Alkali Absorption in Crude Oil Refining

By DAVID WESSON

IN 1899 the writer made some experiments with a view of determining the amount of caustic soda taken up by oils in the process of refining. Experiments were made by adding a definite excess of caustic soda in the form of lye of different strengths to an oil, stirring the oil by hand from time to time, and titrating the excess of caustic soda in the same manner as in determining the free fatty acids. While the method was crude, the results showed that absorption increased with the strength of the lye and also with the temperature. There was an initial absorption greater than that due to the free fatty acids, after which the absorption slowed down, and when the results were plotted in curves the subsequent increase was very slow.

In 1917 the investigation was taken up again with the idea of testing the method under improved conditions.

Apparatus: The apparatus employed was a cylindrical can about 5½ inches in diameter, 10 inches deep, surrounded with a water-jacket and provided with a stirring apparatus worked by an electric motor. Temperatures were controlled by means of a thermometer in the oil and another one in the water-jacket.

Two burettes, 10 or 20 cc. capacity, divided into tenths, preferably those with a very small bore so as to give a long scale. These burettes should be arranged to fill quickly from reagent bottles; those designed by the writer for fatty acid determination are the most convenient.

One Pipette, graduated to deliver 10 grams of crude oil at 20°C.

Some 4-oz. oil sample bottles.

Reagents: Quarter normal HCl. Quarter normal NaOH.

Phenolphthalein solution for indicator. (1 in 100 alcohol.)

Re-distilled denatured alcohol or grain alcohol.

The phenolphthalein solution and the alcohol should be made neutral before using.

Process: About 2,000 grams of oil were weighed into the apparatus and the stirrer started. The temperature was then brought to the desired point for the experiment. Carefully weighed caustic soda of a calculated amount was run in and the time noted. At intervals of 5 or 10 minutes 10 grams of oil and alkali were withdrawn by the pipette and titrated in 4 ounce bottles in the same manner as the titration of fatty acids, using phenolphthalein as an indicator and neutralized re-distilled denatured alcohol as liquid. Titration was first made on the acid side with quarter normal HCl. When there was any doubt about the end point, quarter normal NaOH was added to akalinity and the solution again titrated to the acid side. By having the two burettes side by side it was possible to obtain end points within .1 cc. without any difficulty.

Very Important: After each addition of the acid or alkali the bottles should be corked and shaken very violently in order to get the correct end point. It is also advisable to let bottles stand one-half minute or so when near the end point so as to observe the color in the supernatant alcohol. There

TABLE I

Sp. Gr. Lye.....	1.092		1.117		1.117		1.18	
P. C. NaOH in Yye.....	8.19		10.18		10.18		17.	
P. C. Lye in Oil.....	6.26		5.		5.		3.22	
P. C. NaOH in Oil.....	.510		.509		.509		.548	
P. C. NaOH in Mix....	.472		.485		.485		.534	
Start Time Min.	Temp. Deg.	NaOH Abs.	Temp. Deg.	Abs.	Temp. Deg.	Abs.	Temp. Deg.	Abs.
0	21.3						20.3	
5	21.4	.256			30	.262	21.5	.230
10	21.7	.268	21	.252	30	.278	21.8	.255
20	21.7	.286	21	.276	30	.304	21.6	.286
30	*21.6	.300		.304	30	†.330	21.5	.311
40	21.6			.331	30	.362	21.3	.353
50	21.6	.326		‡.340	30	**.394	21.3	.378
60	§21.5	.352		.379			21.3	¶.405
70								.434
80							21.3	.445
90							30	
100							50	.491
120							60	‖.522

* Breaking fast. † Break started. ‡ Breaking in large flakes. ** Large grain. § Fully broken. ¶ Pinhead break. ‖ Good open break ready to settle.

TABLE II

Table Showing Rate of Absorption of NaOH by Prime Crude at Different Temperatures

Analysis of Oil		
F.F.A.	1.06	1.06
NaOH for F.F.A.	.15	.15
NaOH for Color, etc.	.50	.50
NaOH Used	.50	.50
NaOH Absorbed (analytically)..	.335	.335
NaOH Used in Excess	.165	.165
Sp. Gr. of Lye	1.116	1.116

Absorption at 21° C.		Absorption at 30° C.	
Minutes	Absorbed	Minutes	Absorbed
0	0	0	0
10	.252	5	.262
20	.276	10	.278
30	.304	20	.304
40	.331	30	.330
50	.346	40	.362
60	.379	50	.394

has been noted in titration at times a tendency of particles insoluble in alcohol to retain alkalinity, which is only removed by a thorough shaking.

Calculation of Results: In calculating the amount of caustic soda absorbed by the oil we have to take into consideration that the portion titrated represents the oil plus the added lye. For instance; if we use 5 per cent of lye containing say 10 per cent of caustic soda, we would add .50 per cent NaOH to the oil we start with, but the mixture of lye and oil would amount to 105 grams of material for each 100 grams of oil started with, and the results of our titration would show the amount of caustic in the 105 grams of mixture. It is evident, therefore, that the mixture contains

$$.50\%\ \text{NaOH} \times \frac{100}{105} = 95.2\% \times$$

$.50\% = .476\%$ which is the percentage of NaOH in the mixture. Each centimeter of quarter normal HCl equals .01 NaOH which on the weight taken is .10 per cent NaOH. If we subtract the quantity of caustic as shown by the burette reading from .476 we have the percentage of caustic absorbed in the mixture. As the mixture contains only 95.2 per cent of oil, we must divide this result by 95.2 in order to get the percentage of caustic absorbed by the oil.

Results

The method was tested out carefully on a sample of prime crude taken from refining No. 440, Bayonne, consisting of a mixture of oil from Charlotte and Chester, which analyzed as follows:

Absolute Oil	97.65
Absolute Loss	2.35
Loss not Fat	.97
F.A. as Soap	1.38
F.F.A.	1.06
F.A. as Soap — F.F.A. = Excess F. A. Saponified	.32
NaOH Absorbed	.335
NaOH for F.A. as Soap	.192
F.A. for Organic Matter	.143
NaOH for Organic Matter and F.F.A.	.293
NaOH for F.A. as Soap over F.F.A.	.042

Three strengths of lye, approximating 8 per cent, 10 per cent and 16 per cent NaOH were used, and obtained results shown in Table I.

Discussion of Results

On consulting Curve No. 1 it will be noticed that the fatty acids are neutralized practically instantaneously after the addition of the caustic soda. It will also be noticed that reaction slows down after the first 10 minutes and then proceeds gradually. It was noticed in the operation of the kettles that when NaOH amounting to that shown by the Absolute Test had been absorbed that the oil commenced to break and not until then. In the case of the strong lye, the break was very slow and did not occur until after the temperature had been raised. In the case of the weaker lyes the absorption and break were both quicker at the higher temperature than at the lower.

In looking into the caustic absorption further it would appear from the analysis of the oil that the caustic taken up in refining forms three functions: First, combination with the fatty acids: Second, combination with organic matter not fat: Third, breaking down an organic complex containing fatty acids and forming a small quantity of soap.

In each case it will be noted that there was a gradual rise in the

curve after the necessary amount of NaOH had been absorbed, and soap was constantly formed as long as the operation proceeded. It will also be noted that at the higher temperature the saponification is more rapid, also that the stronger alkali saponifies more oil.

Chart No. 2 shows the results of two experiments on the same oil,

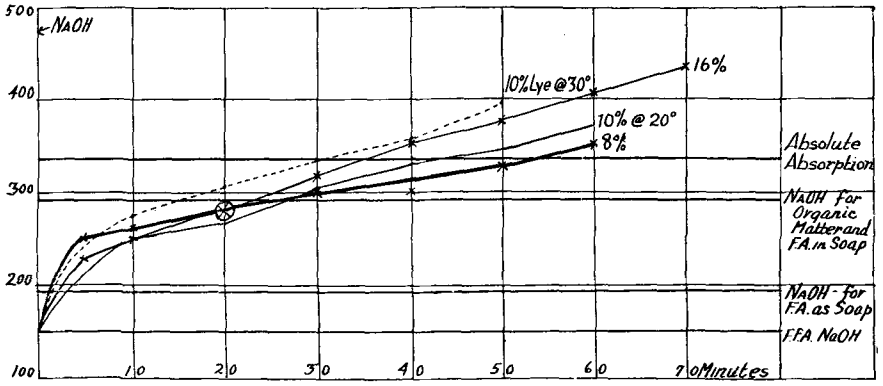


Chart No. 1

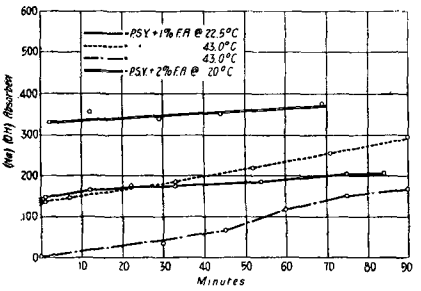


Chart No. 4

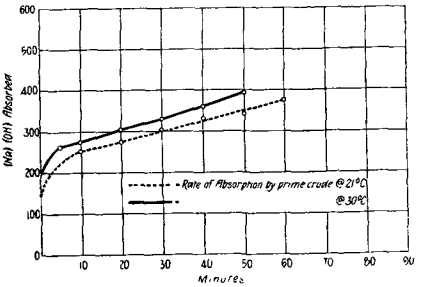


Chart No. 2

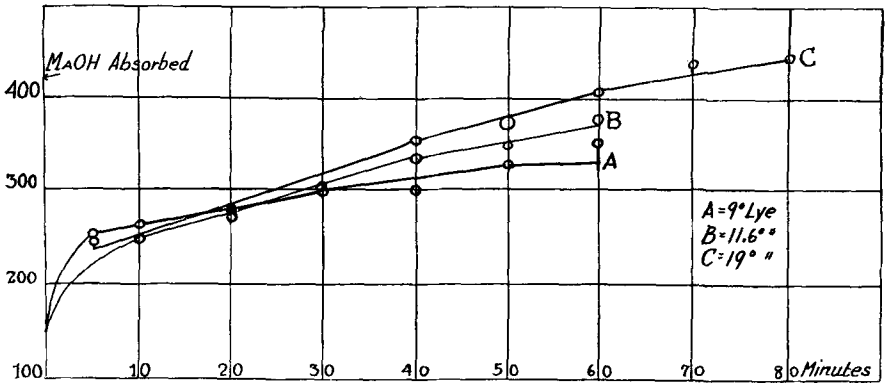


Chart No. 3. Showing the effect of different strengths of lye on the rate of absorption at 21° C.

for the purpose of showing the effect of temperature. The data are given in Table No. II.

The Curves start at the points of the first titration, it being assumed that the NaOH is neutralized at once. It is quite evident that 10°C. speeds up the reaction and saponifies more oil.

In the oil under consideration we note that the Absolute Absorption of F.A. was	.335
F.A. as Soap by Absolute Method was	1.38
Requiring NaOH	.192
Required for combining with organic matter	.143
The F.F.A. in the oil was.....	1.06
Requiring NaOH for neutralization	.150
This added to the NaOH for neutralizing the organic matter gives us	.293
If we subtract this .293 from the total Absolute Absorption we find NaOH	.042
Required for combining with F.A. to make soap.	

It is quite evident, therefore, that any caustic used in excess of the above amounts is going to be used in saponifying oil.

Chart No. 3: This chart was plotted from data below, and shows the effect of strength of lye on absorption. It will be noted that the stronger the lye, the greater the absorption or saponification.

Alkali Absorption of Refined Oil

Experiments were made on Prime Summer Yellow Oil to note the effect of, 1st — Time; 2nd — Temperature; and 3rd—Effect of Free Acid.

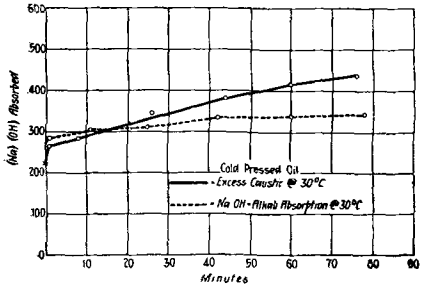
Experiment No. 1: The oil was stirred at 23° for 80 minutes without absorption taking place. The temperature was quickly raised to 40° and then a curve plotted shown as C on Chart. The details of the experiment are given in the table headed Experiment No. 1.

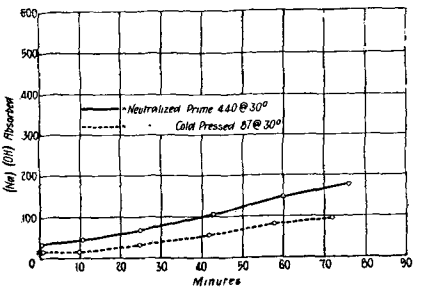
The lye used was 9° and enough

Tabulation Showing Effect of Strength of Lye on Rate of Absorption

	9° Lye	11.6° Lye	19° Lye
F.F.A.	1.06	1.06	1.06
NaOH for F.F.A.	.15	.15	.15
NaOH for Color, etc....	.36	.35	.40
NaOH Used	.51	.50	.55
NaOH Abs. (analyt.)..	.335	.335	.335
NaOH in Excess	.175	.165	.215
Sp. Gr. Lye	1.092	1.116	1.190

Min.	Abs.	Temp. Deg.	Min.	Abs.	Temp. Deg.	Min.	Abs.	Temp. Deg.
0	0	21.3	0	0	21.1	0	0	20.3
5	.256	21.4	10	.252	21.1	5	.250	21.5
10	.268	21.7	20	.276	21.1	10	.255	21.8
20	.286	21.7	30	.304	21.1	20	.286	21.6
30	.300	21.6	40	.331	21.1	30	.311	21.5
40	.300	21.6	50	.346	21.1	40	.365	21.3
50	.326	21.6	60	.379		50	.378	21.3
60	.352	21.5				60	.405	21.3
						70	.434	21.3
						80	.445	21.3





(Left) Chart No. 5. (Right) Chart No. 6. This shows differences in results on neutralized Prime Cottonseed Oil and neutralized Cold Pressed Oil. The oils were simply neutralized for removing the free fatty acid. This experiment would seem to indicate that the Lipoids and other matters in regular Crude Oil tend to increase its rapidity of saponification.

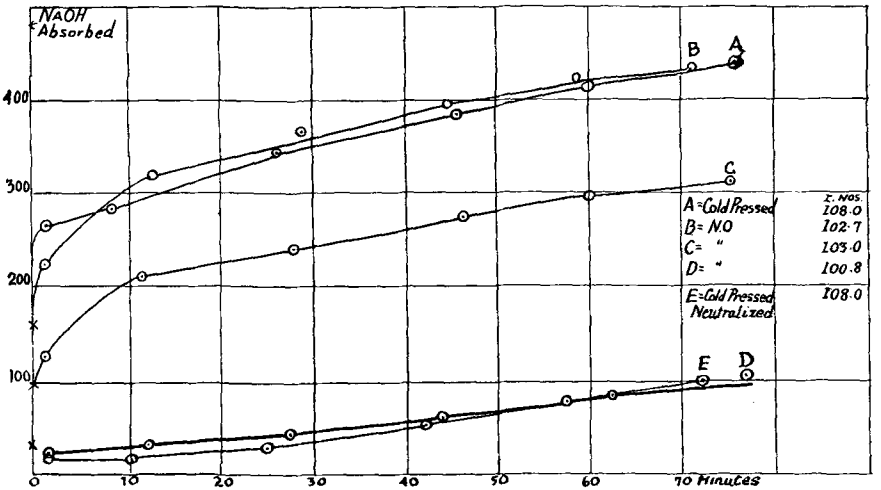
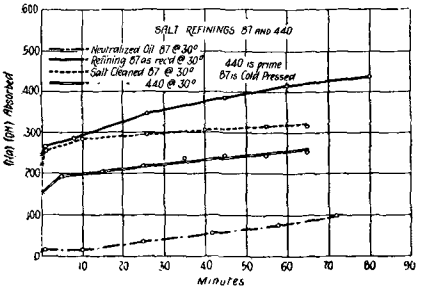


Chart No. 7 is for the purpose of showing the comparison of oils used in Chart No. 6, with varying crudes of different iodine numbers.



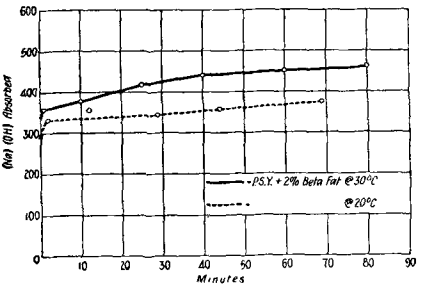


Chart No. 8 shows the effect of first cleaning the oil with a salt wash. Apparently a clean oil saponifies more slowly than an oil which has not been so cleaned.

Chart No. 9 shows the effect of free fatty acid when added to a Prime Summer Yellow Oil. It is interesting particularly in showing the effect of temperature on the reaction.

was used to make .50 per cent NaOH on the oil. The oil was neutral and did not absorb any NaOH analytically.

Experiment Nos. 2 and 3: In these experiments about 1 per cent of distilled fatty acids were added to the crude and the absorption determined, and results plotted in curves A at 22.5°, B at 43°.

It will be noted that in the presence of soap the absorption increases with time, and more rapidly at the higher temperature.

The data are given in the table headed Chart 4.

The theoretical absorption of the mixture is .183 per cent and it will be noticed that this is about where the curves, laid out from the above data, cross. The mixture used at 43° contained .92 per cent F. F. A. That used at 22.5° contained .95 per cent F. F. A. In each case there was present .50 per cent NaOH in excess of that required by the F. F. A. The lye used was 9°.

Experiment No. 4: This was made at 20°, using 2 per cent Fatty Acid in the oil. Results are shown in Curve D. It would appear from the curve that in presence of a large amount of Fatty Acids at low temperature the soap formed surrounds the lye globules and retards absorption.

Experiment No. 4

Prime Refined Oil containing 2 per cent of added fatty acid was treated with caustic to determine the rate of absorption. Used .78 per cent of NaOH, i.e., 0.5 per cent more than was needed to combine with F. F. A.

Minutes	Absorption	Temperature Degrees
0	0	20.0*
2	.330	20.8†
12	.352	20.7
29	.341	20.6
44	.352	20.6
69	.374	20.6

* Start. † Very thick mass to sample.

Cold Pressed Oil

Two tests were run, one in the regular manner, using excess

Experiment No. 1

Table Showing Rate of Absorption of NaOH by P. S. Y.

Minutes	Absorption	Temperature Degrees	
0	0	20.1	
10	0	20.4	
25	0	20.5	
30	0	20.5	
40	0	20.5	
60	0	20.5	
80	0	20.7	
87	0	25.0	
92	0	30.0	To draw curve for absorp-
96	0	35.0	tion we start with 0 Minutes
100	.003%	40.0	0
130	.032	43.6	30
145	.064	43.0	45
160	.117	43.0	60
175	.149	43.4	75
195	.170	44.0	95

EXPERIMENTS ON REFINED OIL—CHART NO. 4

Table Showing Absorption of NaOH by P. S. Y. Containing .93 Per Cent Beta Fat

Curve A—Experiment No. 2 At 22.5° C.			Curve B—Experiment No. 3 At 43 ° C.		
Minute	Absorption	Temperature Degrees	Minute	Absorption	Temperature Degrees
0	0	22.0	0	0	43.0
1	.145	22.0	1	.134	43.2
12	.161	22.3	7	.142	43.2
33	.177	22.4	22	.177	42.9
54	.183	22.5	33	.188	43.0
75	.204	22.5	52	.220	43.4
84	.204	22.5	71	.253	43.8
99	.215	22.5	97	.306	42.3

NaOH, the other using just enough NaOH to neutralize the F. F. A.

These curves are interesting as showing the excessive saponification in one case, and the gradual neutralization in the other.

It is worthy of remark that the cold pressed oil when treated with just enough caustic to neutralize it gave a refined oil, indicating absence of bodies which prevent ordinary crude from acting in the same manner.

In studying Chart 5 it will be noted that where the excess caustic was used, as shown by Curve A, there was a steady increase in the absorption after the addition of the lye, while on Curve B, where just enough caustic was used to meet the requirements of the absorption test, there was a rapid absorption at the start and a very slow increase afterwards during the entire operation of the experiment. The two curves cross each other at .31, which is somewhat below the point

(*Continued on page* 111)

CHART NO. 5

Table Showing Rate of Absorption of NaOH by Cold Pressed Cotton Seed Oil

	Excess NaOH Used	NaOH = Alkali Absorption
F.F.A.	1.55	1.55
NaOH for F.F.A.	.22	,22
NaOH for Color, etc.	.38	.135
NaOH Used	.60	.355
NaOH Absorbed (Analysis)	.355	.355
NaOH Used in Excess	.245	.000
Sp. Gr. Lye	1.091	1.091

Excess NaOH Used			NaOH = Alkali Absorption		
Min.	Abs.	Temp. Deg.	Min.	Abs.	Temp. Deg.
0	0	29.6	0	0	30.8
1	.263	30.5	1	.282	32.0
8	.285	30.5	11	.304	31.9
26	.344	30.5	25	.319	31.8
45	.382	30.9	42	.335	31.3
60	.414	31.0	60	.340	31.0
76	.438	30.7	78	.345	30.0