

the borders of the photograph is mainly due to chromatic aberration. The irregularities in the borders of the lines show that the resolving power of the lens is fairly good and that structures of about $\frac{1}{500}$ mm can be easily resolved. Fig. 2 shows a photograph of some diatomees. The magnification is slightly more than 200, the length of the sides of the triangle being 0.18 mm. The slight indistinctness in the centre of the field of view is partly due to some scratches on the top of the very highly curved lens, partly to the fact that the image does not lie in a plane, but on a curved surface. It is astonishing that a lens with a free aperture of less than half a millimeter can give such a large image without showing a greater curvature than is observed.

Chemistry. — *The Thermal decomposition of Paraffin wax in the Presence and in the Absence of Hydrogen of High Pressure.*
By H. I. WATERMAN, A. J. TULLENERS, and J. DOOREN. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of September 24, 1932.)

In previous communications a comparative examination was made of the gaseous and low boiling products (gasoline), obtained in the thermal decomposition of paraffin wax by berginization (high pressure hydrogen) and by cracking (without addition of hydrogen) ¹⁾. A comparative examination of the higher fractions, which gave analogous results, was described in 1929 ²⁾.

In PERQUIN's Thesis the results of these investigations were summarized as follows:

1. The quantities of the products boiling up to 150° are about the same for berginization and for cracking (32—34% of the paraffin wax after 90 minutes at 450° C.).
2. In both products the presence of considerable quantities of paraffin-hydrocarbons has been detected with great certainty.
3. The products obtained by cracking are considerably less saturate.
4. Besides the higher degree of unsaturation of these cracking-products they differ qualitatively more from the products obtained by berginization, as their boiling-points become higher.

¹⁾ H. I. WATERMAN and A. F. H. BLAAUW, Rec. trav. chim. **45**, 284 (1926); H. I. WATERMAN and J. N. J. PERQUIN, ibid **46**, 813, (1927); Comptes rendus du 7^{me} congrès de chimie industrielle, octobre 1927, Chimie et industrie, numéro spécial, April 1928, p. 244. The same subject is discussed more in detail in J. N. J. PERQUIN's Thesis: Bijdrage tot de kennis van het BERGIUS-proces, Delft 1929.

²⁾ H. I. WATERMAN, T. W. TE NUYL and J. N. J. PERQUIN, Journal of the Institution of Petroleum Technologists **15**, 369—371 (1929).

5. From the higher indices of refraction and specific weights together with the lower aniline-point of the cracking-products after saturation with hydrogen, we may conclude to a more cyclic character of these hydrocarbons.

6. The residues boiling above 150° C. differ greatly in character, the berginized product is solid and resembles paraffin wax, the cracked product is a very mobile liquid.

7. The gasoline-fractions obtained by cracking are less stable than the bergin-products, which manifests itself in the increase of the refraction and the specific weight and in the deposition of a viscid, insoluble residue ("gum").

8. In the C-fractions benzol and toluol were detected in small quantities with certainty.

Now the investigation was taken in hand again, and this chiefly, because it had become possible, to learn more about the nature of the hydrocarbon mixtures by a new method of investigation, and this without being obliged to isolate the separate hydrocarbons¹⁾. Besides more attention could be given to the examination of the higher boiling fractions, because the greatest differences were to be expected here.

We had at our disposal products freed from the lower boiling gasoline. First they were distilled under atmospheric pressure to about 240° C.; then the residue was distilled under a vacuum of 8–10 mm. pressure (vapour temperature from 120–130° to about 210° C.), while the residue of this vacuum distillation was further distilled in cathode light vacuum with internal condensation C. V. D. I. C.²⁾. The liquid-temperature in this last distillation was from 100° to 225° for the cracking product and from 107° to 178° for the berginization product. In this last distillation the residue that was subjected to C. V. D. I. C., was already solid, therefore cooling with cold water was impossible.

A survey of the distillation is found in the following schemes.

The symbol C means cracking and B berginization; A. D. means distillation under atmospheric pressure; L. V. D. distillation under low vacuum (8–10 mm. pressure), the cathode vacuum-distillation being denoted by C. V. D. I. C. (see above).

Of the fractions obtained we have determined the following constants:

n_D^{20} , d_4^{20} , $\frac{n^2-1}{n^2+2} \frac{1}{d}$, aniline point, bromine number, and molecular weight.

This last by the lowering of the point of solidification of benzol for

¹⁾ J. C. VLUGTER, H. I. WATERMAN and H. A. VAN WESTEN, Improved methods of examining mineral oils, especially the high boiling components of non aromatic character, Journal Institution of Petroleum Technologists **18**, 735, (1932); *Chemisch Weekblad* **29**, 226 (1932).

²⁾ Method of H. I. WATERMAN and E. B. ELSBACH, *Chem. Weekbl.* **26**, 469 (1929) and H. I. WATERMAN and J. N. J. PERQUIN, *Technische analysen*, 4th edition, Dordrecht. Ed. G. VAN HERWIJNEN.

Distillation cracking product (847 g.).

Distillation cracking product (847 g.).						
C. A. D.	C. L. V. D. (8 mm.)	Residue L. V. D.	Loss			
360,4 g.	191,6 g.	239 g.	56 g.			
42,5 %	22,6 %	28,2 %	6,7 %			
Fraction I	Fraction II	Fraction III	Fraction IV	Fraction V	Residue	Loss
C. C. V. D. I. C. I	C. C. V. D. I. C. II.	C. C. V. D. I. C. III.	C. C. V. D. I. C. IV	C. C. V. D. I. C. V		
34,1 g.	34,3 g.	34,7 g.	37,0 g.	21,9 g.	69 g.	8 g.
14,4 %	14,4 %	14,5 %	15,5 %	9,2 %	28,9 %	3,3 %
light yellow liquid	light yellow liquid	semi solid	solid	solid		

Distillation berginization process (790 g.).

Distillation berginization process (790 g.).					
B. A. D.	B. L. V. D. (10 mm.)	Residue L. V. D.	Loss		
339,5 g.	223,8 g.	210 g.	16,7 g.		
43,0 %	28,3 %	26,6 %	2,1 %		
B. C. V. D. I. C. I	B. C. V. D. I. C. II	B. C. V. D. I. C. III	B. C. V. D. I. C. IV	Residue	Loss
31,4 g.	31,4 g.	31,6 g.	21,1 g.	88,2 g.	6,3 g.
15,0 %	15,0 %	15,0 %	10,0 %	42,0 %	3,0 %
solid	solid	solid	solid	solid	

the lower fractions, for the higher fractions by the lowering of the point of solidification of naphthalene.

Then the C. V. D. I. C.-fractions were hydrogenated at 225° under high hydrogen pressure (some hundreds of kg/cm²) with nickel on guhr as catalyst, after which all the constants mentioned were determined once more. After the hydrogenation the bromine-number was practically nihil; sometimes feebly negative values were found. With a few exceptions the hydrogenated products were free from aromates. The aniline point predicted (for products free from aromates and olefines) from specific refraction and mean molecular weight was in accordance with the value determined save for a single exception, viz. the hydrogenated C. C. V. D. I. C. V; evidently this fraction was not completely hydrogenated, the calculated aniline point was considerably lower (92.2° instead of 105°). The other observations differed for the completely hydrogenated C. C. V. D. I. C. I—IV inclusive 4° maximally; for the completely hydrogenated B. C. V. D. I. C. I—IV inclusive almost 5° maximally. It appeared from the values for the specific dispersion of B. C. V. D. I. C. III and IV $\frac{n_{G'} - n_c}{d} \cdot 10^4$, that a considerable percentage of aromates could no more be present. For C. C. V. D. I. C. IV the specific dispersion was higher (about 166) after complete hydrogenation. Accordingly for C. C. V. D. I. C. I—III inclusive and for B. C. V. D. I. C. I—IV inclusive the mean formula after complete hydrogenation was derived, and also the mean number of rings per molecule of these products:

Completely hydrogenated products.
Calculated elementary formula and number of rings per molecule.

Formula	Mol. Weight	Mean number of rings per molecule
C. C. V. D. I. C. I $C_nH_{2n-1.2}$	259	1.6
II $C_nH_{2n-1.3}$	278	1.65
III $C_nH_{2n-1.0}$	298	1.5
IV $C_nH_{2n-1.2}$	315	[1.6] ¹⁾
B. C. V. D. I. C. I $C_nH_{2n+1.5}$	311	0.25
II $C_nH_{2n+1.4}$	315	0.3
III $C_nH_{2n+1.6}$	338	0.2
IV $C_nH_{2n+1.5}$	351	0.25

¹⁾ In this case this calculation is not entirely permissible, because, as appears from the specific dispersion, which was too high, the product could not be considered as free from aromates. The error made will, probably not be great in this case.

	C. A. D.	C. L. V. D.	C. C. V. D. I. C. I		C. C. V. D. I. C. II		C. C. V. D. I. C. III		C. C. V. D. I. C. IV		C. C. V. D. I. C. V		B. A. D.	B. L. V. D.	B. C. V.	D. I. C. I	B. C. V. D. I. C. II		B. C. V. D. I. C. III		B. C. V. D. I. C. IV	
<i>t</i>	20°	20°	before 20°	after 20°	before 20°	after 20°	before 40°	after 40°	before 40°	after 40°	before 40°	after 40°	20°	20°	before 40°	after 40°	before 40°	after 40°	before 70°	after 70°	before 70°	after hydro- genation 70° C.
n_D^t	1.4466	1.4730	1.4920	1.4682	1.4929	1.4700	1.4920	1.4669	1.5012	1.4740	1.5133	1.4845	1.4236	1.4416	1.4429	1.4402	1.4431	1.4415	1.4333	1.4321	1.4344	1.4333
d_4^t	0.7988	0.8453	0.8753	0.8536	0.8778	0.8567	0.8694	0.8491	0.8829	0.8611	0.9000	0.8832	0.7565	0.7903	0.7928	0.7919	0.7938	0.7943	0.7788	0.7789	0.7812	0.7819
$\frac{n^2-1}{n^2+2} \frac{1}{d}$	0.3342	0.3319	0.3315	0.3258	0.3310	0.3257	0.3337	0.3267	0.3338	0.3264	0.3341	0.3242	0.3370	0.3345	0.3343	0.3329	0.3340	0.3328	0.3339	0.3331	0.3336	0.3326
Aniline point determined	54.7°	65.8°	66.5°	87.2°	73.7°	90.8°	76.6°	94.5°	79.6°	97.2°	82.0°	92.2°	73.0°	89.2°	99.9°	106.8°	102.7°	108.7°	107.3°	111.7°	110.7°	115.8°
Aniline point read in °C	—	—	—	90	—	93	—	98	—	101	—	105	—	—	—	111.5	—	112	—	116	—	117
Bromine value ¹⁾	16.6	11.6	10.7	0	8.5	0	8.2	0	7.5	0	6.1	0	10.3	6.8	6.1	0	5.4	0	5.1	0	4.7	0
Molecular weight ²⁾	163 (<i>b</i>)	216 (<i>b</i>)	259 (<i>b</i>)	259 (<i>b</i>)	278 (<i>b</i>)	278 (<i>b</i>)	301 (<i>b</i>)	298 (<i>b</i>)	$\left\{ \begin{matrix} 316 \text{ (b)} \\ 322 \text{ (n)} \end{matrix} \right\}$	315 (<i>b</i>)	$\left\{ \begin{matrix} 390 \text{ (b)} \\ 386 \text{ (n)} \end{matrix} \right\}$	379 (<i>b</i>)	153 (<i>b</i>)	229 (<i>b</i>)	312 (<i>b</i>)	311 (<i>b</i>)	$\left\{ \begin{matrix} 319 \text{ (b)} \\ 314 \text{ (n)} \end{matrix} \right\}$	315 (<i>b</i>)	334 (<i>n</i>)	338 (<i>b</i>)	351 (<i>n</i>)	351 (<i>b</i>)
$n_C^{70^\circ}$	—	—	—	1.4658 (20°)	—	1.4681 (20°)	—	1.4534	—	1.4602	—	1.4714	—	—	—	—	—	—	1.4307	1.4298	1.4320	1.4310
$n_D^{70^\circ}$	—	—	—	1.4682 (20°)	—	1.4705 (20°)	—	1.4559	—	1.4629	—	1.4742	—	—	—	—	—	—	1.4332	1.4321	1.4344	1.4333
$n_F^{70^\circ}$	—	—	—	1.4741 (20°)	—	1.4767 (20°)	—	1.4618	—	1.4688	—	1.4810	—	—	—	—	—	—	1.4385	1.4374	1.4398	1.4386
$n_{G'}^{70^\circ}$	—	—	—	1.4790 (20°)	—	1.4817 (20°)	—	1.4665	—	1.4741	—	—	—	—	—	—	—	—	—	1.4416	—	1.44295
$\frac{n_{G'} - n_C}{d^{70/4}} \cdot 10^4$	—	—	—	$\left[\frac{155}{(n_{G'} - n_C)} \cdot 10^4 \right]$	—	$\left[\frac{159}{(n_{G'} - n_C)} \cdot 10^4 \right]$	—	158	—	166	—	—	—	—	—	—	—	—	—	151 à 152	—	153

1) The bromine values of the products after complete hydrogenation were very small or in some cases feebly negative; practically they might be put equal to zero.
2) *b*: benzol solvent.
n: naphthalene solvent.
The molecular weights have been determined only for one single concentration, and not calculated by extrapolation at infinite dilution. This was sufficient for our purpose. For the products hydrogenated with nickel the determination was afterwards repeated by G. J. F. BREEDVELD. His observations follow below. They differ fairly much from the values given, but practically they do not affect the conclusions drawn.

C. C. V. D. I. C.	I (<i>b</i>)	II (<i>b</i>)	III (<i>b</i>)	IV (<i>b</i>)	V (<i>b</i>)	B. C. V. D. I. C.	I (<i>b</i>)	II (<i>b</i>)	III (<i>b</i>)	IV (<i>n</i>)	
<i>A</i>	1.290°; 1.690°	1.102°; 1.490°	1.075°; 1.126°	1.063°; 1.240°	0.747°		1.180; 1.098	1.135; 1.005	1.159; 1.074	1.46; 1.13	In this it was assumed that $K_{benzol} = 50.0$ and $K_{naphthalene} = 69.0$
<i>Molecular weight</i> . . .	274; 278	289; 310	329; 320	353; 365	384		315; 315	333; 321	364; 348	388; 374	

For the rest we point out that the lowering in specific refraction is large with the hydrogenation of the cracking-products, smaller with the berginization-fractions, where the change in n and d is also small.

From this investigation it appears clearly how in berginization the formation of cyclic compounds is hindered.

It should be remembered that both series of experiments were performed at 450° C., an initial pressure of 110 kg/cm² at about 15° C. in the Bergin-series, and an initial pressure of 1 kg/cm² or vacuum in the Cracking-series. The duration of the experiments was 90 minutes at 450° C. In the berginization experiments the maximum pressure was on an average 280—290 kg/cm² at 450° C., and the final pressure on an average 80 kg/cm² at about 15°; in the cracking experiments the maximum pressure was on an average 100—110 kg/cm² at 450° C. and the final pressure on an average 15—18 kg/cm² at about 15°.

By the presence of hydrogen in the berginization, which caused a hydrogen consumption of 1.4⁰/₇, the ring-formation is reduced to one seventh of that in the cracking.

By following this method of analysis we have succeeded for the first time in measuring the cyclisation in the cracking quantitatively and in establishing the inhibitory influence of high pressure hydrogen on this cyclisation quantitatively.

Laboratory for Chemical

Delft, July 1932.

Technology of the Technical University.

Physics. — *On the Directional Effect of the Single Hot Wire Anemometer.*

By M. ZIEGLER (Mededeeling N^o. 25 uit het Laboratorium voor Aero- en Hydrodynamica der Technische Hoogeschool te Delft).
(Communicated by Prof. J. M. BURGERS).

(Communicated at the meeting of October 29, 1932.)

1. *Introduction.*

In hot wire work still little attention has been given to the fact that **exact** measurements with a single wire anemometer are only possible in a two dimensional field of flow, provided the position of the wire is perpendicular to the plane of the motion. The indications of the wire, calibrated in the so-called normal position, that is perpendicular to the direction of flow, then give the absolute value of the velocity for an arbitrary direction of the velocity vector in that plane. However, as soon as a third component of the velocity, i.e. a component parallel to the wire is present, then neither the absolute value of the velocity, nor the resultant of the two components