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BUREAU OF ENGINEERING

REPORT ON

The Carbon and Hydrogen Content of the Fuel Oils in Storage at the Naval Research Laboratory.

NAVAL RESEARCH LABORATORY
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WASHINGTON, D.C.

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TABLE OF CONTENTS

AUTHORIZATION

This problem was authorized by the Bureau of Engineering Project Order 86/31 of June 2, 1931.

PROBLEM

In this report is given the analysis of the fuel oils in storage at the Naval Research Laboratory giving the percent of hydrogen and carbon as determined by complete combustion.

MATERIAL

The fuel oils are described in Report P-25-9. The furnace used was a multiple unit electric furnace with three units controlled by separate rheostats equipped with a clear quartz combustion tube. The catalyst was furnished by the Carbon Monoxide Eliminator Corporation of Baltimore, Md.

METHOD OF ANALYSIS

The furnace was equipped with a quartz combustion tube in order to reach a maximum temperature beyond the softening point of the glass. All combustions were carried out in an atmosphere of oxygen.

Compressed oxygen may contain small amounts of impurities, so in order to insure oxygen free from any hydrogen and carbon compounds the gas was passed through a tube containing copper oxide (wire form) heated to red heat by means of a single unit electric furnace. After passing over the hot copper oxide the oxygen was passed through a suitable drying agent and a CO_2 scrubber before entering the combustion tube.

The furnace as used was so arranged that the longest unit of the three available was in the middle for heating the catalyst.

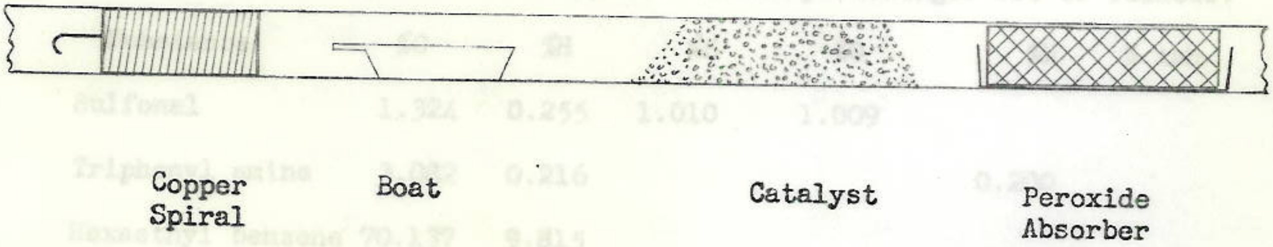
COMBUSTION TUBE

The end of the combustion tube next to the receiving train was loaded with a lead peroxide absorber. Levene and Bieber (Jour.Am.Chem.Soc. Vol.40, 460 (1918)) showed lead peroxide to be an excellent absorber for use in combustion of compounds containing sulfur, nitrogen, and halogens. This absorber consists of a copper gauze wrapper about 12 cm. in length filled with alternated layers of lead peroxide and asbestos impregnated with the peroxide. It has also been found that by the addition of a small amount of red lead to the peroxide there is less chance for low determination of hydrogen.

As lead carbonate decomposes at 315°C, the temperature of the absorber was kept between 330° and 360°C in order to insure that no CO_2 is held in the tube in the form of the carbonate. Lead nitrate has a decomposition temperature of 470°C. Therefore, if the temperature is allowed to go above

470°C the nitrogen compounds will not be held by the absorber. The other lead salts decompose at a temperature above 500°C and will not cause trouble as long as the temperature is held within the limits specified above.

A copper gauze plug is placed in front of the catalyst and the remainder of the tube is clear for the introduction of the sample. After the sample is introduced a copper gauze plug is placed behind it and heated to red heat before burning in order to take care of any gases that might back up in the tube. A platinum gauze wrapper filled with the catalyst was substituted for the copper coil but it was found to absorb moisture during the time of introducing the sample and gave too high results for hydrogen. Since the catalyst is absorbed on pumice it would be expected that more moisture would absorb on it than the copper coil. The following diagram shows the combustion tube loaded and ready for burning the sample.



The receiving train was the same as the drying train for water and carbon dioxide - the products of the combustion. Sulfuric acid was used for water absorption due to the fact that any olefine (products of incomplete combustion) passing through the acid give it a pink to red color. If this should occur the determination was discarded.

PROCEDURE

When the apparatus was assembled and ready for use a blank determination was made. When constant weights were obtained a sample of pure benzoic acid was introduced. After checking benzoic acid with the theoretical value a sample of pure triphenyl amine (a nitrogen compound) was determined.

On assurance that the apparatus was operating correctly a master sample was prepared having a composition of carbon, hydrogen, nitrogen, and sulfur similar to that found in fuel oils. The substances and weights used to make this sample are as follows:

Sulfonal	$(CH_3)_2 C(SO_2C_2H_5)_2$	1.80 gm.
Triphenyl amine	$(C_6H_5)_3 N$	1.75 gm.
Hexaethyl benzene	$C_6(C_2H_5)_6$	40.00 gm.
Benzoic acid	C_6H_5COOH	6.35 gm.
Sodium chloride	NaCl	0.08 gm.
Calcium carbonate	$CaCO_3$	0.05 gm.
	Total weight -	50.03 gm.

From the weights of each ingredient used the total percentage of each element in the sample was calculated. These percentages are as follows:

Substance	%C	%H	%S	%O	%N	% Ash
Sulfonal	1.324	0.255	1.010	1.009		
Triphenyl amine	3.082	0.216			0.200	
Hexaethyl benzene	70.137	9.815				
Benzoic acid	8.738	0.629		3.328		
Sodium chloride						0.160
Calcium carbonate	0.012			0.032		0.056
Total	83.293	10.915	1.010	4.369	0.200	0.216

This master sample was used as a check throughout the work to determine if the apparatus were operating correctly. After the analysis of 4 to 5 oils the master sample was run as a check. The analysis given below will serve to show the accuracy of the determinations. The first set of analyses shows that of pure benzoic acid, giving the mean deviation of the results obtained. The second set of data gives the results obtained from the analysis of the master sample made during the analysis of the fuel oils where it was used as a check.

BENZOIC ACID (Bureau of Standards Sample)

No.	Wt.Sample	%H	Deviation	%C	Deviation
1 without peroxide	0.1729	4.94	-.055	68.72	-.11
2	0.1657	5.08	+.085	68.81	-.02
3	0.1040	4.96	-.025	68.94	+.11
4	0.1034	5.00	-.005	68.84	+.01
	Av.	4.995	.042	68.83	.063
	Calculated	4.95		68.82	

CHECK SAMPLE

No.	Wt.Sample	%H	Deviation	%C	Deviation
1	0.1009	10.89	-.04	83.14	-.22
2	0.1094	11.05	+.13	83.48	+.12
3	0.1058	10.96	+.03	83.41	+.05
4	0.1141	10.92	-.01	83.46	+.10
5	0.1026	10.97	+.04	83.49	+.13
6	0.1124	10.88	-.05	83.24	-.12
7	0.1235	10.88	-.05	83.36	-.00
8	0.1126	11.11	+.18	83.31	-.05
9	0.1073	10.84	-.05	83.34	-.02
10	0.1104	10.83	-.10	83.39	+.03
	Av.	10.93	.068	83.36	.084
	Calculated	10.915		83.281	

DISCUSSION

The analysis of the 29 fuel oils studied in this Laboratory are listed below, showing the size of sample used and average percentages for the two determinations made for each oil. It will be seen from the data below that the average weight of the sample was close to .1000 gram. Water had been determined on all samp les with the centrifuge and found to be absent or a trace except for sample #3.

The ash content is low as shown in the last column. The ash was determined by "ashing" the contents of the alundum thimble after benzol extraction. This assumes that the materials that constitute "ash" are insoluble in hot benzol during the extraction and are not volatile when heated to burn off the organic matter.

Oil Number	Wt. of sample grams	Percent H	C	Wt. of Sample	%H	%C	Average %H	%C	%Ash
3	.1552	11.28	85.75	.1293	11.20	85.69	11.24	85.72	.002
4	.1050	11.28	87.00	.1274	11.32	86.99	11.30	87.00	.000
8	.1005	10.51	85.72	.1148	10.37	85.76	10.44	85.74	-
9	.1679	10.14	86.03	.1531	10.25	86.07	10.19	86.04	.005
12	.1165	11.97	85.60	.1281	11.99	85.47	11.98	85.53	.000
13	.1249	11.59	85.45	.1250	11.58	85.45	11.58	85.45	.008
14	.1096	9.82	87.78	.1163	9.73	87.86	9.77	87.82	.000
15	.1050	11.77	85.92	.1172	11.81	86.18	11.74	86.05	.001
16	.1069	10.74	86.53	.1908	10.71	86.51	10.72	86.52	.021
17	.1507	10.98	86.28	.1306	11.07	86.36	11.02	86.32	.013
21	.1753	11.51	85.53	.1063	11.57	85.63	11.56	85.58	.000
22	.1447	11.50	85.47	.1171	11.55	85.68	11.52	85.57	.001
24	.1635	9.63	87.22	.1846	9.50	87.22	9.56	87.22	.018
25	.1623	10.07	86.94	.1214	10.01	86.62	10.04	86.78	.015
26	.1243	11.68	85.50	.1286	11.69	85.54	11.68	85.52	.019
27	.1253	8.38	90.56	.1124	8.30	90.21	8.34	90.38	.005
27A	.1753	10.76	86.48	.1331	10.74	86.62	10.75	86.55	.045
28	.1006	10.90	86.09	.1072	10.96	85.83	10.93	85.96	.032
30	.1370	11.22	86.25	.1511	11.41	86.18	11.31	86.21	.000
31	.1453	10.51	86.63	.1586	10.50	86.47	10.50	86.55	.000
32	.1148	11.70	85.83	.1080	11.57	85.41	11.63	85.62	.005
33	.1520	9.99	86.94	.1489	10.08	87.21	10.03	87.07	.035
36	.1106	12.83	86.30	.1031	12.80	86.31	12.81	86.30	.000
37	.1173	12.22	86.99	.1215	11.98	86.95	12.10	86.97	.003
38	.1282	8.57	89.87	.1142	8.57	89.64	8.57	89.75	.000
39	.1261	8.53	89.66	.1735	8.56	89.92	8.54	89.79	.003
41	.1175	11.31	85.11	.1003	11.16	84.83	11.23	84.97	.012
44	.1576	11.51	85.49	.1121	11.56	85.51	11.53	85.50	.006
45	.1240	11.66	85.53	.1079	11.76	85.55	11.71	85.54	.013

When the oils are listed according to groups as they have been reported in previous reports which classify them as to straight run, cracked, and blends, it is found that there is some difference in the carbon and hydrogen content. The cracked oils all run lower in hydrogen. This would be expected since in the process of cracking some of the hydrogens are stripped from the molecules. In the case of blends it would be reasonable to conclude that those blends having a low hydrogen content must have a cracked residuum as the base. All straight runs give a higher percentage of hydrogen. The following data gives the oils listed according to their groups:

Group (a) - Cracked

No.	Source	Mol.wgt. avg.	PERCENT				TOTAL
			H	C	S	N	
9	Venezuela	404	10.19	86.04	2.69	0.42	99.34
14	West Texas	273	9.77	87.82	2.08	.16	99.83
16	Los Angeles	417	10.72	86.52	1.04	.88	99.16
24	" "	366	9.56	87.22	1.29	1.10	99.17
27	" "	307	8.34	90.38	.86	.28	99.86
27A	" "	413	10.75	86.55	1.06	.86	99.22
33	" "	358	10.03	87.07	1.32	.99	99.41
38	Mid Continent	285	8.57	89.75	1.22	.12	99.66
	Average -		9.74	87.66			
Group (b) - Blend of Cracked Base							
8	Venezuela	370	10.44	85.74	2.56	0.41	99.15
17	Los Angeles	403	11.02	86.32	1.09	.77	99.20
25	" "	395	10.04	86.78	1.24	1.05	99.11
	Average -		10.50	86.28			
Group (c) - Straight Run							
12	West Texas	381	11.98	85.53	2.33	.16	100.00
13	" "	510	11.58	85.45	2.53	.25	99.81
15	Los Angeles	382	11.74	86.05	1.16	.56	99.51
21	Ventura	477	11.56	85.58	1.94	.64	99.72
22	"	418	11.52	85.57	1.73	.60	99.42
26	Los Angeles	377	11.68	85.52	1.30	.65	99.15
30	SanJoaquin Valley	367	11.31	86.21	1.02	.62	99.16
32	" " "	391	11.63	85.62	1.52	.66	99.43
36	Mid Continent	419	12.81	86.30	.51	.13	99.75
37	Gulf Coast	371	12.10	86.97	0.34	0.11	99.52
45	Signal Hill	387	11.71	85.54	1.39	-	-
	Average -		11.78	85.85			
Group (e) - Blends (Unknown Base)							
3	Navy (West Coast)	364	11.24	85.72	1.39	0.64	98.99
4	Navy (East Coast)	306	11.30	87.00	1.39	0.17	99.86
28	Los Angeles	397	10.93	85.96	1.30	.86	99.05
31	" "	377	10.50	86.55	1.39	.80	99.24
39	Mid Continent	314	8.54	89.79	1.23	.15	99.71
41	Navy (West Coast)	350	11.23	84.97	1.32	-	-
44	Los Angeles	381	11.53	85.50	1.46	-	-

Assuming that the sulfur compounds present have one atom of sulfur to the molecule and the nitrogen compounds have one atom of nitrogen to the molecule, the percentage of the oil which is due to sulfur and the percentage due to nitrogen can be calculated. As an illustration, the master sample will serve to show this. The total weight of the substances used to prepare the sample is 50.03 grams and 1.75 grams of this weight is due to triphenyl amine. If we calculate the percent of the mixture which is due to triphenyl amine we find it to be 3.49%. By this same reasoning with the above assumption and the use of the average molecular weights the following data have been obtained:

No. Oil	Percent of Oil due to Sulfur Compds.	Nitrogen Compds.
3	15.8	16.6
4	13.3	3.7
8	29.6	10.8
9	34.0	12.1
12	27.7	4.4
13	40.3	9.1
14	17.7	3.1
15	13.8	15.3
16	13.6	26.2
17	13.7	22.1
21	28.9	21.8
22	22.6	17.9
24	14.8	28.8
25	15.3	29.6
26	15.3	17.5
27	8.2	6.1
27A	13.7	25.4
28	16.1	24.4
30	11.7	16.3
31	16.4	21.5
32	18.6	18.4
33	14.8	25.3
36	6.7	3.9
37	3.9	2.9
38	10.9	2.4
39	12.1	3.4
41	14.4	-
44	17.4	-
45	16.8	-

From a study of these figures we see that a large percent of the compounds which go to make up the oils may be due to sulfur and nitrogen compounds. For example, oil #13 shows that approximately 50% of the oil may be made up of sulfur and nitrogen compounds. The data shows the sulfur compounds occur in a higher percentage than the nitrogen compounds. Therefore, in any complete study of fuel oils, sulfur, and nitrogen compounds can not be ignored.

CONCLUSIONS

1) That this data shows that a cracked fuel oil has a higher percentage composition of carbon and a lower percentage of hydrogen than a straight run fuel. The data is summarized below:

Sample Number	Average percent H	Average percent C
Cracked - 8	9.74	87.66
Straight run - 11	11.78	85.85

2) That fuel oils consist of a considerable percentage of hydrocarbon compounds containing sulfur or nitrogen or both in the molecule.