paraffin goes up with the lengthening of the carbon chain - in contrast to that of the halogen alkyls -- and that the selectivity goes up, too (in this respect, they behave like halogen alkyls).

Table 15

Solvent		Paraffin % by weight	Separation Temperature °C.
Methyl rhodanide	CH_3SCN	1.5	45
Ethyl rhodanide	CH_3CH_2SCN	12.5	45
n-propyl rhodanide	$CH_3(CH_2)_2$ SCN	18.5	45
n-octyl rhodanide	$CH_3(CH_2)_7$ SCN	55	45

The introduction of a rhodane group into a hydrocarbon results in a much greater reduction of the dissolving power for paraffin than that of halogen. The selectivity of rhodane compounds is poorer than that of the corresponding halogen compounds.

Table 16

Solvent		Paraffin % by weight	Separation Temperature °C.
Methyl bromide	CH_3 Br	68.5	50
Methyl rhodanide	CH_3 SCN	2.2	50

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The paraffin-solubility curve of methyl rhodanide lies above the melting point of paraffin.

If a rhodane group is substituted for another hydrogen atom of the hydrocarbon, the separation curve is shifted into a higher temperature range, sometimes to such an extent that the critical temperature of the paraffin solubility curve can not be determined experimentally (it lies above 260 °C. with pentamethylene-dirhodanide).

The difference in the solvent capacity for paraffin and in selectivity obtained by substituting fluorine atoms to chlorine atoms, may be most clearly observed by comparing trichlororhodane with its fluorine-substitution products, which we had prepared for the first time. Trichlororhodane is of a very good selectivity. If an F-atom is substituted to a Cl-atom, the solubility for oil and paraffin goes considerably down (much more for oil) while the selectivity becomes considerably poorer. If another F-atom is introduced, the solubility for oil and paraffin as well as the selectivity are improved once more; with respect to selectivity, it surpasses even trichlororhodane. If the third chlorine atom is replaced by fluorine, the steepness of the paraffin solubility curve is altered. In contradistinction to the oil solubility curves of the fluorination products, that of the trichlororhodane has a negative "temperature coefficient." The fluorination products are of interest because they have a low boiling point (35°C, 13°C, -6°C); the heat of evaporation may be utilized for cooling purposes.

(b) Isocyclical rhodane compounds

The rhodane group has also a more important effect upon the paraffin-solubility of benzol derivatives than a halogen substituent.

Table 17

Solvent		Paraffin % by weight	Separation Temperature °C.
Chlorobenzol	C_6H_5Cl	30	30
Rhodanobenzol	C_6H_5SCN	0.5	30

V. Mustard Oils and Nitriles

We studied only allyl isothiocyanate, as a representative of the mustard oil group. The course of the solubility curve ressembles the picture obtained with various halogenides. The temperature range of the paraffin melting point is not exceeded.

The introduction of a cyanogen residue affects very strongly the solvent power for paraffin. The paraffin-solubility curve of acyclic and cyclic compounds, e.g. of acetonitrile, allyl cyanide and benzyl cyanide, lies considerably above the melting point of paraffin. In this case, the paraffin solubility curve takes the form of a parabola. Solvent power and selectivity are dependent upon the nature of the residue which is combined with the CN-group.

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If in aceto nitrile, chlorine is substituted to one hydrogen atom, the solvent power for paraffin and oil goes up and the selectivity is increased. When chlorine is substituted for all the hydrogen atoms, the selectivity becomes still better and the paraffin solubility become so great that the solubility curve drops below the melting point of the paraffin.

VI. Sulfohalogenides

The sulfohalogenide group reduces the solvent power for paraffin more than the rhodane group, but not as much as the cyanogen group. The paraffin solubility curves of methyl sulfochloride and of ethyl sulfochloride lie attemperatures which are so high that the separation temperature could be established only for low paraffin concentrations. With propyl sulfochloride, the hydrocarbon chain prevails already to such an extent that the paraffin solubility curve exceeds the temperature range of the melting point of paraffin only with medium concentrations of the solid hydrocarbon. Paraffin is somewhat less soluble in sulfofluoride than in sulfochloride. Sulfofluorides are more hydrolysis resistant than sulfochlorides. The paraffin solubility is increased by halogenation of the alkyl.

Table 18

Solvent		Paraffin % by weight	Separation Temperature °C.
Methyl sulfo chloride	CH_3SO_2Cl	5	110
Chloromethylsulfochloride	CH_2ClSO_2Cl	5	68.5
Trifluoromethylsulfochloride	Cl_3SO_2F(?)	5	8

In the homologous series of sulfohalogenides, the selectivity is improved with a lengthening of the carbon chain. Halogenation, in particular, chlorination has an analogous effect.

If another sulfo-halogenide residue is introduced into a molecule, the solubility of the paraffin is so low that an experimental measurement can be made only if the two substituents are combined with a phenyl residue.

VII. Carbon Bisulphide and Derivatives

In the patent literature (1), the use of carbon bisulphide for dewaxing has been frequently recommended. This compound is distinguished by its considerable solubility for paraffin and its selectivity; in this regard, only methane and ethane are superior.

By a halogenation of the carbon disulphide, the paraffin solubility is considerably reduced, by chlorine more than by fluorine. The selectivity of the halogenation product — the fluorination products have been prepared for the first time — is much higher than that of the original substance.

(1) German Patents 532,606; 647,631; U.S. Patent 2,191,136; French Patent 781,258, 822,934; British Patent 356,205; 511,170; Can. Patent 160,666.

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Table 19

Solvent		Paraffin % by weight	Separation Temperature °C
Carbon bisulphide	CS_2	73	20
Thiophosgen	$CS\ Cl_2$	14	20
Thiocarbonyltetrachloride	$CS\ Cl_4$	8.5	20
Thiocarbonyltriochloromonofluoride	$CS\ Cl_3\ F$	17.5	20
Thiocarbonyldichlorodifluoride	$CS\ Cl_2\ F_2$	17	20

VIII. Nitro Compounds

The solubility of oil and paraffin suffers a considerable reduction if a nitro group is introduced into an organic molecule. In the tested specimens, at least, some part of the paraffin-solubility curves will lie above the melting point of paraffin; but 1-nitrooctane is an exception from this rule.

Table 20

Solvent		Paraffin % by weight	Solution Temperature °C Paraffin	Oil	Temperature Difference Paraffin-oil °C
Nitromethane	CH_3NO_2	35	186.5	164.5	22
Chloropierine	CCl_3NO_2	35	34	-32.5	66.5
1-nitrooctane	$CH_3(CH_2)_7NO_2$	35	44.5	-25	69.5
3-nitropyridine	$C_5H_4N{\cdot}NO_2$	35	180.5	137	43.5
1-nitronaphthalene	$C_{10}H_7NO_2$	35	109.5	67.5	42
Nitrobenzol	$C_6H_5NO_2$	35	56	27.5	28.5

There is a noteworthy improvement in the dissolving power for oil and paraffin and in the selectivity when nitromethane is converted to chloropicrine.

IX. Amines and acid amides

The amino group exercises a great effect upon the solubility of hydrocarbons. At temperatures below 160°C, neither oil nor paraffin are dissolved by ammonia. But if a methyl group is introduced into ammonia, the dissolving power of the compound is so great that the solubility curve of paraffin comes to lie below the melting point of paraffin. The rate of solubility of hydrocarbons in ethylene diamine is very low. If the molecule contains a hydroxyl group along with the amino group, hydrocarbons cannot be solvated by ethalomine or thiethanolamine.

In a corresponding manner, it is the association of nitrogen and oxygen in acid amides which causes hydrocarbons to be insoluble in the lower members of the homologous series, e.g. in formamide. The same behavior is displayed by sulfamides (they do not dissolve hydrocarbons, up to propyl sulfamide).

In aromatic compounds the dissolving power for paraffin is much reduced by the amino groups. In the aniline-points method, the limited solubility of paraffinic

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components of an oil is utilized for analytical purposes.

In comparison to the basic hydrocarbon, the paraffin solubility is much reduced by the introduction of an amino-group.

Table 21

Solvent		Paraffin % by weight	Separation Temperature °C.
Benzol	C_6H_6	40	29.3
Aniline	$C_6H_5NH_2$	40	118
Cyclohexane	C_6H_{12}	40	25.7
Cyclohexylamine	$C_6H_{11}NH_2$	40	37

If a methyl-group is introduced into aniline, forming o-toluidine, its dissolving power for hydrocarbons is substantially increased. A similar effect is obtained by substituting an alkyl group to a hydrogen atom of the amino group, e.g. ethyl aniline.

X. Oxides

It is a well-known fact that solvents the molecules of which contain oxygen, are of a poor dissolving power for hydrocarbons. It was therefore to be expected that in general the paraffin solubility curves of this type of compounds would lie above the melting point of paraffin. The examination of propylene oxide showed that the influence of the oxygen contained in this molecule is not yet sufficiently prevalent. In practical application of the interactions discussed in II, halogen has therefore been introduced into the propylene oxide molecule in order to reduce its dissolving power for paraffin.

Table 22

Solvent		Paraffin % by weight	Separation Temperature °C.
Propylene oxide	$CH_2\overset{O}{\frown}CH - CH_3$	completely mixable	55
Monochloropropyleneoxide	$CH_2\overset{O}{\frown}CH - CH_2Cl$	3.7	55
Dibromopropylene oxide	$CH_2\overset{O}{\frown}CH - CHBr_2$	1.6	55
Trichloropropylene oxide	$CH_2\overset{O}{\frown}CH - CCl_3$	completely mixable	55

Our prior experience has been reconfirmed; i.e. the dissolving power is initially reduced by the introduction of halogen and will go up again if more halogen atoms are introduced.

By virtue of the shorter hydrocarbon chain, the effect of the halogen and of the oxygen is so prevalent in brombethylene oxide that both oil and paraffin are dissoluble at temperatures up to 240° C.

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As a specimen of unsaturated compounds we have studied allylene oxide. Its dissolving power is lower than that of the saturated propylene oxide, conformant to the experiences registered in Table 8. The selectivity of the compound is, however, comparatively poor.

Table 23

Solvent		Paraffin % by weight	Separation Temperature °C.
Propylene oxide	$CH_2 \overset{O}{\diagdown\diagup} CH-CH_3$	77	45
Allylene oxide	$CH \overset{O}{\diagdown\diagup} C-CH_3$	2	45

XI. Aldehydes

We tested two aldehydes. In both cases, the effect of the hydrogen upon the solubility was comparatively slight and insufficient to shift the paraffin-solubility curve into the temperature range above the melting point of paraffin.

Table 24

Solvent		Paraffin % by weight	Separation Temperature °C.
Butyraldehyde	$CH_3CH_2CH_2C\overset{O}{\diagdown H}$	25	40
Crotonaldehyde	$CH_3CH=CH-C\overset{O}{\diagdown H}$	10.9	40

Here, too, as in Table 9, the unsaturated compound is of a lower dissolving power for paraffin.

XII. Ketones

(a) Aliphatic ketones

Ketones have been used as dewaxing agents already at an early date. They are extensively used by the oil technicians, and in a conventional laboratory method for determining the paraffin content.

The paraffin solubility curve of acetone lies above the melting point of paraffin; its selectivity is comparatively poor. By lengthening one or both of the alkyl groups the selectivity can be substantially improved. This device will however increase the paraffin solubility at the same time, so that the solubility curve will fall below the melting point of paraffin.

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Table 25

Solvent		Paraffin % by weight	Separation Temperature °C.
Acetone	$(CH_3)\ CO\ (CH_3)$	1	35
Methylethylketone	$(CH_3)\ CO\ (C_2H_5)$	9	35
Dipropylketone	$(C_3H_7)\ CO\ (C_3H_7)$	26	35

We expected the paraffin solubility curve to be displaced into a higher temperature range by virtue of the following devices: introduction of more hydrogen, introduction of halogen, of a rhodane group, or of another substituent which represses the solubility.

By comparing acetone and acetyl acetone we see that the introduction of the acetyl residue does not substantially alter the paraffin solubility but will substantially improve the selectivity.

But if another acetyl group is introduced into the molecule, the dissolving power of Diacetylacetone for paraffin and oil is so low that measurements become impossible.

The dissolving power of halogenated ketones goes down, at first, in analogy to prior experiences, dropping to a minimum and then rising once more.

Table 26

Solvent		Paraffin % by weight	Separation Temperature °C.
Acetone	$CH_3.CO.CH_3$	9.2	50
Chloroacetone	$CH_2.CO.CH_2\ Cl$	11.2	50
Trichloroacetone	$CH Cl_2.CO.CH_2\ Cl$	2.5	50
Hexachloroacetone	$CCl_3.CO.C\ Cl_3$	90	50

With an increase in the number of halogen atoms in the molecule, the selectivity of the halogen compound is constantly improved, reaching its optimum value in hexachloroacetone. For instance, the difference in the curve values for a 20% oil-paraffin solution is 17° C. with acetone and 64° C. with hexachloroacetone.

If butanone is halogenated, the same phenomenon reappears, which had been found with hydrocarbons: the introduction of halogen effects at first a decrease in dissolving power.

Table 27

Solvent		Paraffin % by weight	Separation Temperature °C.
Butanone	$CH_3.CO.C_2H_5$	79.5	45
3-bromobutanone	$CH_3.CO.CH\ Br\ CH_3$	70	45
3,3-dibromobutanone	$CH_3.CO.C\ Br_2\ CH_3$	1.6	45

The reduction in dissolving power is accompanied by a reduction in selectivity.

The paraffin solubility of rhodaneacetone for paraffin is poor; the shape of the solubility curve is unusual.

New points of view failed to be discovered by the examination of unsaturated ketones such as mesityl oxide or phorous. The first-names ketone is of outstanding selectivity and superior to the last-names compound in this respect.

(b) Aromatic ketones

The paraffin solubility goes up if one methyl group of acetone is replaced by a phenyl residue (forming acetophenone). The introduction of another phenyl group (transition to benzophenone) has the surprising effect of reducing the solubility to the temperature range of acetone. But the selectivity of benzophenone is substantially superior to that of acetone.

Table 28

Solvent		Paraffin % by weight	Separation Temp. Paraffin	Separation Temp. Oil	Differ. in Temp. Oil - Paraffin °C.
Acetone	$CH_3.CO.CH_3$	40	65.2	45	20
Acetophenone	$C_6H_5.CO.CH_3$	40	49.5	18.5	31
Benzophenone	$C_6H_5.CO.C_6H_5$	40	66.5	30	36.5

A favorable effect on the dissolving power for paraffin and on the selectivity was to be expected by virtue of a halogenation of the ketones in question.

Table 29

Solvent		Paraffin % by weight	Separation Temperature °C.
Acetophenone	$C_6H_5.CO.CH_3$	Completely mixable	60
ω - bromoacetophenone	$C_6H_5.CO.CH_2Br$	1.3	60
$\omega\omega$ - dibromoacetophenone	$C_6H_5.CO.CHBr_2$	1.8	60
$\omega\omega\omega$ - trichloroacetophenone	$C_6H_5.CO.CCl_3$	22	60

With an increase in the number of halogen groups introduced into a molecule a minimum of solubility for paraffin will occur at first, and then once more an increase. The selectivity of $\omega\omega$-dibromoacetophenone is the highest, that of acetophenane the lowest one.

XIII. Alcohols and phenals

A lengthening of the carbon chain in the homologous series of alcohols (1) is tantamount to an increase in their dissolving power for paraffin and in their selectivity. Their behaviour is analogous to that of the rhodane compounds.

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With respect to solvent power, n-butyl alcohol stands between propyl alcohol and amyl alcohol in the homologous series of alcohols. It is unnecessary to believe that the behavior of butyl alcohol is bassically different from that of amyl alcohol.

Table 30

Solvent		% by weight paraffin or oil resp.	Separation temperature °C Paraffin	Oil	Differ. in Temp. oil - Paraffin △ °C.
Methyl alcohol	CH_3OH	5	142.5	112.5	30.5
Ethyl alcohol	C_2H_5OH	20	92.4	64.8	27.6
n-propyl alcohol	C_3H_7OH	20	49.5	-11	60.5
n-butyl alcohol	C_4H_9OH	20	47.5	-36	83.5
n-amyl alcohol	$C_5H_{11}OH$	20	46	-39	85
n-hexyl alcohol	$C_6H_{13}OH$	20	43.3	-47	90.3
n-octyl alcohol	$C_8H_{17}OH$	20	42.5	-	-

Among the aromatic alcohols benzyl alcohol is distinguished by its slight solubility for paraffin and its fair selectivity.

The same is true of phenol. Its solvent power for paraffin is somewhat lower than that of benzyl alcohol. The solvent power for paraffin is higher in m-cresol, by virtue of the pressure of the methyl group, whereas the selectivity is nearly unchanged.

By chlorinating phenol, the solvent power goes up. The solubility curve of o-chlorophenol lies below the melting point of paraffin. The solvent power of p-chlorophenol is like that of phenol, but its selectivity is better.

XIV. Acetals

The study of diethyl acetal shows clearly how great are the differences in paraffin solubility and selectivity which are generated by the introduction of chlorine into a molecule, depending upon the position of the constituent.

TABLE 31

Solvent		Paraffin resp. Oil % by weight	Separation Temperature °C. Paraffin	Oil	Differ. In Temp. oil - paraffin △t °C.
Diethyl acetate	$CH_3CH(OC_2H_5)_2$	45	179.5		7.5
Acetaldehyde-bis-beta chloro-ethyl acetate	$CH_3CH(OCH_2CH_2Cl)_2$	45	85.5		32
Dichloroacetal dehyd-diethyl acetate	$OH\ Cl_2CH(OC_2H_5)_2$	45	45		91.5

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XV. Acid and Acid Halogenides

The solvent power of the lower members of the fatty acid group, e.g. formic acid and acetic acid, both for oil and paraffin, is very low, by virtue of the presence of the two oxygen atoms of the carboxyl group. If the alkyl group which is combined with the acid residue, is increased, the solvent power for hydrocarbons goes up. The selectivity of propionic acid is good. The solvent power is improved by the exhausting chlorination of the alkyl or a decrease in the number of the oxygen atoms by a transition to an acid halogenide. The selectivity of acetyl fluoride is rather poor. By combining the carbonyl group with an aromatic rest, selectivity and solvent power are good, e.g. benzoyl fluoride.

XVI Esters

The paraffin-solubility of esters with a short carbon chain is so low, by virtue of the presence of the carboxyl-group oxygen, that the separation temperatures are higher than the melting temperatures of paraffin. The presence of two immediately adjacent carboxyl groups adds to this effect. The selectivity of methyl formiate, ethyl formiate and methyl acetate, for instance, is poor; that of ethyl acetate, n-butyl-acetate and i-amyl acetate is better in the given order. The selectivity of triacetine is good, even though the critical dissolving temperature is high. Attention must be paid to tri-o-tolyl phosphate; its selectivity is outstanding, even though the solubility curve for paraffin lies below the melting point of paraffin.

XVII. Ethers

We found in our studies regarding the solubility of paraffin in diethyl ether and di-n-propyl ether that their solubility curves lie below the melting point of paraffin. We tried to modify solvent power and selectivity by introducing halogens. Both properties turned out to be affected by the position of the halogen in the molecule. The effect of halogen occupying a position in the middle was lower than that of a terminal substituent. Lower solvent power for paraffin goes hand in hand with poorer selectivity.

The paraffin solubility curve of monomethyl ether and of monoethyl ether lies above the melting temperature of paraffin.

TABLE 32

Solvent		Paraffin resp. oil % by Wt.	Separation Temperature °C Paraffin	Oil	Differ in Temp. Oil - Paraffin Δt °C
α,α'- dichloro ethyl ether	$(CH_3 CH Cl)_2 O$	40	37	-32.5	69.5
α,β- dichloro ethyl ether	$(CH_2 Cl. CH Cl)(C_2H_5) O$	40	41	-37	78
β,β'- dichloro ethyl ether	$(CH_2Cl. CH_2)_2 O$	40	69	40	29

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Anisol has been studied as an aromatic ether. Its selectivity is good; but its paraffin-solubility curve lies below the melting temperature of paraffin.

XVIII. Thioethers

If dimethyl ether is transformed into dimethyl sulfide, its solvent power for hydrocarbons goes down. The solvent powers of diethyl ether and dimethyl sulfide for paraffin or oil are rather equal. The solvent power of higher members of the homologous series is better (that of diethyl sulfide is better than that of dimethyl sulfide).

The chlorination of dimethyl sulfide has the usual effect. The introduction of two chlorine atoms reduces the solubility of paraffin. If four symmetrical hydrogen atoms are replaced by chlorine, the solubility is improved to such an extent that it exceeds that of the original material. Hexachlorodimethylsulfide has the greatest solvent power for paraffin. Among the various chloro-substitution compounds s-tetrachlorodimethyl sulfide has the best selectivity.

TABLE 32a

Solvent		Paraffin % by weight	Separation Temperature °C
Dimethylsulfide	$(CH_3)_2$ S	23	40
Dochlorodimethylsulfide	(CH_2Cl) S	5.5	40
Tetrachlorodimethylsulfide	$(CH\ Cl_2)$ S	41	40
Hexachlorodimethylsulfide	$(C\ Cl_3)_2$ S	47.5	40
Diethylsulfide	$(C_2H_5)_2S$	75	40
Dimethylsulfide	$(C\ H_3)_2\ S_2$	58	40

A comparison of dimethyl sulfide and dimethyl disulfide shows that the solubility of hydrocarbons is promoted by the presence of the s-atom.

XVIII. Heterocyclical Compounds

(a) Pyridine, chinoline andol and their derivatives

A comparison of benzol and pyridine shows that the introduction of nitrogen into the benzene ring causes the solvent power of paraffin considerably to go down. However, it does not yet exceed the melting temperature of paraffin. For this purpose, it is necessary to introduce another solubility-suppressing group, such as the amino group or a bromchalogen or iddohalogen.

The selectivity of amino pyridine is still greater than that of pyridine iodide, even though its paraffin solubility has been decreased very much.

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TABLE 33

Solvent		Paraffin % by weight	Separation Temperature °C
Pyridine	$C_5H_5N.H$	14	45
2-fluoropyridine	$C_5H_4N.F$	10.5	45
2-chloropyridine	$C_5H_4N.Cl$	15	45
2-iodopyridine	$C_5H_4N.I$	1	45
2-aminopyridine	$C_5H_4N.NH$	nearly 0 (1.6)	45 (120)

The introduction of an alkyl group into pyridine increases its solvent power for paraffin and improves its selectivity.

The hydration of pyridine (piperidine) has the same effect; both the selectivity and the solvent power for paraffin go up.

By introducing the benzoyl group into piperidine, the solvent power for paraffin goes down substantially. Indeed, there is also an important reduction in the dissolving power for oil; but the selectivity remains satisfactory.

TABLE 34

Solvent		Paraffin % by weight	Separation Temperature °C
Piperadine	$C_5H_{10}.NH$	40	31
Benzoyl piperidine	$C_5H_{10}.NC_6H_5CO$	40	108

A comparison of chinoline and isochinoline shows that in this case it does not make a great difference in the solvent power where the nitrogen atom is placed in the nucleus of the molecule; the selectivity is the same, too, even though the course of the oil curve is different. The selectivity is much improved by hydrogenation (tetralydrochinoline); the solvent power for paraffin does not change. By partial hydrogenation and introduction of a methyl group, chinaldine is formed, displaying a further increase in selectivity with higher paraffin solubility.

The paraffin solubility curves of all the above-mentioned chinoline derivatives remain below the melting temperature of the solid hydrocarbons. The curves lie above this temperature only when a solubility-repressing group, such as the methoxyl-group is introduced (forming 2-methoxychinoline) or the OH-group (forming 8-oxychinoline).

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TABLE 35

Solvent		Paraffin % by weight	Separation Temperature °C
Chinoline	C_9H_6NH	14.5	45
2-methoxychinoline	$C_9H_6N.)OCH_3$	5	45
3-oxychinoline	$C_9H_6N.OH$	less than 1	45

We found a surprisingly high value of the critical temperature necessary for the solution of paraffin in studying indol. It was contrary to our expectations, as based on the prior measurements made of non-substituted heterocyclic nitrogen derivatives; the selectivity was satisfactory.

The effect of water upon solubility and selectivity of a water-soluble nitrogen compound

In the patent literature we find several recommendations with respect to water soluble selective solvents, advising the use of aqueous solvents in order to improve the separation of paraffin (1). The addition of water represses the solvent power for paraffin. But the selectivity becomes much poorer at the same time. According to our observations, that gives a paraffin with a rather high oil content.

(1) German Patents 123,101; 140,546; 140,927; 549,451; 689,063; 705,058; French Patent 842,450.

TABLE 36

Solvent	Paraffin resp. oil % by wt.	Separation Temperature °C Paraffin	Oil	Differ. in Temp Oil - Paraffin Δt °C
Chinoline	30	46	13.5	32.5
Chinoline + 10% by wt. water	30	99.5	86	13.3

(b) Heterocyclic compounds containing more than 1 atom of nitrogen

It was to be expected that the solvent power would go down if the number of nitrogen atoms in a molecule would go up. The paraffin-solubility curve of the non-substituted compounds with one nitrogen atom in the molecule (pyridine, chinoline) exceeds nowhere the temperature range of solid hydrocarbons. The separation temperature of piperazine is so high that it could not be measured. Nearly the entire paraffin-solubility curve of chinoxaline lies above the melting points of the paraffins used, in contradictinction to that of chinoline. By hydrogenating the ring which contains the two nitrogen atoms, forming tetrahydrochinoxaline, the solvent power for paraffin becomes still lower (in analogy to chinoline, on the one hand, and to tetrahydrochinoline, on the other hand). The introduction of a methyl group into the nitrogen-containing ring (2-methyl-chinoxaline) raises again the solvent power to such an extent that the entire paraffin curve lies again below 52°C. The selectivity of the compounds in question does not differ very much. The selectivity of 1-methyl-benzimidamol is fair; it has next to no solvent power for paraffin.

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Molecules with more nitrogen atoms, such as Azimidobenzol are of a very slight solvent power for paraffin and oil.

(c) Heterocyclic compounds with nitrogen and sulfur

Measuremsnts of 2-bromothiazol confirmed the similarity existing between pyridine and thiazol-derivatives also with respect to their solvent powers. The paraffin-solubility curves of Piazthiol, 4-phenylthiazol and 2,5-dimethyl-1,3,4-thiazol, in particular, those of the two last-named compounds lie entirely in the range of liquid paraffin.

(d) Heterocyclic oxygenous compounds

The paraffin-solubility curve of furane lies below 51°C. Its solvent power for paraffin is considerably reduced by the introduction of solubility-repressing groups. The paraffin-solubility curves of furfurol, furfuralcohol and furfuroldiacetate lie in the range of liquid paraffin for nearly all concentration.

The study of 1,4-dioxane confirms our prior experience that the solvent power for paraffin goes down at first, if halogens are introduced (2,3-dichlorodioxane).

By introducing 2 methyl groups into γ-pyrone the infinitesimally small solvent power of this substance for paraffin is raised to such an extent that the critical dissolving temperature of 2,6-dimethylpyrone lies at 163°C.

Piperonal has a strikingly low solvent power for paraffin and a very high selectivity.

In comparing 1,4 dioxane and ethylene methylene dioxide, we observe that the effect of oxygen is much stronger in a ring of five than in a ring of six; it represses the paraffin solubility, while the selectivity is satisfactory.

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Translation Book 176
Reel 113
Doc. 7
8 Drawings - 5 Tables

August 3, 1948

0581

Federal Institute for Petroleum Research
Institute for Technology Hannover
July 7, 1944

The refining of petroleum and lignite-tar fractions with liquid hydrofluoric acid to produce Diesel-fuel, lubricants and fuel oil for the armed forces.

Because of the constantly increasing demand for fuel and lubricants, it is necessary to utilize all the available sources of supply. For this reason lignite is used for supplementing the supply of fuels and lubricants. The consumers used to be prejudiced against lignite products, in particular against lignite-carbonization benzine and lignite Diesel fuel. But at the present time, these products have been generally accepted.

Already during the First World War a lignite product, montan wax, has been used as a lubricant for automobile motors; it has been mixed with machine-oil distillate and spindle oil.

At the present, the following methods are known for producing lubricants from lignite-carbonization tar (some processes using carbonization tar proper as raw material, others paraffin prepared from tar):

(1) Lignite [illegible] refined with selective solvents.

(2) Tar oil paraffins are [illegible] and changed to lube-like materials by means of catalysts.

(3) Mixed polymerizates of low unsaturated aliphatic hydrocarbons obtained from lignite petrol [illegible] tar-oil compounds containing [illegible] substitution like [illegible] of carbazole.

[illegible] of lignite tar oils

Fair lubricating oils [illegible] are prepared by refining lignite tar oils with [illegible].

Selective solvents, such as liquid sulfur dioxide, methanol, ethanol, furfurol, aniline and phenol [illegible] dissolve only the lubricating oils contained in mineral oils or [illegible]. The refined products contain mainly the paraffinic hydrocarbons, [illegible] the greater part of the aromatic and unsaturated hydrocarbons [illegible] nitrogen and sulfur compounds. Selective solvents are more suitable [illegible] solid-layer refining process for removing just those tar fractions [illegible] the Diesel fuels and lubricants less desirable for motors.

The Deutsche Erdöl - A.-G. in Hamburg already in 1936 a method of producing high-grade lubricants [illegible] tar products obtained by selective refining.

This process and additional studies made at the Institute of Lignite and Petroleum Research at Berlin (1) have furnished the proof that good Diesel fuel may be obtained by refining [illegible] with solvents.

M. Pier and F. Christmann(5) took unsaturated hydrocarbons which they had obtained by reiterated cracking of lignite-paraffin gatsch, and used them as starting material for high-grade lubricants. The cracking products are treated with liquid sulphur dioxide and polymerized with aluminum chloride. The viscosity-temperature curve of the lubricants thus obtained is better than that of a Pennsylvania lubricant.

H. Harder and O. Herbst (6) report about lubricants which have been manufactured by means of refining lignite-carbonization tars with acids and solvents and condensing them with aluminum chloride. The lignite lubricants are suitable for the lubrication of bearings; the output obtained was 8-9% of the tar. By the reformation with aluminum chloride the viscosity has been increased; but the temperature function of the viscosity would not be improved by increasing the amount of catalyst used.

Catalytic Polymerization of Unsaturated Olefinic Hydrocarbons and Lignite Tar Oils to Lubricants

Some variegated [illegible] and processes are used for reforming olefinic hydrocarbons, by themselves or also in combination with aromatics.

The Badische Anilin- und Soda-Fabrik (7) produces lubricants from dewaxed lignite-tar distillates by [illegible] polymerization at elevated temperature.

[illegible] manufactures high-grade lubricants by treating chlorinated [illegible] (cracking) in the presence of cyclic hydrocarbons or olefins. [illegible] used were e.g. aluminum [illegible], [illegible], boron fluoride, phosphorus [illegible], [illegible], molybdenum oxide and [illegible] (9) prepared high-molecular lubricants by treating [illegible] with acids which contained an organic acid group with [illegible] to a metal-metal bridge.

H. Harder and [illegible] (10) report about the reformation of lignite-carbonization tar oil [illegible] of sulfuric acid. They intended to prepare [illegible] by the mixed polymerization of aromatic compounds [illegible] and olefins, in the presence of sulfuric acid. [illegible] with unsaturated hydrocarbons in the presence of [illegible] a motor oil and a Diesel fuel which was then [illegible]. The yields, however, were low, as cold tar would be [illegible].

Along with [illegible] aluminum chloride, zinc chloride, iron chloride, boron [illegible], [illegible] or liquid hydrofluoric acid (in one [illegible] (11) has [illegible] the last years the importance of concentrated [illegible] recognition, especially in U.S.A. H. Simons [illegible] "Alkylates, if well [illegible] one of our best popular industrial products."

Good lubricants are obtained by the polymerization of olefins with HF in the presence of solvents [illegible] of which is lower than that of the olefins (13), or by treating [illegible] with anhydrous HF, metal halogenides and acids (12).

H. Feichtinger (13) reformed unsaturated hydrocarbons which had been prepared by chlorinating lignite paraffins and subsequently splitting-off gaseous hydrochloric acid in the heat, with lignite Diesel fuel, or Diesel fuel by itself, in the presence of concentrated HF. He produced a substantially improved Diesel fuel and a good lubricating oil.

We may briefly mention the processes for purifying hydrocarbons with HF. F. Hofmann and W. Stegemann (14) purified benzol with HF. They found gaseous or liquid hydrofluoric acid to have a considerable polymerizing effect upon the unsaturated impurities contained in benzol. The polymerization effect can be enhanced by the addition of metal halogenities. The same scientists polymerized also the unsaturated compounds of the tar oils with HF, thus obtaining a stable oil.

Polymerization and Condensation Reactions with Concentrated Hydrofluoric Acid.

Hydrofluoric acid resembles sulfuric acid with respect to its dehydrogenating effect. Sulfuric acid is apt to sulfonate or to oxydize aromatic compounds; but in conversions with HF, fluor-containing products are obtained only at definite reaction conditions, e.g. under gauge pressure at high temperatures — oxidation is impossible.

If HF is used [illegible] aluminum chloride, boron trifluoride and other halogenides, similar products are usually obtained. Aromatic rings are not coupled; aromatic rings [illegible] usually not hydrolyzed.

Compounds with unsaturated halogens may be converted into saturated fluoride compounds by the addition of HF; otherwise, they will be polymerized (15). K. Klatt (160) reports that aromatic compounds and not polymerizations are formed by HF and compounds which [illegible] in contrast to the unsaturated hydrocarbons.

J. A. Simons [illegible] (17) employed HF for the alkylation of exogenous hydrocarbons. In contrast to the methods using sulfuric acid, yields have been obtained of up to [illegible] with optimal hydrocarbon mixture. If slight amounts of water were contained in the concentrated HF, the alkylation was not affected.

Aromatic compounds [illegible] alkylated in different ways (18).

(1) [illegible]
(2) [illegible]

(3) [illegible]
(4) [illegible]
(5) [illegible]
[illegible]

Even though olefines are polymerized in the presence of HF, alkylation will take place if the olefine is slowly added to the aromatics in the presence of HF. Polyalkylated compounds are obtained by the condensation of olefins with aromatic compounds (19).

By the action of various olefins on benzol in the presence of HF, the corresponding alkyl benzols are formed. There are no side reactions (or very few of them) such as, the addition of HF to olefins or polymerization. Benzol with propylene gives mono-iso-propylbenzol, with isobutene, mono-t-butylbenzol and di-t-butylbenzol; with pentene, a mixture of alpha and beta phenyl pentane; with trimethyl ethylene, mono-t-amylbenzol and Di-t-amylbenzol. Cyclohexylbenzol has been obtained by the condensation of benzol with cyclohexene. The material to be alkylated reacts in benzol; the reactions take place even though only slight amounts of HF be present (20). Phenol and di-i-butylene yield p-t-butylphenol in the presence of much HF; with 70% HF, p-t-octylphenol. If phenol is converted with di-i-butylene in a larger amount of HF, t-butylphenol is formed with a small amount of HF, dodecylphenol (21). A satisfactory output of n-propylbenzol is obtained by condensing cyclopropane with benzol.

E. Isobutyl [illegible] is alkylated by passing [illegible] HF gives

[illegible]

[illegible]

The corresponding [illegible]

Table [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

If the original compound contains an active centre, the solubility is reduced by introducing a negative substituent (phenol is readily solvable, nitrophenol poorly, benzoic acid readily, bromobenzoic acid poorly). If the original compound fails to contain an active centre while the negative substituent contains such a centre, the solubility is enhanced (benzol is poorly solvable, nitrobenzol readily)(16). When none of them contains an active centre, the solubility goes down (benzol is poorly solvable, bromobenzol indissoluble)(27).

Specifications Made for Selective Solvents

It is a familiar fact that selective solvents must meet the following specifications in the refining of Diesel oil and lubricants.

(1) High solvent power and good selectivity, slight amounts of solvent being necessary.

(2) Low solubility for the refined fractions so that a maximum output of valuable refined material may be obtained.

(3) Low boiling point, in order to avoid losses in refined material when the solvent is removed by distillation.

(4) Favorable operating temperature and pressure.

(5) Quick separation of the heterogeneous phases.

(6) Low molecular and evaporation heat.

(7) Demulsification.

(8) Applicability of many different starting materials.

(9) No chemical reactions with the substances to be refined.

(10) No corrosion.

(11) Not harmful to health.

(12) Low price.

There is hardly a solvent which will readily meet all the specifications in question. For each special purpose a suitable solvent will have to be selected. The most important physical data for some solvents are given in Table 1.

HF meets satisfactorily the specifications 1-10.

Our studies have shown that concentrated HF may be used successfully as a catalyst and selective solvent for starting materials of all kinds. The results of these studies will be published at a later date. With respect to its corrosive effect, it may be stated that highly concentrated HF is non-corrosive for iron and behaves in this regard like liquid sulfur dioxide. HF, when it has evaporated from the extract and the refined matter, must be kept anhydrous by a treatment with thionylchloride. If the same sanitary precautions are observed as in the Edeleanu-process, there will not occur any major sanitary injuries. Both sulfur dioxide and HF evolve injurious vapors. The vapors will have a caustic effect on the skin if their action lasts for a longer period of time; the effect