

# SINCLAIR REFINING COMPANY

May 25, 1948

1820

S-113

Translation Book 1,  
Reel 186  
Frame 2420-2474

Breaking of oil-water emulsions when working with the pile system for carbonization of oil shale.

## Causes of Emulsification

Report Prof. Mally  
Tubingen 7-15-44

Chem. Institute of University of Tubingen  
Authors: Brockhausen and Coworkers

## Summary

Objectives of the project were the investigation of the connection between the presence of cokelike components in the condensate (1) evolved in the carbonization of shale and its tendency to form emulsions.

Results: The determination of the content of coking products in various crude tars (1) and the determination of the residual sludge obtained by various water-removing methods, gives a picture as follows:

Starting Material (1) from carbonization test	Coke in the (2) Condensate	Separation Method (3)	Residual sludge after separation
Schon Mill	0.2%	Carbonizing	20.5%
" M.c. 17a	0.02%	"	6.4%
" M.c. 17b	0.015%	"	6.7%
" M.c. 17c	0.02%	"	9.45%
" (No. unknown)	0.02%	"	5.0% (*)
" "	0.02%	Dismulgen	7.5%
" "	0.02%	"	9.0%
" "	0.02%	Carbonized shale powder	15.0% (**)
" "	0.02%	Granule size 0.3 mm	23.0%

(\*) Content of ashes: 0.027%

(\*\*) Content of ashes: 0.05%

The determination showed the cokelike portion to contain 10% of ashes. The coking products are insoluble in benzine.

(1) It seems that not the crude tars served as test materials but the so-called oil-sludges which are left over after the separation of a part of the water-free oils.

(2) No details known about the analytical method applied.

(3) No further details.

When the water is removed by centrifuging, the coking products gather in the slight layer of sludge which separates the oil layer from the water layer after their separation. Oil which has been freed from water will form a stable emulsion with water if coking products are added again.

Conclusions: The presence of cokelike components in the condensate promotes emulsification and stabilizes the sludge thus formed (4).

(Signature)

Causes of Emulsification

Report of the U-Laboratory Schenberg  
10-12-44

Dr. Eisinger

Summary

Objective of the project: Demulsification tests were made with the objective of clarifying the effect of various components and solid impurities contained in the shale-tar condensate upon the emulsifiability of shale tar.

Results: Samples of a water-free crude shale tar have been under certain conditions emulsified with

- (1) distilled water
- (2) carbonization water
- (3) a 1% sodium-chloride solution
- (4) carbonization water to which 0.1% (based on the tar) of solid impurities from the tar have been admixed
- (5) carbonization water containing 1% of solid impurities from the tar.

We measured the settling velocities of the clear water separated out during every minute. We found this velocity to be highest with carbonisation water, less with sodium-chloride solution and much lower with distilled water. The results were still poorer when 0.1% of impurities were added to the carbonisation water even though the demulsification velocity was greater during the first five minutes. In the presence of 1% of impurities oil would still be separated out.

Conclusions: Certain substances are dissolved in the carbonisation water which promote the settling of the crude-tar emulsion. Sodium chloride has a similar effect as these substances. We cannot say what causes this effect, whether their character as electrolytes or the increase in density caused by them (5). The solid impurities contained in the crude tar strongly repress demulsification. This effect increases with the amount of impurities; the settling difficulties which are characteristic for crude tar, appear in the presence of a higher rate of impurities.

Conducting the experiments.

A carbonization condensate has been permitted to stand for several days, whereby water and tar separated. As the specimen in question water-free tar was decanted from the uppermost layer; it was of a density of 0.952 (20°), a viscosity of 3.2°E (20°) and 1.6°E (50°) and its neutralization number of 0.558. The carbonization water, drained from the bottom had pH 7 (determined with universal indicator).

(5) Carbonization water Schenberg:  $d_{20} = 1.01 = 1.06$ ; 1% sodium-chloride solution:  $d_{20} = 1.0053$ .

With reference to the Herschel (7) demulsification test (6) we have emulsified each time 40 cm<sup>3</sup> of tar with 40 cm<sup>3</sup> of the aqueous phase, stirring them for five minutes. After the termination of the stirring we determined every minute the amounts of the aqueous phase settled up to that time. By multiplying the registered quantity with 60 and dividing it by the operating period in minutes, the respective settling velocities are obtained in cm<sup>3</sup>/hour. The maximum value obtained is the "demulsification number".

Settling period minutes	Distilled water		Carbonization water		1% Na Cl Solution		Carbonization water and solid contaminations 0.038 g = 0.1% 0.38 g = 1%		after two hours no separation of aqueous phase but only of ab. 30 cm <sup>3</sup> of waterfree tar over a permanent tar emulsion
	Aqueous phase used		water		Solution		contaminations		
	a cm <sup>3</sup>	b cm <sup>3</sup> /hr.	a cm <sup>3</sup>	b cm <sup>3</sup> /hr.	a cm <sup>3</sup>	b cm <sup>3</sup> /hr.	a cm <sup>3</sup>	b cm <sup>3</sup> /hr.	
1	1	60	2	120	0	0	1	60	
2	3	90	11	330	6	180	4	120	
3	6	120	25	500	18	360	10	200	
4	10	150	36	540	30	450	14	210	
5	16	192	40	480	38	456	17	204	
6	24	240	-	-	(8)40	400	20	200	
7	32	275	-	-	-	-	23	197	
8	38	285	-	-	-	-	25	189	
9	39(?)	260	-	-	-	-	26	174	
10	-	-	-	-	-	-	27	162	
20	-	-	-	-	-	-	32(9)	96	
Time required for complete separation									

a = separated aqueous phase.  
 b = settling velocity = demulsification number.  
 (Diagram may be supplied upon request. M.B.)

- (7) The separated aqueous layer was permeated with fine lamellae, like with cells.
- (8) Only slight formation of lamellae.
- (9) Over this sharply separated aqueous layer lay 16 cm<sup>3</sup> of bluish-tar rich in water and between the two a mixed layer of 8 cm<sup>3</sup>, consisting of both substances. The uppermost layer consisted of 24 cm<sup>3</sup> of water-free tar.

Practical suggestions for the liberation of crude oil from water.

Report of I. G. Farbenindustrie  
2-11-44

Summary

Objective of the project was the ascertaining of the most favorable conditions for the breaking of shale oil-water emulsions by means of Dismulgen.

Results: Dismulgen VIII turned out to be most effective demulsifying agent. Under conditions as follows a good separation of water and oil was obtained in two different shale-oil emulsions.

<u>Starting Material</u>	<u>Shale Oil Emulsion Metzingen</u>	<u>Shale Oil Emulsion Braunschweig</u>
water content of the starting material	19.2%	67%
Amount of Dismulgen VIII added (5% aqueous warm solution)	0.025-0.05%	0.05%
Settling conditions	2 hr. at 60°C	sh. 16 hr. at 90°-95°C
Result of separation	separation into pure oil (water content 0.02%) and clear water with smutty spots.	Separation into oil (water content 0.11%, specific gravity 0.980), a thin layer turbid with flakes and clear water.

By settling at elevated temperatures with an addition of Dismulgen VIII, an emulsion will be separated into water and oil sufficiently accurately for practical purposes, taking a shorter or longer period of time, in accordance with its stability.

Ditto

Report Dr. Grudelt, (G. B. Chemis, Berlin)  
Metzingen, 4-12-44

Summary

Objective of the project: The impurities contained in carbonization tar were to be removed by filtering, since they seemed to affect its emulsifiability.

Results: The attempt to filter uncentrifuged oil -- no details are given -- through a filter cloth was a failure. The impurities passed through the filter.

In Odenfurt, however, carbonization tar had been successfully freed from water (from 17% to 0.2%) by centrifuging it with a separator - Nobel-Centrifuge at normal temperature, and that had likewise been tried at Dillingen with a Humboldt-centrifuge. We succeeded in our attempts by applying the following method.

At first, the oil was centrifuged, separating thereby into three layers. The uppermost layer was clear oil, the bottom layer was clear water, the medium layer, one fifth of the feed-stock by weight, contained water, sludge and oil. This layer was sucked off to a suction filter covered with filter cloth. The sludge was left upon the filter cloth and the filtrate immediately started separating into two clear layers of water and oil.

Conclusions: Carbonisation tar can be filtered through a filter cloth for the purpose of separating out the water only after being previously subjected to centrifuging.

Ditto

Report Prof. Heine (Technical Institute of Berlin)  
Emslingen, 1-15-14

Summary

Objective of the project: Clarifying the possibility of removing water from crude shale tars by means of centrifuging.

Results: A complete separation into oil-free water and water-free oil could be obtained with three different shale tar-water emulsions, using a Krupp Separator with 6,400 r.p.m. at an optimum operation temperature of 70° and an optimum throughput of 25 l/hr. of crude tar together with 250 l/hr. of hot water.

Conclusions: In order to obtain rates of throughput suitable for large-scale operations, with this method it is necessary

- (1) to use a larger centrifuge
- (2) to reduce the ratio of additional water: tar as much as possible
- (3) to heat the tar to 80° before centrifuging.

It is most suitable to centrifuge the carbonization products after they have been separated from the carbonization aggregate, cooling them to 100°C. The hot water to be added may be taken from waste water of the centrifuge. Since it grows somewhat cooler during the centrifuging process, some heat must be supplied in order to reestablish the operational temperature. For each centrifuge separately it is necessary to find out the optimum number of rotations, the optimum adjustment of the rings and the optimum operational temperature.

Mode of Operation

Three crude tars have been investigated having a water content of 70%, 76% and 11.5% respectively. We used a Krupp Separator-Centrifuge with 6,400 r.p.m. The difference in density between the water-free tars and water being so slight, we had to use the separator ring No. 8 having the smallest interior diameter and a large amount of hot water. The latter served also for heating the tar. The optimum throughput ratio was found to be 250 l of hot water and 25 l of crude tar per hour, the optimum operational temperature about 70°. Crude tar and additional water must always flow into the centrifuge under the same pressure in order to maintain their ratio as constant as possible. For this purpose we use a container with automatic influx control.

The water-free oil thus obtained was perfectly free and showed between level glass plates neither bubbles nor impurities. Only traces of water could be found in the oil by means of the xylene methods.

Report Prof. Hally  
Tübingen, May 8, 1914

Ditto

Operator: Brockhausen

Summary

Objective of the project: The investigation of possibilities of removing water from oil sludge by means of filtration through a filter cloth or sawdust or by means of a treatment with saw dust.

Results: The water content of an oil sludge containing 70% of water could be reduced to 16% of water by heating it with saw dust. Filtration over saw dust was a failure, hot filtration through a filter cloth unsatisfactory.

Conclusions: The methods in question are failures.

Mode of Operation

After the addition of sawdust to the oil sludge and after heating it to the optimum operational temperature range of 40-50°, an oily layer separated soon from the aqueous; the sawdust which was obviously moistened by the oil swelled in the process. After separating the layers in the separator funnel, the saw dust was removed from the oily layer by means of filtration.

Report Prof. Hally  
Tübingen, May 11, 1914

Ditto

Operator: Goldhofer

Summary

Objective of the project: Investigation whether oil sludge can be freed from water by a treatment with bleaching earth or carbonized-shale dust.

Results: It was possible to reduce the water contents of two samples of Schenborg pile-oil sludges from 67% and 28% resp. to 4-6% by digesting them with bleaching earth or carbonized-shale dust (3%) at an elevated temperature. In one case, by a repeated treatment with carbonized-shale dust the water content was reduced to 1%.

Conclusions: The effect of slight quantities of bleaching earth or carbonized-shale dust in digesting oil sludge is a good one.

Mode of Operation

The oil sludge was heated to about 60°, the agent added and stirred at this temperature for about five minutes. After the filtration through a filter cloth the separation of the layers occurred in the separator funnel. The separated water looked sandy and contained 1.5% of oil. It has not been determined how much of the oil has been retained by the dehydration agent.

Test 1.) Addition of bleaching earth to 200 g oil-sludge at 18°C.

Amount of bleaching earth added	4g = 2%	5g = 2.5%	6g = 3%
Raising the temperature under stirring to 40°			
Water content after water removal	6%	5%	5%
Under stirring the temperature is raised to 60°; water content in the oil after water removal	5%	5.5%	5.5%

2.) Ditto: The bleaching is added at 60°, digesting time 5 min.

Amount of bleaching earth added	4g = 2%	5g = 2.5%
Water content after separation	4%	4.5%

3.) Ditto: 5g of sintered oil-shale slag (ground) added five minutes digesting. Water content in the oil after water removal at 60° 5%

4.) Ditto: Water removed with carbonized-shale dust.

The oil sludge was treated with 1.5% carbonized-shale dust at a temperature which went up to 60°. The oil obtained after filtering through the suction filter and separating the filtrate in the separator funnel amounted to 4%. The dehydrated oil has been treated with 1.5% carbonized-shale dust at 60°, filtered on the suction filter and separated in the separator funnel. The oil contained 1% of water.

Ditto

Practical suggestions for removal of water from crude oil.

Boal reports  
June 1944

#### Summary

Objective of the project: Pilot plant experiments concerning the effect of Diamulgan upon the removal of water from crude tar by settling.

Results: The crude tar Schen M. 2. 15 has been heated and 0.05% of Diamulgan has been added to it. It was allowed to settle for 18 hrs. Then, 50.9% of the oil contained in the tar had separated out in the form of heavy oil (water content: 0.4%) and 19.1% in the form of oil sludge (water content: 58%). Without Diamulgan we obtained only 11.6% of heavy oil (water content: 5.6%) and 38.4% of oil sludge (water content: 65%).

The separation of the crude-tar sample Schen P. M. 20 was more satisfactory with Diamulgan, but also without Diamulgan. We obtained: (a) with Diamulgan, after heating and 12 hours settling, 93.5% of the oil content as heavy oil (water content: 1%) and 6.5% as oil sludge (water content: 48.4%); without Diamulgan after heating and 8 hours settling, 85% as heavy oil (water content: 1%) and 15% as oil sludge (water content: 20.5%).

A settling test with the crude-tar sample Schom M.c. 17, after heating and adding 0.05% Dismulgan illustrated the decrease in water content in the oil-sludge layer from the bottom to the top. The uppermost layer contained no water at all.

Conclusions: In principle, the pilot-plant results were like those obtained in the laboratory. However, the effect of Dismulgan varies within a wide range with different types of tar.

#### Mode of Operation

#### Fischer carbonization analysis of the oil shale used (100g)

	<u>Schom M.C. 15</u>	<u>Schom R.M. 16</u>	<u>Schom M.C. 17</u>
Water	1.8%	3.4%	2.4%
Residue	90.1%	89.8%	90.17%
Carbonization Water	2.5%	1.25%	1.3%
Tar and Oil	3.54%	3.65%	3.87%
Gas and Losses	2.06%	1.9%	2.26%

#### Carbonization Gas Analysis

	<u>Schom M.c. 15</u>	<u>Schom R.M. 16</u>	<u>Schom M.c. 17</u>
H <sub>2</sub> S	0.58% by vol. (8.82 g/m <sup>3</sup> )	0.47% by vol. (7.9 g/m <sup>3</sup> )	0.79% by vol. (14.5 g/m <sup>3</sup> )
CO <sub>2</sub>	18.92% by vol.	12.03% by vol.	20.91% by vol.
C <sub>m</sub> H <sub>n</sub>	0.3 "	0.3 "	0.4 "
O <sub>2</sub>	3.6 "	5.9 "	1.9 "
CS <sub>2</sub>	2.9 "	3.3 "	4.2 "
H <sub>2</sub>	3.5 "	2.5 "	3.2 "
C <sub>m</sub> H <sub>n</sub>	1.7 "	0.6 "	2.1 "
C <sub>m</sub> H <sub>n</sub> + 2	1.1 "	0.3 "	0.2 "
N <sub>2</sub>	67.4 "	74.6 "	66.3 "
C-number	-	1.5	1.1
Benzine in gas	7.82 g/m <sup>3</sup>	4.08 g/m <sup>3</sup>	8.14 g/m <sup>3</sup>
Heating value (Lurgi)			
H <sub>1</sub> lower	404 K cal/m <sup>3</sup>	273 K cal/m <sup>3</sup>	440.6 K cal/m <sup>3</sup>
H <sub>1</sub> lower upper, C <sub>m</sub> H <sub>n</sub>	373 "	243 K cal/m <sup>3</sup>	400.6 "
Heating value (Graf. Vienna)			
H <sub>1</sub> upper	657 "	-	-
H <sub>1</sub> upper, C <sub>m</sub> H <sub>n</sub>	589 "	-	-

Settling Tests

	Schom M.c. 15		Schom R.M. 16	
	without Dismulgan	with 0.05% Dismulgan(*)	without Dismulgan	with 0.1% Dismulgan
Temperature	Elevated Temp. (**)	Addition made at surface temp. of 67°; going down to 50° after 4 hours	Elevated temperature	Addition made at 62° heated for 7 hours more
Settling period	?	18 hr.	ab. 8 hr.	12 hrs. (***) (?)
Total condensate	546 kg	1884 kg	430 kg	2517 kg
Heavy oil	116 kg	484 " = 25.7%	352 "	1102 " = 43.7%
Oil Sludge	430 "	270 " = 14.3%	78 "	147 " = 5.8%
Water	-	1130 " = 60%	-	1268 " = 50.5%
Water content of the heavy oil	5.6%	0.4%	1%	1%

(\*) The Dismulgan has been added in the form of an aqueous solution.

(\*\*) The only remark made regarding temperature. "Heated up as usual in the sedimenting vessel."

(\*\*\*) The original does not show, whether this period of time includes the 7-hour heating period or whether this period must be added to the settling period of 12 hours.

Water content of	65%	58%	20.5%	13.1%
the oil sludge				
In the heavy oil was found a portion of the total oil contained in the crude tar (without benzine) amounting to	41.6%	80.9%	85%	93.5%
In the oil sludge was	58.4%	19.1%	15%	6.5%

The condensate from the test Schom M.c. 17 has been mixed with 0.9 kg of Dismulgan (0.5 kg/l) in the heated sump. When it was added, the temperature at the surface was 60°. The heating was continued for 4 hours until the temperature at the surface reached 80. Then the condensate was pumped into the sedimenting container, once more allowed to settle and then discharged bucket by bucket (1 bucket = about 10 kg). After each bucket the water content has been determined. It was found to be

after 2 buckets	41.6% water
" 4 "	40.0 "
" 5 "	38.5 "
" 7 "	37.0 "
" 9 "	4.25 "
" 12 "	2.05 "
" 15 "	0.0 "

The best of the condensate has been drawn off as heavy oil containing 0.1% water. 83.3% of the total oil contained in the crude tar has been obtained as heavy oil, and 16.7% in the oil sludge

Ditto

Dr. Spengler, Prague  
July 17, 1944

Objective of the project: The optimum conditions for the quick and simple removal of water from Schomberg pile-tar by means of settling and/or centrifuging.

Results: The starting material contained about 55% of water. When it was permitted to stand for 3 days the quantity of practically waterfree oil obtained depended to a large extent upon the height of the liquid column. With equal quantities of oil the separation was taking place more rapidly in large vessels than in narrow vessels. An increase in temperature, e.g. heating it to 70°C for 3/4 of an hour before it is allowed to stand for three days (\*) increased the settling velocity. Dismulgan II and Dismulgan III (in quantities of 0.1%) proved to be the most effective additives among various Dismulgans. Heating (\*) the oil before the settling stage, the quantity of water-free oil could be further increased.

The separation of the oil could not be increased by adding more than 0.1% of Dismulgan.

In all the above mentioned tests, along with the water-free oil layer we would obtain an oil layer averaging 80% of water. If these two layers were separated and 0.1% of Dismulgan VIII was added to the watery oil layer, a complete separation of oil and water took place within 2-3 hours. With a Dismulgan concentration of 0.1% only, oil free water separated out, but the separated oil would still contain 40% of water.

By centrifuging directly the crude tar or by centrifuging the oil layer which contains much water, it was possible to remove much of the water but not all of the water. In both cases, a practically complete separation of oil and water would only occur when Dismulgan VIII was added. An oil layer having a high water content would evolve at the settling, with or without Dismulgan addition; by gentle stirring, e.g. by the slow raising and lowering of a coarse sieve, a considerable portion of oil free water can be separated out from this layer.

We tried also to separate the oil by the addition of water-soluble salts or mineral acids, succeeded in it to a certain extent. But owing to the high consumption of chemicals, these experiments had to be discontinued.

### Conclusions:

(1) Centrifuging: At 20° (or rather, at 60-70°) the shale oil is centrifuged, 1% (V) of Dismulgan VIII being added. The immediate yield consists in 93-98% of an oil containing about 0.1% of water. The drawback in this procedure lies in the comparatively high consumption of Dismulgan and of energy.

(\*) The original (from which a coordinator at the University of Tübingen has compiled these reports M.P.) does not indicate when this heating took place.

(2) Settling. Shale oil is permitted to stand for 1-2 days at 20° (or rather for 2-3 hours at 60-70°) in insulated and heated vats of 1 m height, being slowly stirred upwards and downwards (perforated sieve with 1 cm perforation, 30 lifts/hour). The shale tar is condensed in such a manner that it issues from the condensation unit at 60-70°, the cooling water attaining the same temperature. This cooling water is passed through the vats, heating them. Three layers are formed in the vats: on top 26-30% oil with less than 0.1% water; at the bottom 30% pure water; in the middle 40-45% of an oil-water mixture.

The layers are separated. The middle layer is mixed with 0.1% of Dismulgan VIII and allowed to stand at about 60-70° without stirring (\*) under otherwise identical conditions. After about 1 hour, the complete separation into oil containing about 0.1% of water and into pure water is terminated. At 20°C, the settling will take 3-4 hours. (The intermediate layer may also be directly separated by means of centrifuging, instead of by means of another settling process.)

(The description of the various tests is given at great length and may be translated upon request. Frame 2437-41 M.B.)

Ditto

Report: U-Labor Schombert  
July 13-18, 1941.

Operator Dr. v. Radinger

Summary

Summary: The demulsifying effect of Dismulgan upon crude-tar shale was to be improved, by treating the tar at the same time with other substances, in particular with sand.

Further experiments were aimed at finding out whether a mere filtering of the crude tar over sand, gravel, iron shavings or excelsior would remove the water.

Results: If a tar emulsion contained 0.05% of Dismulgan VIII or less, no substantial separation of tar and water took place in the heat (\*\*). With an addition of 1% of sand, however, water separated out, the more so the less Dismulgan had been added. With a Dismulgan content of 0.005% or 0 some tar was obtained, along with about 61% of volume of water and 8-11% by volume of an intermediate layer. Even in the most favorable cases, this tar would still contain 25% of water by weight.

The filtration experiments using sand failed, because the surface of the filter was soon plugged up. The same drawback has been experienced with gravel, at 60-70° as well as at room temperature, however not to the same extent. With one pass, about 42% by volume of water were separated out; but the tar thus obtained would still contain more than 25% of water. With every pass through the gravel filter some water would again be separated out, passings crude tar (water content: 70%) at about 20° through a filter filled with excelsior moistened with water, resulted also into the separation of an aqueous phase one of an oil phase (water content: 12.7%). Iron shavings were useless as filter material.

(\*) The same author mentioned in a report dated 8-26-44 that gentle upwards and downwards stirring like in the first settling period ought to be applied.

(\*\*) Apparently the emulsion was of a particularly stubborn character.

Conclusions: Merely by treating crude tar with sand a certain but insufficient separation of water and tar could be achieved. The presence of Dismulgan VIII seems to have rather a disturbing effect thereby. Filtering through sand, gravel, or excelsior yielded considerable quantities of water and a tar of high water content.

Mode of Operation

3500 cc of crude tar could not be freed from water by the addition of 10 cc of 2% of Dismulgan VIII solution (0.05%). On heating the sample which contained the Dismulgan for 24 hours to 80-90° and on adding 2-3 spoonful of washed sand (grain size: 0.3-1.0 mm), the separation took place within a few minutes. Sand of finer grain size, however, was a failure, because it remained suspended in the oil, or the sand will entrain the oil when it settles at the bottom of the container.

In another case, the tar which contained the Dismulgan failed to be demulsified by this sand treatment. Once more 0.05% of Dismulgan were added and now the water separated out; if more Dismulgan was added, more water separated out. However even at 70-80° only a part of the water was separated out. Only when it was allowed to stand for 1 hour at 90° a complete separation into yellowish clear water and practically water free slight-viscous tar would take place, the sand sinking to the bottom, while a sludgy intermediate layer appeared, occluding sooty particles. The intermediate layer was soluble (??) in benzine benzol and xylene and easy to filter, a black sludge being left behind. If the intermediate layer was filtered through sodium chloride at 100°, immediately a salt solution and pure oil separated. In the sodium chloride remained a black residue which was extracted with a mixture of benzol, xylol, benzine and ether. A black sludge was left; it left a zuddy residue on being incinerated.

(Rest may be translated. M.B.)

Report U-Laboratory Schomberg  
November 1914

Ditto

Operator: Dr. v. Radinger

Summary

Objective of the project: It was to be found out whether the aqueous crude shale tar can be freed from water by filtration over glass wool as well as over excelsior.

Moreover, we had to find out how the xylene-insoluble water-soluble constituents, ashes and hard asphalt are distributed among the various water-free tar portions and the aqueous tar residues.

Results(\*): (1) Filtration with glass wool and filtration with excelsior had practically the same effect on aqueous crude tar. Approximately 90% of the tar have been obtained practically free of water. No tar-free water has been separated.

(\*) The results are not quite reliable, since owing to technical defects the analyses could not be carried out quite reliably.

(2) If the aqueous tar residue (I) was permitted to stand for 9 days, about 5% of the tar would separate out once more. This tar portion contained 10% of water.

(3) By reacting the aqueous tar residue (II and III) with 1% concentrated hydrochloric acid, the rest of the tar was obtained free of water.

(4) During the 9-day settling period of the aqueous tar residue (I) the smut, consisting of xylene-insoluble and water-insoluble substances was enriched in the aqueous tar residues (II + III) while the separated-out tar portion of low water contents contained only one tenth of the smut. Similar relations have been found to be true for the contents in ashes.

(5) Of the three tar portions obtained which are low in tar contents, that obtained with hydrochloric acid contained less impurities and was of a somewhat lower density and viscosity. The first tar portion obtained by the filtration through glass wool is the poorest in hard asphalt, ashes, etc. of the second tar portion with a 1% water content, obtained by the nine-day settling period from the tar residue (I) contains two or three times as much of them.

Conclusions:

(1) In filtering crude shale tar, excelsior may be replaced by glass wool.

(2) The major quantity of water-free tar (90%) separates out by settling for a few hours after filtration.

(3) If the aqueous tar residue is allowed to settle for several days, one half of the water-free tar may be recovered. But this tar portion contains water (about 10%) and more asphalt and ashes than the first, practically water-free tar portion.

(4) By adding 1% concentrated hydrochloric acid to the aqueous tar residue, the tarry portion which could not be separated by filtration may be directly obtained practically free from water.

Mode of Operation

(Not translated, H.B.)

Ditta

Report Prof. Heinze, Technical Institute, Berlin

8-24-44

Objective of project: Can water be removed from crude tar (tube-pile processed) by means of settling or filtering?

Results: Three settling tests (24 hours) showed that only a small quantity of water and about 62.5% of the oil separate out from the crude tarry at 50° (without additives) about 51% of water and 72% of oil; at 80° (with the addition of 0.05% of Dismulgan VIII) about 92% of the water and 98% of the tar.

Nine filtration tests made with wood shavings, bleaching earth, sand, iron shavings, excelsior and paper, show that the separating effect of wood shavings is about as satisfactory as that of Dismulgan. The separating effects of bleaching earth, sand and paper filters were satisfactory, too; but troubles developed, because the filters became plugged up. The results obtained with iron shavings and excelsior were not satisfactory.

Conclusion: Water can be removed from crude tar by settling; but only if Dismulgan VIII is added.

Wood shavings on a support of paper or glass wool are the best filter material.

Mode of Operation

Starting material was crude tar with a water content of 60%, obviously an oil sudge.

Tests:

(4) sucking off the crude tar (temp. 80°) on a suction filter over 2% wood shavings placed upon a paper filter

(5) sucking off the hot crude tar over wood shavings with a thin glass wool layer as a base

(6) filtration of the hot crude tar over shavings in a glass funnel having a glass wool stopper in the funnel canal.

Tests	Clear water % by weight	Clear oil % by weight	Emulsion % by weight	Oil lost by filter material % by weight
4	52	37	6	5
5	55	45	-	7
6	53	38	6	3

(Rest not translated M.E.)

Report I.O. Farbenindustrie  
Sept. 4, 1944

Ditto

Summary

Objective of project: Working out instructions for the removal of water with Dismulgan.

Results: The prior statement that the best dehydration effect is obtained by adding 0.05% of Dismulgan in a 5% solution at 80°, has been confirmed.

Further tests showed that Dismulgan VII (1%) and Dismulgan VII<sup>0</sup> (0.75%) are practically of the same effect. In contrast to the water obtained with Dismulgan VIII, the water obtained with Dismulgan VII is quite clear.

Conclusions: Whenever it is of importance to obtain perfectly clear water, Dismulgan VII and Dismulgan VII O (in larger quantities) are more suitable demulsifiers than Dismulgan VIII.

Mode of Operation

(Not translated, M.B.)

Report: A.L. G. Dahms  
5-11-44

Ditto

Objective of project: Can crude tar be freed from dust and water by filtration on a heated frame filter press (Rohrman filter press)?

Results: Filtration in the cold is possible. However, it does not result in a clear separation of oil and water. It is more suitable to add a filtering auxiliary agent, such as kieselgur, and to use a special filter medium. It is an advantage to heat the filter gently with steam. Oil heated to 70-80° can also be filtered readily. A shale-tar sample freed from water on the filter press was of an abnormally high viscosity.

Conclusions: It is indeed possible to remove the water from the crude tar by passing it through a heated filter press. But this process is impractical because it causes an increase in viscosity by virtue of the occurrence of heat polymerization.

(Rest not translated, M.B.)

Report U-Laboratory Schenberg  
9-19-44

Ditto

Dr. Lutskendorf

Summary

Objectives of project: The establishment of the most favorable conditions under which crude shale tar can be freed from water by adding Dismulgan.

Results: Tar containing 37% by volume of water could be separated into practically entirely water free tar and water which still contained some tar by adding 0.05-1% of Dismulgan VIII. An amount of water-free tar which was lower by 4.5% was separated out by adding 0.5-1% of Dismulgan VII O; the amount of residual tarry water was increased by the absorption of water from the Dismulgan solution.

Tar containing 15.6% of water has been separated by the addition of 0.025-0.5% of Dismulgan VIII into practically waterfree tar and partly tarry water.

(Rest not translated, M.B.)

Report of Doelt  
9-26-44

Ditto

Summary

Objective of project: Separation of shale-oil sludge by centrifuging.

Results: Oil sludges from Schomberg carbonization piles could be separated at temperatures of from 60 to 94° on Krupp-Separators with 5,500 r.p.m. In one pass, the water content of the oil could be reduced to 2%. The aqueous phase left the centrifuge in the form of a porous paste; it contained some oil. The major part of its water content could be decanted after heating it to 70-80°. In the residue remained 4-6% of oil, based on water.

In accordance with the rate of solid impurities contained in the oil sludge, the interior drum would be put out of commission within 1/4-1 hour.

Conclusions: Oil sludge can be separated by centrifuging, and it is not necessary to re-centrifuge the oil thus obtained. However the centrifuge can not be in operation for more than an hour because of the impurities deposited in it. Then, it must be cleaned. That is why two centrifuges would have to be installed for working up the sludge formed. The aqueous phase issuing from the centrifuge ought to be heated in a special container to 70-80°; thereupon the major part of the water would separate out, go to the drain, and the rest of the oily water could be burnt on the pile, if it should not prove economically profitable to work it up with Dismulgan.

Mode of Operation

The Krupp-Separator (Size 7) (1.5 m<sup>3</sup>/hr; 5,500 r.p.m.) had

an onset period	10 min.
running-in period without drums brakes	30 "
running-out period with drum brake	50 "
time needed for disassembly of drum	10 "
time for cleaning	10 "
time for assembling	10 "

80 minutes are necessary before this centrifuge can be put into operation again after being used.

(Rest not translated M.B.)

Washing of shale tars freed from water by means of an acid treatment.

Report of the U-Laboratory Schomberg  
11-5-44

Dr. v. Radiger

Summary

Objective of the project: Crude shale tar freed from water with a slight quantity of concentrated sulfuric acid is of considerable value (e.g. acid number 5.1). Moreover, such a type of tar can hardly be distilled for at distillation temperatures of less than 200° the tar will evolve considerable quantities of SO<sub>2</sub>, H<sub>2</sub>S and water vapor and will froth over.

Can the tar be made more readily distillable by washing out the acid?

Results: (1) When the acidic water-free tar is subjected to several washings with water, its distillability will be improved when the concentration of the sulfuric acid used for removing the water was less than 0.5%.

(2) The acidic tar becomes readily distillable by being steeped in alkali liquor (excess) and subsequently washed with water several times at 60-80°.

(3) No trouble resulted due to emulsification.

Conclusions: It is suitable to subject shale tar which had been freed from water with sulfuric acid to an alkali liquor treatment and to wash it subsequently with water, before it is worked up or distilled.

#### Mode of Operation

The starting material used was a mixture of various pile tars which had been dehydrated by adding 1% by volume of concentrated sulfuric acid. The aqueous crude tar and the water-free tar had the following characteristics:

	<u>Aqueous Crude Tar</u>	<u>Tar dehydrated with 1% H<sub>2</sub>SO<sub>4</sub></u>
Density (20°)	0.970	0.964
Water content, % by weight	9.2	0.2
Hard asphalt	0.9	0.92
Impurities	1.05	0.13
Acid No. mg KOH/-	2.7	1.2
Saponification No.	12.8	13.3
Engler viscosity (20°)	4.18	4.70
Engler viscosity (50°)	1.75	1.80
Solidification point	-3°	-2°

We conducted three series of tests. Each time, 300 cm<sup>3</sup> of water-free acidic tar (alkali required for neutralization 1.475 g KOH) have been vigorously shaken with alkali liquor at 60-70°, then, they have been left standing for 2-3 hours at 80°. Most of the settled liquor has been drawn off. Then the tar has been mixed three times with 100 cm<sup>3</sup> of tap water each time and heated to 70-80° for 1 hour and then again separated from the wash water. (This mode of operation would hardly be suitable for large scale operations, in particular because of the high temperature involved.) Then, we determined the reaction of the last wash water, the water contents of the washed tar and its distillability.

#### Series I (Alkali excess)

Ten acidic-tar samples of 300 cm<sup>3</sup> each were mixed with 2g KOH each in aqueous solution, using a liquor concentration of 1-10%, each time increasing the concentration by 1%. In all cases the liquor separated completely from the tar; with 1% and 2% liquor the separation started slowly. The washing with water proceeded smoothly, the layer being quickly formed. The last washing waters were neutral, the tars free of water. They distilled off without disturbance.

Series II (Alkali deficiency)\*

Each time 300 cm<sup>3</sup> of acidic tar have been mixed with 1% alkali liquor in quantity mixing from 20 cm<sup>3</sup> to 200 cm<sup>3</sup>, by 20 cm<sup>3</sup> each time (corresponding to 0.2-2g KON). No permanent emulsification occurred. As was to be expected the last washing waters turned out to be sour with amounts of liquor up to including 190 cm<sup>3</sup> (= 1.4 g KOH). The acidity and distillability have not been determined.

Ditto

Report Prof. Heinze  
Nov. 30, 1944

Technical Institute Berlin

Summary

Objective of project: What changes undergo shale tars when they are dehydrated with hydrochloric acid.

Results: Comparative tests were made, on one case removing the water by filtration over wood shavings, the second time with 1% concentrated hydrochloric acid. They showed that the dehydration with hydrochloric acid caused a slight lowering of the solidification point of the tar and a decrease in its coking residue (Conradson) and of the contents in sulfur and in substances normally insoluble in benzine.

Table

Dehydration Method	With 1% Concentrated Hydrochloric Acid		Over Wood Shavings	
	Schomberg	Schorzingen	Schomberg	Schorzingen
	Tar	Tar	Tar	Tar
Solidification Point	-139	-109	-120	-90
Coking residue % by weight	3.08	1.98	3.26	2.18
Sulfur, % by weight	4.03	4.20	4.11	4.69
Benzine insoluble substance % by weight	1.00	0.90	1.28	0.92

Conclusions: Shale tar does not undergo any substantial changes by a treatment with 1% concentrated hydrochloric acid. The acid effect is insofar a favorable one, as the solidification point of the tar is lowered. Moreover, it will contain less impurities, less sulfur and less benzine-insoluble substances.

Mode of Operation

(Not translated, M.B.)

(The next report (v. Radinger) discusses the changes undergone by a tar produced by the pile process and by a tar produced in a "Hubofen", if both of them are treated with 1% of 37% hydrochloric acid at 70° (as compared with the centrifuging method).

\* There is nothing unusual to report about Series III, each time 100 cm<sup>3</sup> alkali liquor (1-10%).

The density was somewhat lower and likewise the viscosity. The contents of xylene-insoluble substances, hard asphalt and saponifiable substances went down. No acidic constituents. With the tar produced by the pile process the solidification point would become a few points higher -- this result is contradicted by the preceding report -- but it would become lower with Hubofen - tar M.B.)

Ditto

The sulfur distribution in the Schandalah - "Hubofen" - Carbonization condensate when it is dehydrated with acid.

Summary

Objective of project: The distribution of sulfur and/or sulfur compounds in the Schandalah carbonization condensate after its dehydration with acids.

Results: In the original Schandalah carbonization condensate (water contents: 7%) about 3/4 of the entire sulfur was present in the form of tar-soluble sulfur compounds and 1/4 as water-soluble sulfur compounds. The (waterfree) tar would thus contain about 3.4% of sulfur, the water portion about 0.4%.

2. On treating the condensate with about 37% hydrochloric acid, 96% sulfuric acid, or 25% nitric acid, we have found that:

- a. SO<sub>2</sub> was the only gaseous sulfur compound observed. The quantity of SO<sub>2</sub> gases present was practically independent from the type of acid used and only correlated to its quantity. With larger amounts of acids, larger amounts of SO<sub>2</sub> were found.
- b. With increasing quantities of acid, the water soluble portion of the sulfur decreased. There were 0.1% of sulfur (based on water) present in their carbonization water separated by centrifuging. On using nitric acid, the amount of water-soluble sulfur compounds was somewhat higher, probably due to the oxidating effect of this acid.
- c. The sulfur content of the solid acid, separated out when the acid was dehydrated, varied only within a narrow range. Nitric acid treatment resulted in a somewhat higher sulfur content of the separated-out acidic portion.
- d. Apparently, the sulfur content of the tar increases at the expense of the amounts of sulfur contained in the carbonization water.

Mode of Operation

(Not translated, M.B.)

(It seems that the final decision favored the use of Dismulgan VIII, even though this chemical was scarce in wartimes and hard to obtain. Dismulgan was produced from ethylene oxide.)

Dismulgane VIII was used as a 5% aqueous water solution, which was added to the emulsion.)