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A report on the investigation of the emulsion technology of water in oil (fuels) emulsions

Herman Charles Mouwen
Lehigh University

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A REPORT ON THE INVESTIGATION OF THE
EMULSION TECHNOLOGY OF WATER
IN OIL (FUELS) EMULSIONS

by

Herman Charles Mouwen

A REPORT ON THE INVESTIGATION OF THE
EMULSION TECHNOLOGY OF WATER
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Herman Charles Mouwen

A REPORT OF RESEARCH

Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Master of Science

Lehigh University
Bethlehem, Pennsylvania

1955

CERTIFICATE OF APPROVAL

This report of research is accepted and approved
in partial fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering.

Aug 26, 1958

Date

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SUMMARY

Many fuels when mixed with small quantities of water form an emulsion of water in oil. This water frequently originates from condensation, water-washing treatments or pumping operations involving water displacement method. The water in oil emulsion is usually obtained by pumping the two components through pipe lines during routine storing and re-fueling operations. An experimental procedure for analyzing the various degrees of emulsification of fuels has been used to investigate the many variables which may enhance this emulsification tendency. The procedure includes the use of a Klett-Summerson Colorimeter to measure the light transmission of a turbid emulsion. The term, degree of emulsification, as used in this report describes the dispersion of an arbitrary amount of water in fuel as measured by the colorimeter. The colorimeter reading, therefore, not only reflects the particle size distribution of the water but also the amount of water dispersed. Also, the stability of the emulsions of different fuels is described by taking these colorimeter readings at different time intervals after the initial emulsification.

From the recorded data, the term Emulsifying Factor (E) has been related to the five-minute Klett-Summerson Colorimeter readings (K) of the various fuel samples emulsified with water. This relationship is:

$$\text{Log}(K) = .00397(E)$$

where E, the Emulsifying Factor is a function of the Volume Average Boiling Temperature of the fuel and the Interfacial Surface Tension between the fuel and water. The important

variables which may enhance emulsification are discussed and finally, the above relationship was used to compare the calculated and experimental Klett readings of several industrial solvents and fuels not considered during the correlation of the above relationship.

The above correlation permits a dependable prediction as to the degree of emulsification of many fuels, from gasolines to diesel oil, with water. This prediction may be further applied as a guide to the present performance of coalescing filters used to break these type emulsions.

INTRODUCTION

Opposite the fact that hydrocarbon emulsions have such a wide application is the problem of removing the water from certain hydrocarbon emulsions in which the water is the dispersed phase. Many applications of fuels and solvents cannot tolerate the presence of water. Decanting operations fail as soon as the fuel or solvent becomes thoroughly mixed with water during routine operations. Before the problem of separation is considered, the various fuels and solvents must be considered from the standpoint of emulsion tendencies with water.

A procedure has been devised to measure the degree to which the various fuels and solvents will emulsify with water. Considering the situation and origin of the water which may possibly be present, the analysis was based upon studying a mixture of fuel and water, the amount of water to be 3% by volume. Therefore, a water in oil emulsion is almost forced as a result of the relative amounts of the two components present.

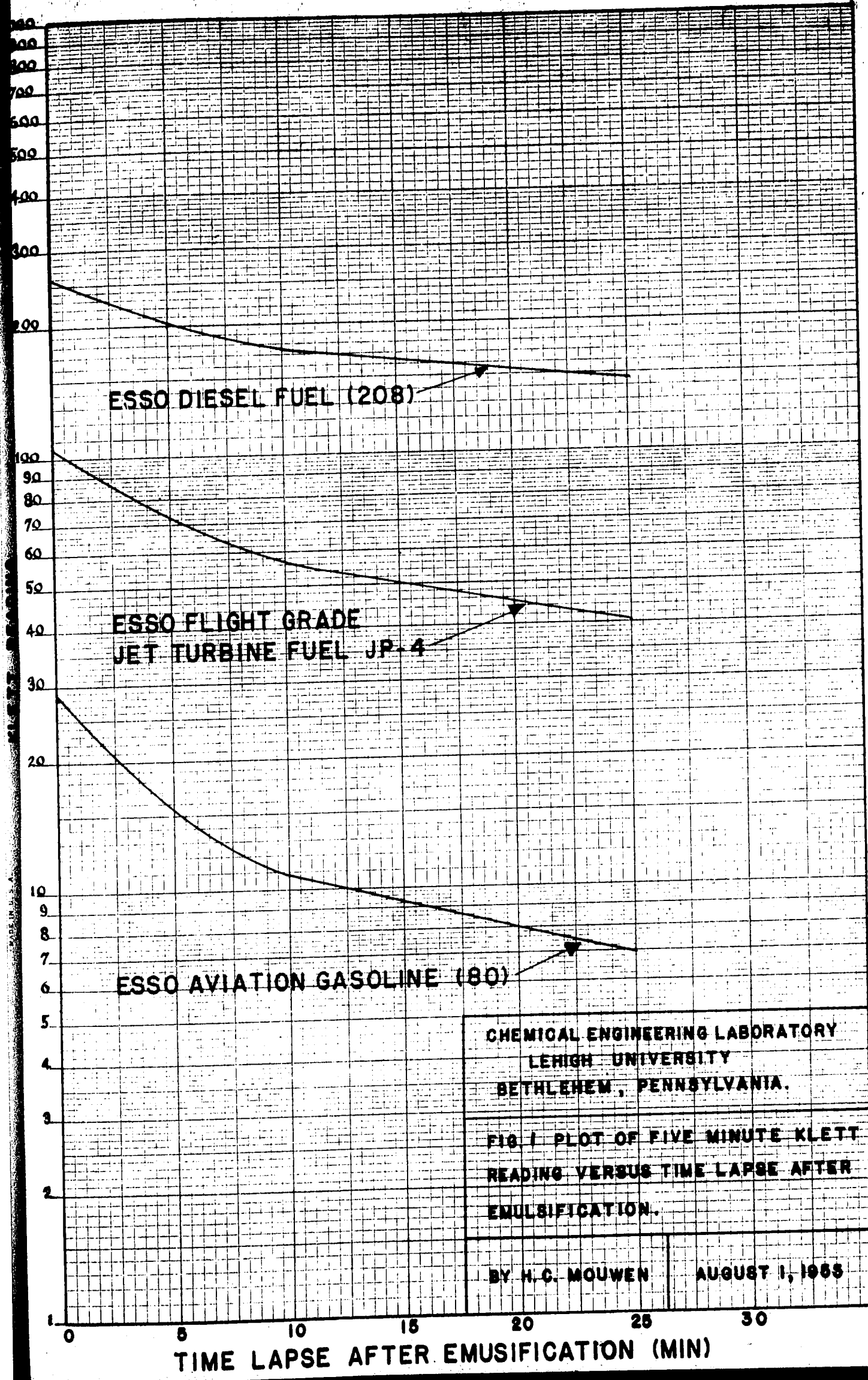
This mixture is blended for ten seconds in a Waring blender and immediately analyzed using a Klett-Summerson colorimeter to measure the percent light transmission through the emulsified mixture. The measurements are continued for a time lapse after the initial mixing and a settling curve can be described for each fuel analysis. Several runs of each fuel are made to insure reproducible results. It is surprising to note that reproducibility was easily obtained using this procedure. Naturally, consistency and accuracy of laboratory techniques is of extreme importance during the analysis.

The initial consideration of jet turbine fuel and water emulsions has led to the inclusion of fuels which range from gasoline to gas oils. The jet fuel blends seem to lie in the middle of this range. If we consider the fuel range to be:

Gasoline
Kerosene
Gas Oils (Diesel Fuels)

then our jet turbine fuels fall in the kerosene grouping. This fact is also brought out when we consider the emulsifying tendencies of these fuels.

Suppose a typical sample of each fuel given above are plotted with the Klett readings as the ordinate and the time lapse after emulsification as the abscissa. The results of this plot are shown in Figure 1. Thus the wide spread of the emulsifying tendencies of these fuels must be the result of some variable or variables which are characteristic of the various fuels. The total volume of the fuel and water mixture which was analyzed was 100 milliliters, therefore only 3 milliliters of water was used in making the emulsions. In the case of the diesel oil and water emulsion, about 1.5 milliliters of water immediately settles to the bottom of the blending jar after mixing. When the gasoline and water was mixed about 2.5 milliliters of water immediately settles. The increasing emulsifying characteristics are the result of a greater volume of water being dispersed in the continuous phase of fuel. A microscopic inspection of a laboratory emulsion of jet turbine fuel and water revealed water particles which ranged from 20 microns to 6 microns. The ocular spacing was 6.35 microns for each space and very few particles were seen which seemed to be less than one space in diameter.



CHEMICAL ENGINEERING LABORATORY
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA.

FIG. 1 PLOT OF FIVE MINUTE KLETT
READING VERSUS TIME LAPSE AFTER
EMULSIFICATION.

BY H.C. MOUWEN AUGUST 1, 1955

TIME LAPSE AFTER EMUSIFICATION (MIN)

Since the initial problem was concerned with jet turbine fuels and their emulsifying tendencies, the various refineries were contacted for samples of these fuels with an inspection report for each sample of fuel. The response was outstanding and a very complete collection of jet turbine fuels was obtained from various refineries within the country. Later contacts were made for samples of gasolines, diesel fuels and kerosenes also accompanied by a refinery inspection report. Table I lists the fuel samples obtained together with the important inspection data furnished by the refinery along with the fuel samples. These fuels were analyzed according to a procedure as outlined in this report under Experimental Procedure. The data was recorded and simultaneously inspected for any possible correlation between the chemical and physical properties of the fuels and the emulsifying characteristics of the fuels and water. Table II lists the more important data which were recorded as a result of the analyzing procedure and the accompanying inspection report of the fuel.

One of the first important variables studied in this problem was the interfacial surface tension between the fuel and the water. As is known, this tension, acting as a contractile force, draws one of the components of an emulsion system into a series of spherical droplets and separates an intimate mixture of two immiscible liquids into two single phases separated by the smallest possible interface (1). This means that the higher the value of the interfacial tension the greater is the tendency for small droplets to agglomerate with resultant decrease in total surface. The greatest emulsifying tendency would be expected in systems exhibiting interfacial tensions approaching zero, in

TABLE I

Fuel	Esso-Spcl. Cut Kerosene	Esso-Flight Grade JP-4	Esso-Referee Grade JP-4	Texaco JP-4 Lockport, Ill.	Texaco JP-4 Wilmington, California	Soc-Vac. JP-4 East Chicago, Indiana	Soc-Vac. JP-4 Beaumont, Texas	Soc-Vac. JP-4 Paulsboro, N. J.
Sample No.	1	2	3	4	5	6	7	8
Gravity, °API	43.7	50.2	45.5	52.6	49.7	53.8	54.2	51.5
Exist. Gum (mg/100 ml)	0.2	1.0	4.2	0	1.0	0.2	1.0	--
Viscosity (centistokes at 70°F)	--	--	--	--	--	--	--	--
Aromatics %	14.4	14.8	25.7	10.4	14.7	7.1	9.6	--
Olefins %	6.7	5.5	10.4	--	--	1.4	0.7	--
Distillation								
IBP °F	323	122	153	136	129	128	147	116
5% Evap.	--	--	--	--	--	175	--	--
10%	372	240	250	196	212	210	195	192
20%	389	285	285	232	259	243	212	240
30%	403	309	308	--	--	268	--	280
40%	412	324	328	--	--	283	--	306
50%	423	336	345	329	349	298	271	324
60%	435	347	368	--	--	313	--	344
70%	443	357	388	--	--	334	--	362
80%	456	370	414	--	--	361	--	386
90%	471	397	462	433	452	404	456	436
95%	487	427	503	--	--	434	--	--
FBP	495	470	524	483	492	474	523	508
Loss %	2.0	1.0	1.0	0.8	1.0	1.0	--	--
Residue %	1.0	1.0	1.0	0.7	1.0	1.0	--	--
Note				A-B	B	A		

TABLE I (cont'd.)

Fuel	Phillips Pet. Blend F-81	Blend F-82	Blend F-85	Blend F-86	Blend F-87	Blend F-100	Blend F-141	Blend F-176	Blend F-179	Blend F-219
Sample No.	9	10	11	12	13	14	15	16	17	18
Gravity, °API	45.9	57.2	53.0	50.6	47.3	57.1	58.3	57.5	48.0	47.1
Exist. Gum (mg/100 ml)	--	--	0.8	3.1	5.9	--	--	0.3	20.3	--
Viscosity (centistokes at 70°F)	1.75	0.73	--	1.33	1.41	--	0.67	0.95	1.54	1.62
Aromatics %	24.4	25.7	14.8	23.7	19.8	2	23.9	8.4	21.0	25.9
Olefins %	--	--	1.7	1.8	4.7	--	--	0.6	3.5	--
Distillation										
IBP °F	141	162	125	131	126	132	150	135	124	139
5% Evap.	209	185	184	192	186	156	174	201	185	169
10%	228	191	217	222	215	165	178	223	227	183
20%	252	198	252	262	257	192	184	252	284	208
30%	295	203	280	295	292	239	189	270	328	249
40%	400	207	316	327	333	412	192	287	365	325
50%	434	211	358	356	370	441	195	307	388	375
60%	447	216	391	382	402	450	200	324	404	403
70%	456	228	418	407	425	459	204	339	421	430
80%	469	322	447	436	446	473	218	356	442	458
90%	492	449	483	476	470	502	424	383	472	489
95%	513	475	515	509	492	529	463	418	500	511
FBP	536	502	547	542	532	539	479	513	522	539
Loss %	0.6	0.3	0.8	1.0	1.1	0.9	0.8	0.5	0.5	0.3
Residue %	0.4	0.7	1.1	1.1	0.9	1.1	1.2	1.0	0.2	1.0

MISSING

PAGES

TABLE I (cont'd.)

Fuel	Purolator Lab Sample Avi- ation Gasoline	Purolator Lab Sample 2-Diesel Fuel	Purolator Lab Sample JP-5	Purolator Lab Sample Varsol
Sample No.	29	30	31	32
Gravity, °API	--	--	--	--
Exist. Gum (mg/100 ml)	--	--	--	--
Viscosity (SUS at 77°F)	27.3	35.6	32.6	29.1
Aromatics %	--	--	--	--
Olefins %	--	--	--	--
Distillation				
IBP °F	106	352	340	316
5% Evap.	--	--	--	--
10%	162	404	384	328
20%	183	432	398	329
30%	198	454	410	330
40%	208	470	420	332
50%	217	486	430	336
60%	222	502	442	338
70%	230	514	456	343
80%	235	536	471	346
90%	250	560	472	358
95%	--	--	--	--
FBP	297	570	480	386
Loss %	2.45	1.1	0.7	0.4
Residue %	1.3	2.9	4.3	1.1

A Refinery reported Dupont No. 22 additive added to fuel

B Refinery reported Santolene "C" added to fuel

TABLE II

Fuel Sample No. from Table I	Klett Readings at Time Lapse						Interfacial Sur- face Tension (γ) (dynes/cm)	Volume Average Boiling Temp. (°C)	Fuel Avg. Mole Wt.	Avg. Mean Boiling Temp. (°F)	Notes
	0 Min	5 Min	10 Min	15 Min	20 Min	25 Min					
1	120	92	91	79	69	63	41.1	416	168	420	
2	102	72	55	54	45	40	27.1	332	130	311	
3	170	113	103	80	72	63	21.6	361	134	330	
4	82	53	40	32	23	22	35.9	302	123	287	
5	118	81	61	47	38	29	34.7	316	128	304	
6	84	47	39	30	26	23	31.6	302	121	284	
7	60	40	28	21	17	14	31.7	301	107	237	
8	105	69	53	45	38	33	21.7	318	124	289	
9	275	174	134	115	93	80	22.6	375	142	350	
10	102	57	39	29	20	17	20.6	273	118	265	
11	170	102	81	60	50	44	21.0	349	133	313	
12	123	81	63	48	42	35	22.0	349	133	319	
13	133	89	69	50	38	30	22.3	350	129	312	
14	159	114	103	84	77	68	15.5	361	132	307	
15	44	26	21	12	10	7	35.1	250	112	248	
16	50	35	24	18	13	10	35.2	308	126	289	
17	572	460	339	230	182	152	19.8	359	138	334	
18	117	76	60	44	36	28	32.2	345	124	300	
19		34					28.3	239			
20		402					21.1	503			
21		98					39.5	427			
22		178					24.7	427			
23		23					35.1	215			
24		23					35.4	223			
25		262					34.3	479			
26		103					39.6	420			
27		244					28.3	480			

TABLE I (cont'd.)

Fuel	Purolator Lab Sample Avi- ation Gasoline	Purolator Lab Sample 2-Diesel Fuel	Purolator Lab Sample JP-5	Purolator Lab Sample Varsol
Sample No.	29	30	31	32
Gravity, °API	--	--	--	--
Exist. Gum (mg/100 ml)	--	--	--	--
Viscosity (SUS at 77°F)	27.3	35.6	32.6	29.1
Aromatics %	--	--	--	--
Olefins %	--	--	--	--
Distillation				
IBP °F	106	352	340	316
5% Evap.	--	--	--	--
10%	162	404	384	328
20%	183	432	398	329
30%	198	454	410	330
40%	208	470	420	332
50%	217	486	430	336
60%	222	502	442	338
70%	230	514	456	343
80%	235	536	471	346
90%	250	560	472	358
95%	--	--	--	--
FBP	297	570	480	386
Loss %	2.45	1.1	0.7	0.4
Residue %	1.3	2.9	4.3	1.1

A Refinery reported Dupont No. 22 additive added to fuel

B Refinery reported Santolene "C" added to fuel

TABLE II

Fuel Sample No. from Table I	Klett Readings at Time Lapse						Interfacial Sur- face Tension (γ) (dynes/cm)	Volume Average Boiling Temp. (°F)	Fuel Avg. Mole Wt.	Avg. Mean Boiling Temp. (°F)	Notes
	0 Min	5 Min	10 Min	15 Min	20 Min	25 Min					
1	120	92	91	79	69	63	41.1	416	168	420	
2	102	72	55	54	45	40	27.1	332	130	311	
3	170	113	103	80	72	63	21.6	361	134	330	
4	82	53	40	32	23	22	35.9	302	123	287	
5	118	81	61	47	38	29	34.7	316	128	304	
6	84	47	39	30	26	23	31.6	302	121	284	
7	60	40	28	21	17	14	31.7	301	107	237	
8	105	69	53	45	38	33	21.7	318	124	289	
9	275	174	134	115	93	80	22.6	375	142	350	
10	102	57	39	29	20	17	20.6	273	118	265	
11	170	102	81	60	50	44	21.0	349	133	313	
12	123	81	63	48	42	35	22.0	349	133	319	
13	133	89	69	50	38	30	22.3	350	129	312	
14	159	114	103	84	77	68	15.5	361	132	307	
15	44	26	21	12	10	7	35.1	250	112	248	
16	50	35	24	18	13	10	35.2	308	126	289	
17	572	460	339	230	182	152	19.8	359	138	334	
18	117	76	60	44	36	28	32.2	345	124	300	
19		34					28.3	239			
20		402					21.1	503			
21		98					39.5	427			
22		178					24.7	427			
23		23					35.1	215			
24		23					35.4	223			
25		262					34.3	479			
26		103					39.6	420			
27		244					28.3	480			

TABLE II (cont'd.)

Fuel Sample No. from Table I	Klett Readings at Time Lapse						Interfacial Sur- face Tension (γ) (dynes/cm)	Volume Average Boiling Temp. (°F)	Fuel Avg. Mole Wt.	Avg. Mean Boiling Temp.(°F)	Notes
	0 Min	5 Min	10 Min	15 Min	20 Min	25 Min					
28		111					39.6		414		
29		16					37.0		210		
30		299					25.2		480		
31		200					25.8		428		
32		75					33.1		340		
Texaco Kerosene	171	123	107	100	93	89	40.5	-	-	-	(1)
Shell Kerosene	177	122	111	101	95	90	36.2	-	-	-	(1)

Note 1 - This fuel meets British Spec. No. 2482 DERD, no inspection report accompanied these fuels

which there would accordingly be no tendency for the droplets to merge with resultant decrease in surface.

Consideration of the above theory was made by investigating the results of adding to a sample fuel long-chain primary and secondary amines which would vary the interfacial surface tension. The results showed that although the value of the interfacial surface tension may be decreased to almost one-fifth of its original value, the emulsifying tendency was only moderately increased. Again, the results also indicated the difference between straight-chain and branched-chain stabilizing compounds which may be present in the fuel and enhance the emulsification.

TABLE III

FUEL USED: Socony-Vacuum Jet Turbine Fuel JP-4
East Chicago Refinery, Indiana

*AMINE ADDED	γ (dynes/cm)	Klett Rdg (5 minutes lapse)
None	31.6	47
ARMEEN 10D(1.66 gm/l)	6.0	110
ARMEEN 12D(1.95 gm/l)	6.0	117
ARMEEN 16D(2.50 gm/l)	6.0	130
ARMEEN 16D(5.0 gm/l)	5.7	138
ARMEEN 2C(4.50 gm/l)	18.2	137
ARMEEN 2C(2.00 gm/l)	16.9	118
ARMEEN 2T(5.30 gm/l)	25.6	240
ARMEEN 2T(2.00 gm/l)	21.0	140

*See Appendix for ARMEEN composition

A further condensation of this topic and the data of Table III are included in the Discussion of Results of this report. But it should be understood that the theory of lower interfacial surface tensions producing greater emulsifying tendencies does not always hold. It is certain that the molecular structure of any agent present in the fuel which may enhance emulsification plays an

important part in the degree to which a fuel and water will emulsify.

The interfacial surface tensions were measured over the range 0°C to 60°C and no significant influence of temperature on the values of the interfacial surface tension was noted. Several of the systems were also studied with regard to the influence of mutual saturation. No significant effect was observed on the interfacial tension whether the constituents were brought in contact without mixing or were adequately mixed to assure mutual saturation. Along the lines of interfacial surface tension it should be mentioned that the spreading coefficient and work of adhesion were calculated for several fuels but bore no observable relationships. Of course, these two properties are a function of the fuel and water surface tensions measured in air and their interfacial surface tension. Thus no new consideration was being made when the spreading coefficient and work of adhesion were calculated. They have been proposed by theoretical workers in the field, but seem to offer no help here. The interfacial surface tension (γ) as used in the final correlation of data was that value as measured by a DuNouy Tensiometer between the fuel and water at 30.0°C.

In the case of the fuels studied so far in contact with both pure water and synthetic sea water, the interfacial surface tension does not accomplish complete correlation with the light transmission characteristics as measured for the emulsions. There is a clear indication that lower values of the interfacial tension do occur in those systems which form the more stable emulsions. The imperfect correlation does not weaken the indication

that interfacial tension is one of the major factors, but is a consequence of the fact that there are other factors which must be recognized.

Among the other important variables which were studied and are discussed are viscosity, existent gum content, density and fuel additives. The effects of the above variables as found during this investigation range from negligible to very important. Indeed, it was found that fuel additives can be the most important single variable in studying the tendencies of fuels to emulsify with water. Those additives studied and believed to be completely typical included:

Santolene "C"	Monsanto Chemical Co.
Dupont Fuel Additive No. 2	
Ionad 17	Shell Oil Co.

The study of fuel additives was not nearly exhausted on the basis that the many other major effects, due to the fuel's physical and chemical properties, were complicated enough without introducing a new variable.

Finally, after a thorough and complete search of the variables which may enhance the emulsification of fuel and water, a correlation was made between the five-minute Klett Reading (K) and the Emulsifying Factor (E). This emulsifying factor is a function of the volume average boiling temperature of the fuel and the interfacial surface tension between the fuel and water. A fairly dependable prediction may be made concerning the fuel's tendency to emulsify by using the calculated relationship.

The five-minute Klett Reading rather than the initial reading is chosen because it is considerably freer of the uncertainty of the operator's consistent speed in transferring

the emulsion from the mixing vessel into the measuring instrument. It retains the greater indication of emulsification characteristic of the early period and is considered a much safer criterion than the initial reading.

EXPERIMENTAL PROCEDURE

The degree to which fuel and water emulsify was determined by measuring the light transmission through the turbid emulsion with a Klett-Summerson Colorimeter. The following procedure was used during this investigation:

APPARATUS: Klett-Summerson Colorimeter Model (Glass Cell)
Blue Filter (No. 42) for colorimeter
Solution Cell, 10 mm wide for colorimeter
Reduction Plate, 7.5 mm wide for solution cell
Waring Blendor
Constant Temperature Bath at 30.0°C
Stop Watch

The colorimeter instruction book outlines the general procedure for turbidimetric analysis and this procedure closely follows the instruction book outline.

After the colorimeter galvanometer has been adjusted to the zero reading and the instrument has been turned on for a few minutes, the clear fuel under investigation is used in the solution cell with the reduction plate to adjust the instrument for a zero reading for the clear fuel. The 2.5 mm solution depth enables the severest emulsions to be analyzed with fair accuracy. Once the instrument has been adjusted using the clear fuel, it is ready for reading the percent light transmission through a turbid emulsion of fuel and water.

A mixture of 100 cc of fuel and water (3% water by volume), both at the test temperature (30.0°C), is poured into the Waring Blendor and mixed for 10 seconds. After mixing, a portion of the emulsion is immediately poured into the solution cell with the reduction plate and a colorimeter reading is taken. The stop watch used to time the Waring Blendor mixing is allowed to continue to record the time lapse after emulsification. After

the initial reading is recorded, the solution cell is placed in a constant temperature bath (30.0°C) until it is time for the next reading. Colorimeter readings are taken every 5 minutes for 25 minutes. The solution cell is returned to the constant temperature bath between all readings. A thermometer may be used to record the initial temperature of the fuel and water emulsion in the Waring Blendor after the test portion has been removed and inserted in the colorimeter for the initial reading. Three runs are made for each fuel under investigation so that reproducible results are obtained. At times, more than three runs may be necessary in order to obtain cnecking results.

The recorded data should include:

EXAMPLE:

MIX TIME	EMULSION TEMP.	TIME LAPSE	KLETT READING	REMARKS
10 sec	28°C	0 min	160	Reading unsteady
		5 min	142	Reading steady
		10 min	119	" "
		ETC.	ETC.	

A plot of Klett readings versus time lapse may be made to observe the initial degree of emulsification and the settling rate of the emulsion. This plot gives some indication of the stability of the emulsion. Of course, for experimental purposes, many variables may be changed, for example, mix-time; quantity of water; total volume of mixture; etc. Figure 1 represents the initial data taken for the formulation of this procedure for various fuels. This procedure as outlined has given reproducible results after extensive experimental investigation and should be closely adhered to so that the emulsion technology may be investigated on a sound basis.

The interfacial surface tensions between the sample fuels and water were determined by using a DuNouy Tensiometer. This ring-method determination of surface tension presented no difficulties in measuring interfacial tensions. The proper correction for the ring was made for all readings. All determinations were made at 30.0°C and several fuels were investigated over the range 0°C to 60.0°C with no significant influence of temperature being noted. The two components, fuel and water, were also examined when mutually saturated with respect to each other and again no changes were observed.

All viscosity measurements made during the investigation were obtained by using an Ostwald Viscometer placed in a constant temperature bath at 30.0°C.

This experimental procedure was designed to obtain the invaluable data necessary to formulate final conclusions regarding the technology of fuel and water emulsion. It was the result of a separate phase of the general investigation and was adopted only when the data did indicate that it was possible to measure a fuel's tendency to emulsify with water.

DISCUSSION OF RESULTS

Some interesting observations were made during the investigations of the various fuels and these observations evolved in a more or less orderly fashion, though unfortunately indicating that several factors contribute to the emulsification tendency.

Since the interfacial surface tensions of the fuels and water do not correlate the fuels with their emulsifying characteristics completely, it is theorized that the molecular attraction must be about the same for many fuels of the same chemical type at the boundary of the fuel and water.

TABLE IV

Isoparaffin Fuels	γ (dynes/cm)	Klett Reading (at 5 minutes)
Sample No. 9	22.6	174
" " 10	20.6	57
" " 11	21.0	102
" " 12	22.0	81
" " 13	22.3	89
" " 14	15.5	114
" " 17	19.8	460*

Normal Paraffin Fuels	γ (dynes/cm)	Klett Reading (at 5 minutes)
Sample No. 15	35.1	26
" " 16	35.2	35
" " 18	32.2	76

*Fuel Sample No. 17, see Existent Gum Content Table I.

From Table IV it seems that the theory of the similar fuels having the same molecular attraction at the boundary could very well explain the reason for like hydrocarbon-type fuels having the same interfacial surface tension. The data of Table III presents the results of an experiment carried out to investigate this theory of like hydrocarbon fuels having about the same interfacial tensions.

A specified quantity (.01 mole) of primary (RNH_2) and secondary (R_2NH) amines was added to a sample of jet turbine fuel JP-4. The interfacial surface tension was measured as well as the light transmission of an emulsion of the fuel with water in accordance with the Experimental Procedure. The primary amines were straight-chain compounds varying in the number of carbons and likewise, the secondary amines also varied in number of carbons.

The results of adding the straight-chain amines to the fuel sample is a depression of the interfacial surface tensions to about the same value regardless of the carbon chain length and the amount of amine added with respect to chain length. In other words, the addition of 1.66 grams/liter of a 10 carbon straight-chain amine yields about the same interfacial surface tension with water as when 2.5 grams/liter and 5.0 grams/liter of a 16 carbon straight-chain amine was added.

Again, it is shown that additions of a secondary amine also resulted in fuel samples having interfacial surface tension values which range from about 17 to 26 dynes/cm. This is still considered a fairly close grouping of values although the spread is much greater than in the case of the primary amines.

Both amine additions gave positive adsorption at the boundary of the fuel and water, that is, their additions decreased the original interfacial tension. It certainly is obvious that the straight-chain amines caused a greater decrease in the free energy of the boundary surface than the branched-chain or secondary amines. This change is attributed to greater concentration and molecular attraction (or repulsion) at the fuel water

interface in the case of straight-chain molecules. The concentration of secondary or branched-chain molecules at this interface would not be nearly as great as primary or straight-chain molecules.

The above discussion can also be applied to the data of Table IV with respect to like hydrocarbon fuels having about the same interfacial surface tension. In this case the branched-chain type fuel or isoparaffin fuel has the lower value of the interfacial tensions. But the fact must be recognized that the investigation using the addition of the amines did cause greater amounts of the amines to be added to the fuel than would ever be found in a standard product. Undoubtedly, these greater amounts did cause concentration and molecular orientation effects at the fuel and water interface.

The above presentation does clearly show that the interfacial surface tensions of the fuels and water do not completely correlate the fuels with their emulsifying characteristics. This statement is substantiated by observing the values of the Klett readings for both Tables III and IV. Especially of interest is the results of the amine additions and their effect on the emulsifying tendencies of the sample fuel. The plain fuels' Klett reading of 47 was increased to 110 by the addition of ARMEEN 10D. But the addition of amines of longer carbon-chains only increased the Klett reading to a maximum of 138. Hence, the length of the carbon chain does not seem to affect the emulsion tendencies in any great manner.

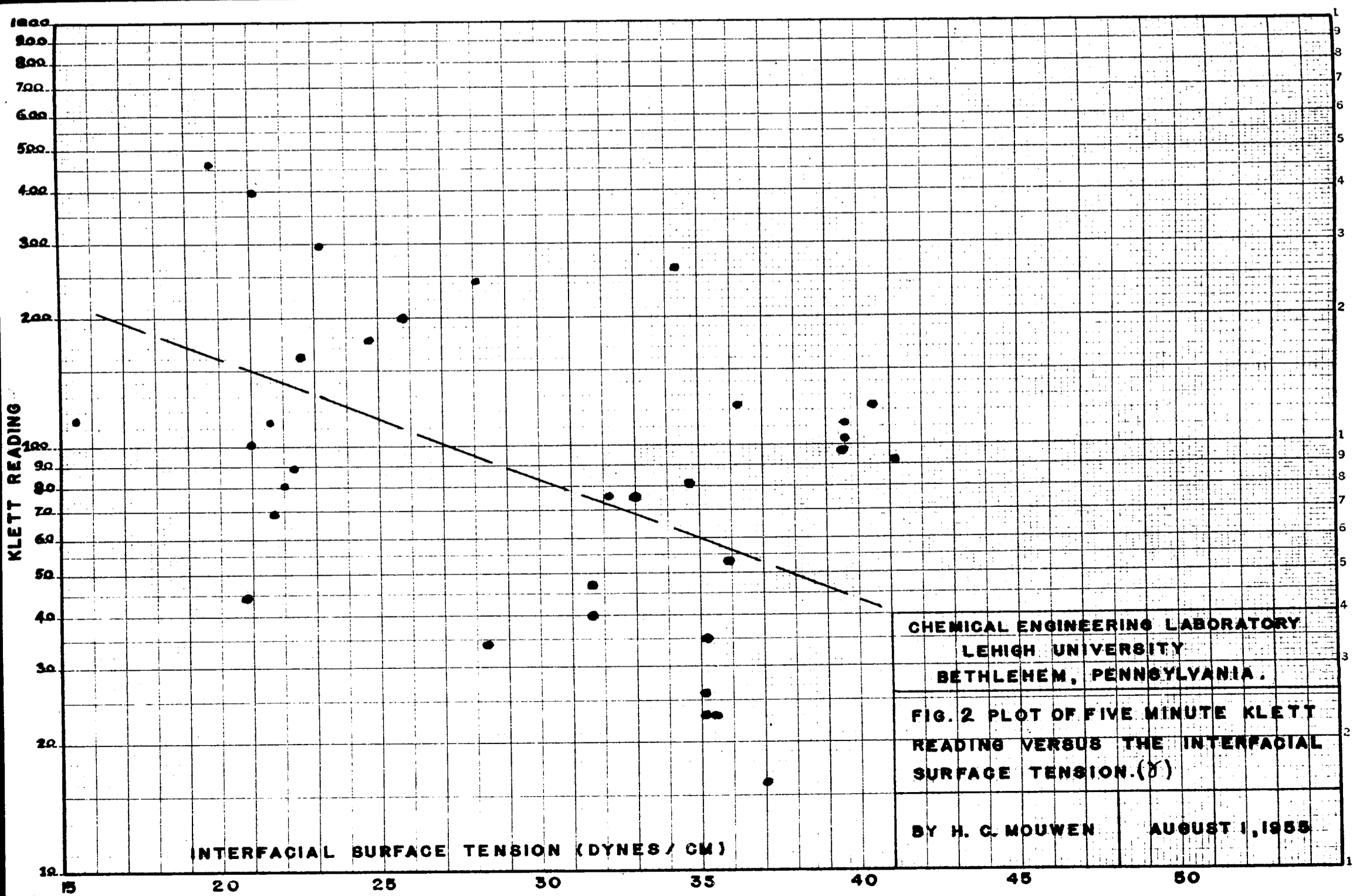
When the secondary amine additions are considered, the range of the Klett readings is greatly increased. First, the addition of 2.00 grams/liter of ARMEEN 2C and 2T caused a range

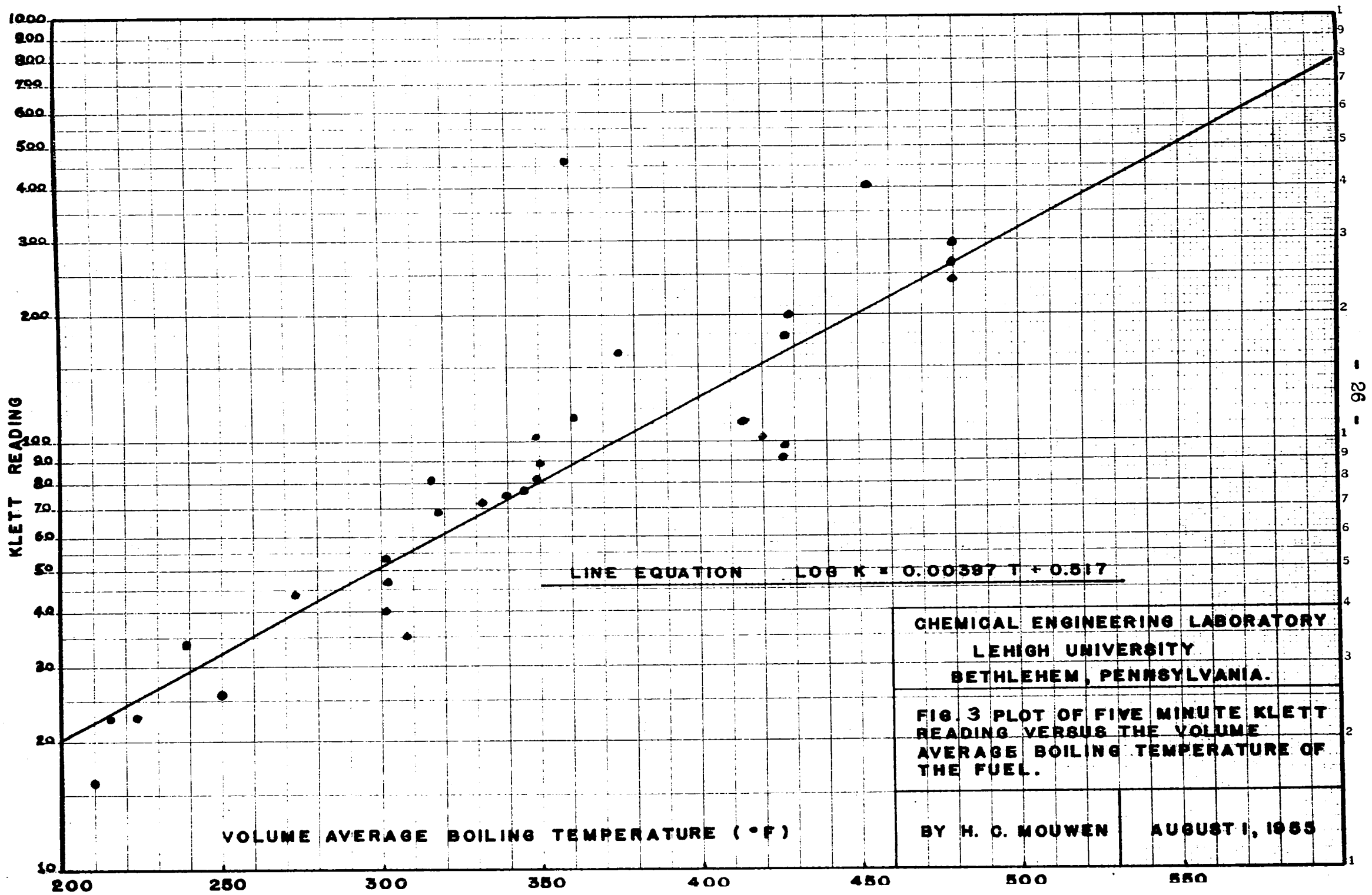
of 118 to 140. Then, the additions of 4.50 and 5.30 grams/liter of ARMEEN 2C and 2T respectively caused the range to spread greater, from 137 to 240. Hence, in the case of branched-chain compounds the effect of a longer carbon chain is realized. These results do agree with the "oriented wedge" theory of emulsification (2). This theory states that if the cross sections of the two parts of a stabilizing molecule are such that the hydrocarbon portion has a larger cross section than the polar group, then a water in oil emulsion will be stabilized. Hence, the addition of ARMEEN 2T (18-C, sec amine) did cause greater stabilization of the emulsion to take place than when ARMEEN 2C (12-C, sec amine) was added. ARMEEN 2T with mainly 18 carbon atom chains would be greater in cross section than ARMEEN 2C with only 12 carbon atoms in its chain since the addition of carbon atoms to a secondary amine also causes a larger cross section. Then again, the additions of straight-chain molecules as ARMEEN 10D, 12D, and 16D (primary amines) would not increase the emulsion stabilization since increasing the carbon chain length would not greatly affect the size of the cross section of the molecule. In the above discussion, two terms were related which relation is justified but not apparent. The term, stability of the emulsion, and the term, degree of emulsification (as reported by the Klett readings) are clearly related by the definition of the latter term as given in the Summary of this report.

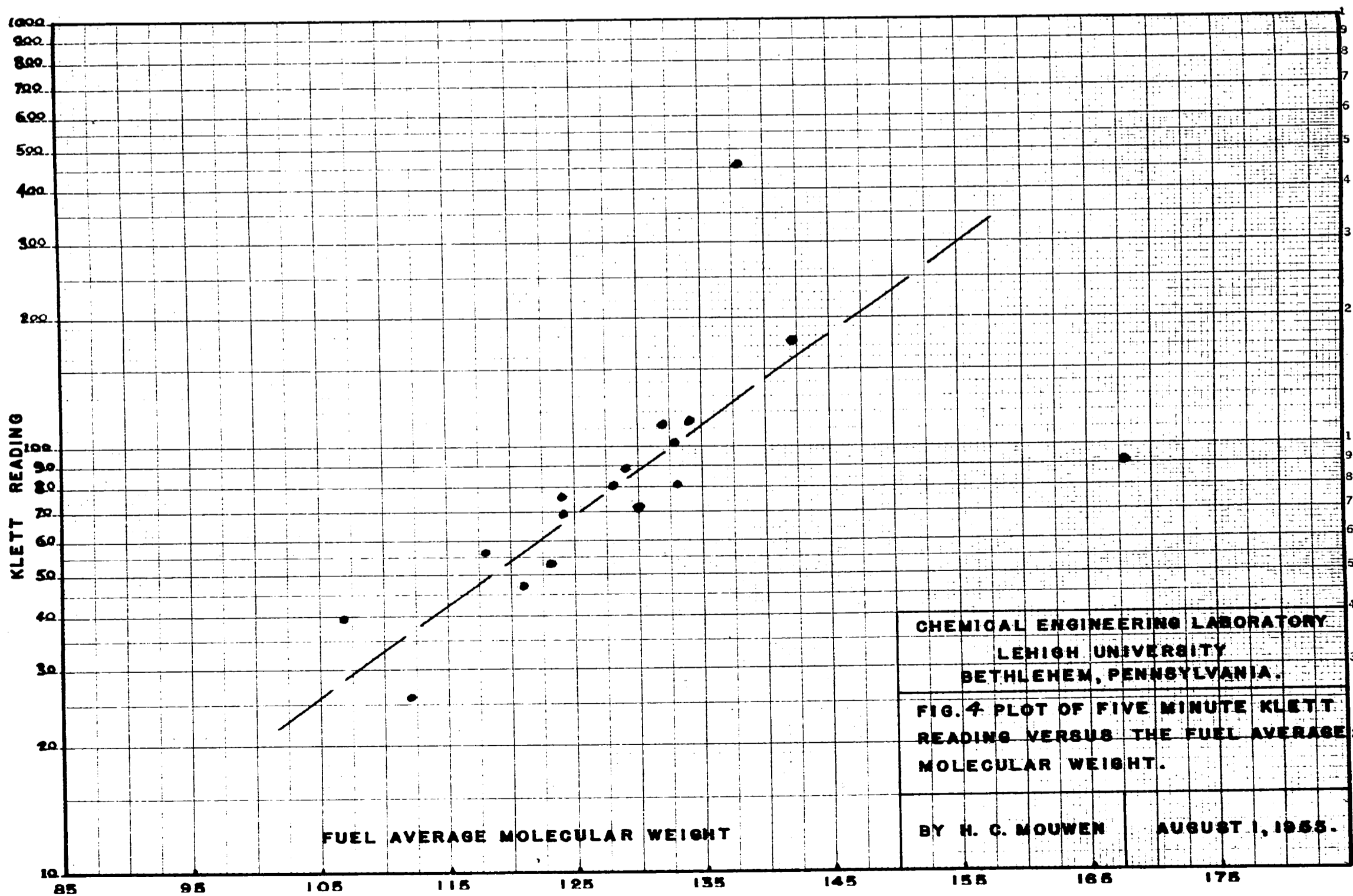
It was mentioned that lower values of the interfacial surface tension do occur in those systems which form a more stable emulsion. This trend can be shown by plotting the five-minute Klett readings versus the interfacial surface tension for

the fuels investigated. This plot is shown in Figure 2. It must also be realized that a complete correlation just between the interfacial surface tension and the fuel's tendency to emulsify with water is not obtained. The second parameter necessary to make the correlation more complete was found by plotting the five-minute Klett reading versus the volume average boiling temperature of the fuel. This plot is shown in Figure 3. Actually this was the first plot which appeared to give signs that some relationship could be made. The evolution continued and from one of the generally used correlations (3) (called mean average boiling temperature) between boiling behavior and the molecular weight, a plot was made of the five-minute Klett reading versus the fuel average molecular weight (Figure 4).

Theoretically, these relationships did bear significance. The more stabilizing compounds whether longer in chain length or wider in cross section, by virtue of their greater molecular weight, will normally exhibit a higher boiling point. A simple procedure to illustrate the above statement is to compare Fuel Sample No. 14 and No. 10. Observing the boiling temperature for both fuels at the 50% evaporated point, it is seen that No. 14 boils at 441°F and No. 10 boils at 211°F. It seems reasonable to assume that any unknown stabilizing compounds distilling over at 441°F would be longer in chain length or wider in cross section or perhaps just more complex than those coming over at 211°F, as would also be characteristic of the hydrocarbons. The ultimate result is shown by the recorded five-minute Klett readings; No. 14 has a value of 114 while No. 10 is 57. Many such procedures may be made with the reported data.







Since the fuel's average molecular weight is a function of the boiling temperature, the volume average boiling temperature was chosen as one parameter. By the Method of Least Squares, the best straight line was calculated for the data shown in Figure 3. This line has the equation:

$$\text{LOG K} = 0.00397 T + 0.517$$

where K - is the five-minute Klett reading
T - is the volume average boiling temperature ($^{\circ}\text{F}$)

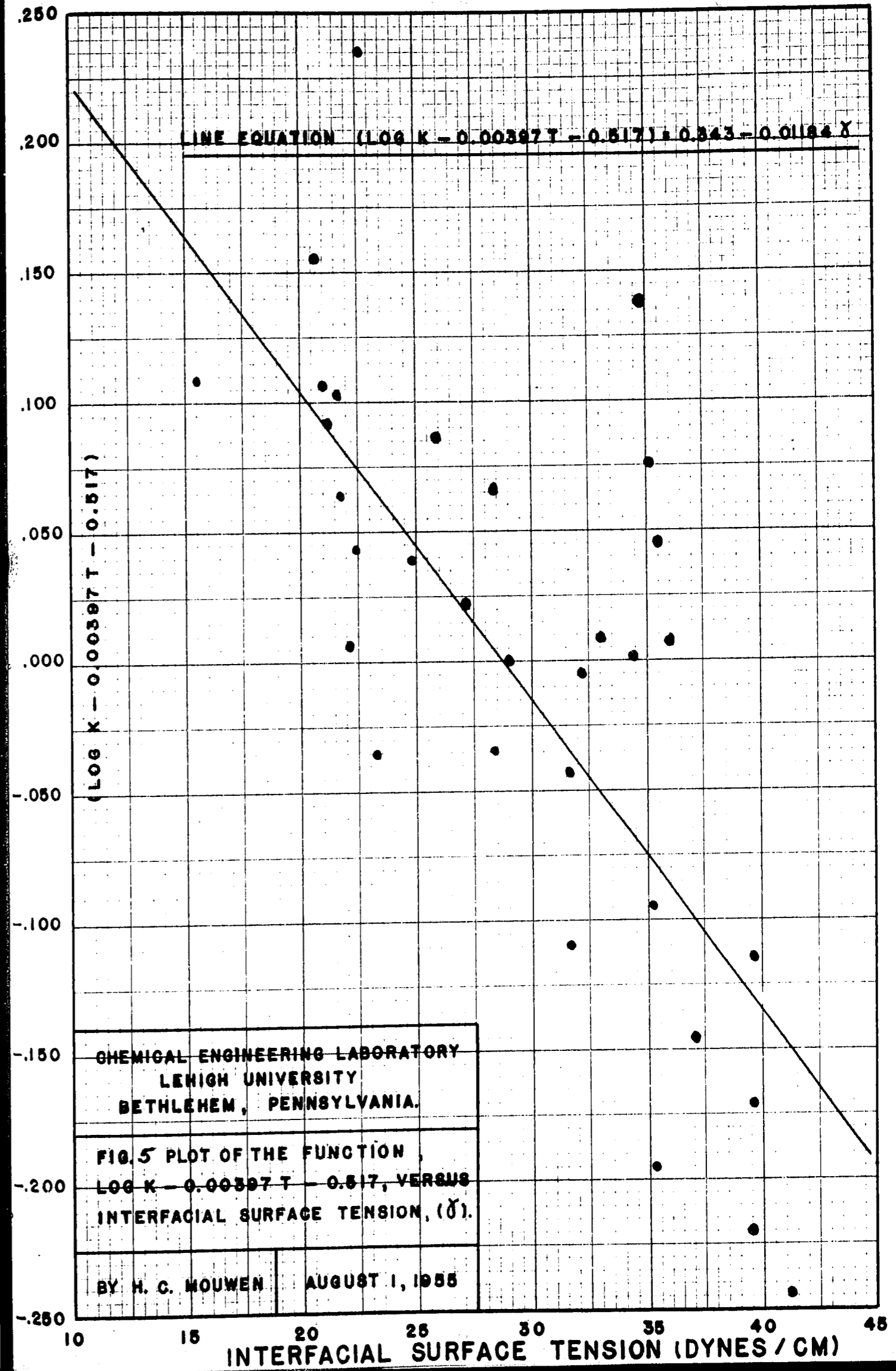
Many points on this plot reflected fuels whose interfacial surface tensions were not in line with like-type fuels and these points did fall out of the straight-line relationship. It was found that some factor of the interfacial surface tension could be used to adjust the volume average boiling temperature and place these "fall-out" points on the straight line. By trial and error the best relationship was obtained from a straight line (Method of Least Squares) by plotting the function $(\text{LOG K} - 0.00397T - 0.517)$ versus the interfacial surface tension. This plot is shown in Figure 5. From this plot the final relationship was obtained to be:

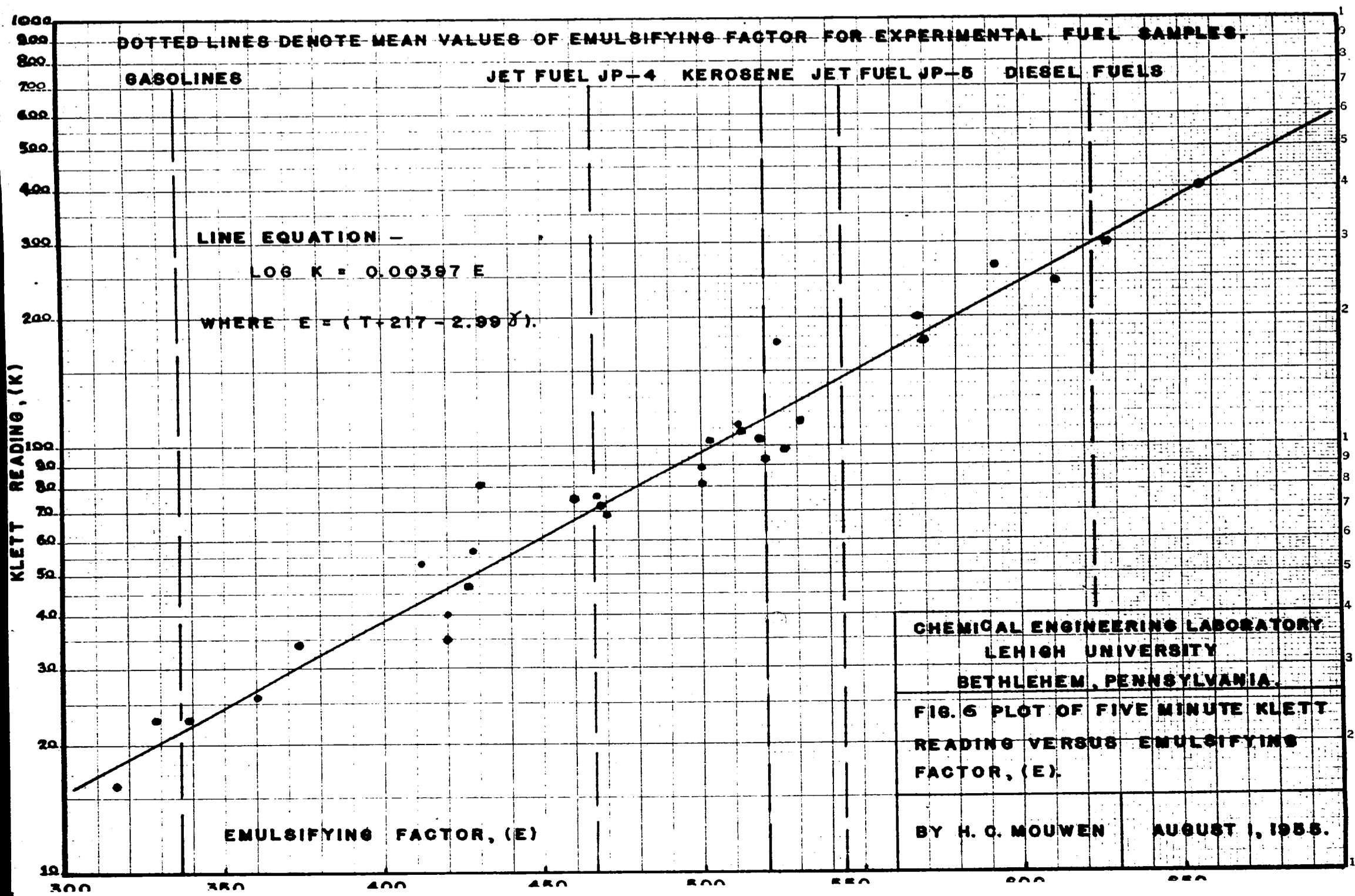
$$\text{LOG (K)} = .00397 (E)$$

where K - is the five-minute Klett reading
E - is the emulsifying factor and is equal to $(T + 217 - 2.99\gamma)$

and T - is the volume average boiling temperature ($^{\circ}\text{F}$)
 γ - is the interfacial surface tension between the fuel and water (30°C) (dynes/cm)

This final relationship with the experimental points plotted is shown in Figure 6. Also shown are the mean values of emulsifying factors for all the experimental fuel samples. These values allow the first rough estimation to be made concerning a fuel's





tendencies to emulsify with water. A more dependable prediction is made by knowing the volume average boiling temperature of the fuel and water at 30°C and then calculating the Klett reading.

The next relationship which could evolve would be between the Klett reading and the Flow Rate of a Coalescing Unit. There would be, undoubtedly, a maximum Klett reading for each flow rate. Any fuel and water emulsion producing a higher Klett reading than the maximum would not be successfully coalesced at the flow rate corresponding to the maximum Klett reading.

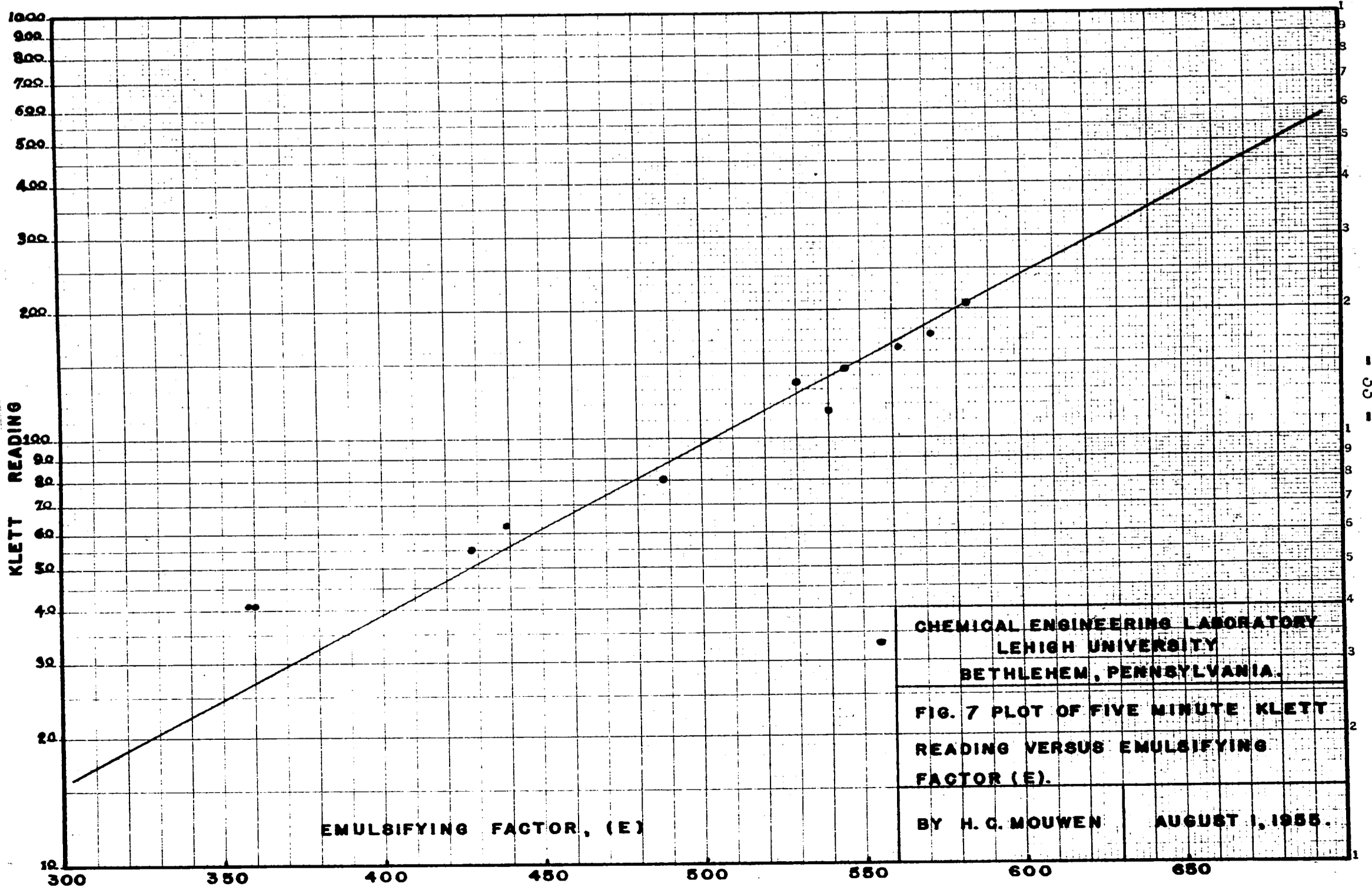
As a final check, several industrial solvents and substandard jet turbine fuels not used during the correlation of the emulsifying factor were investigated. The data necessary to find the emulsifying factor was obtained and the Klett readings were calculated. Then the solvents and fuels were analyzed according to the Experimental Procedure and the experimental Klett readings were obtained. The results are given in Table V.

TABLE V

SAMPLE	γ	T	E	K _{EXP}	K _{CAL}
SOLVENTS					
HISOLV T - toluol	32.5	233	358	42	26
aromatic petroleum naphtha					
HS 8 - low boiling	33.5	238	360	42	26
petroleum aromatic, solvency adjusted					
HS 30 - highly refined	34.0	308	428	55	50
aromatic petroleum naphtha					
HS 534 - aromatic	31.1	359	488	80	86
petroleum naphtha, solvency adjusted					
FUELS (substandard Jet Turbine Fuels JP-5)					
ESSO Kerosene (low S, hi aromatic)	36.1	453	562	162	170
" " (low S, low aromatic)	39.2	455	555	33	160
" " (naphthenic)	36.0	461	572	175	186
" " (mixed aromatic-paraffinic, high S)	24.5	439	583	205	205
" " (low aromatic-paraffinic, high S)	38.8	439	540	115	140
" Spirits (mineral spirits, low solvency)	42.5	346	439	63	55
" Spirits (mineral spirits, insecticidal carrier)	40.1	448	545	144	146
" Alkylate Bottoms (isoparaffinic)	27.2	394	530	135	128

The experimental and calculated values of the Klett readings are plotted in Figure 7.

The calculated values of the Klett reading do check fairly well when the type of analysis is considered. Emulsions are difficult to produce, analyze and reproduce. No logical reason for the exceptionally low value of the Klett reading for the Esso Sample (low S, low aromatic) can be given. All possible reasons were investigated and no answer is available. The results of the industrial solvents were interesting since these types of solvents were never included in this investigation. HISOLV T and HS 8 are two samples that do fall out to some extent but the chemical compositions of these solvents are not known except that their solvency has been adjusted to suit industrial specifications.



Consideration of the viscosity of the fuels leads to the conclusion that it is a significant factor in the rate of the breaking of an emulsion under the influence of gravity, but that it does not appear to be a primary factor in or cause of formation of emulsions from the point of view of interfacial forces. Figure 1 shows the stability curves for the emulsions of diesel oil and water, and gasoline and water. The settling curve for the gasoline is much steeper than that for the diesel fuel. The viscosity (at 30°C) of the fuel samples used in the laboratory for these data were:

Gasoline	5.0 millipoises
Diesel Oil	18.3 millipoises

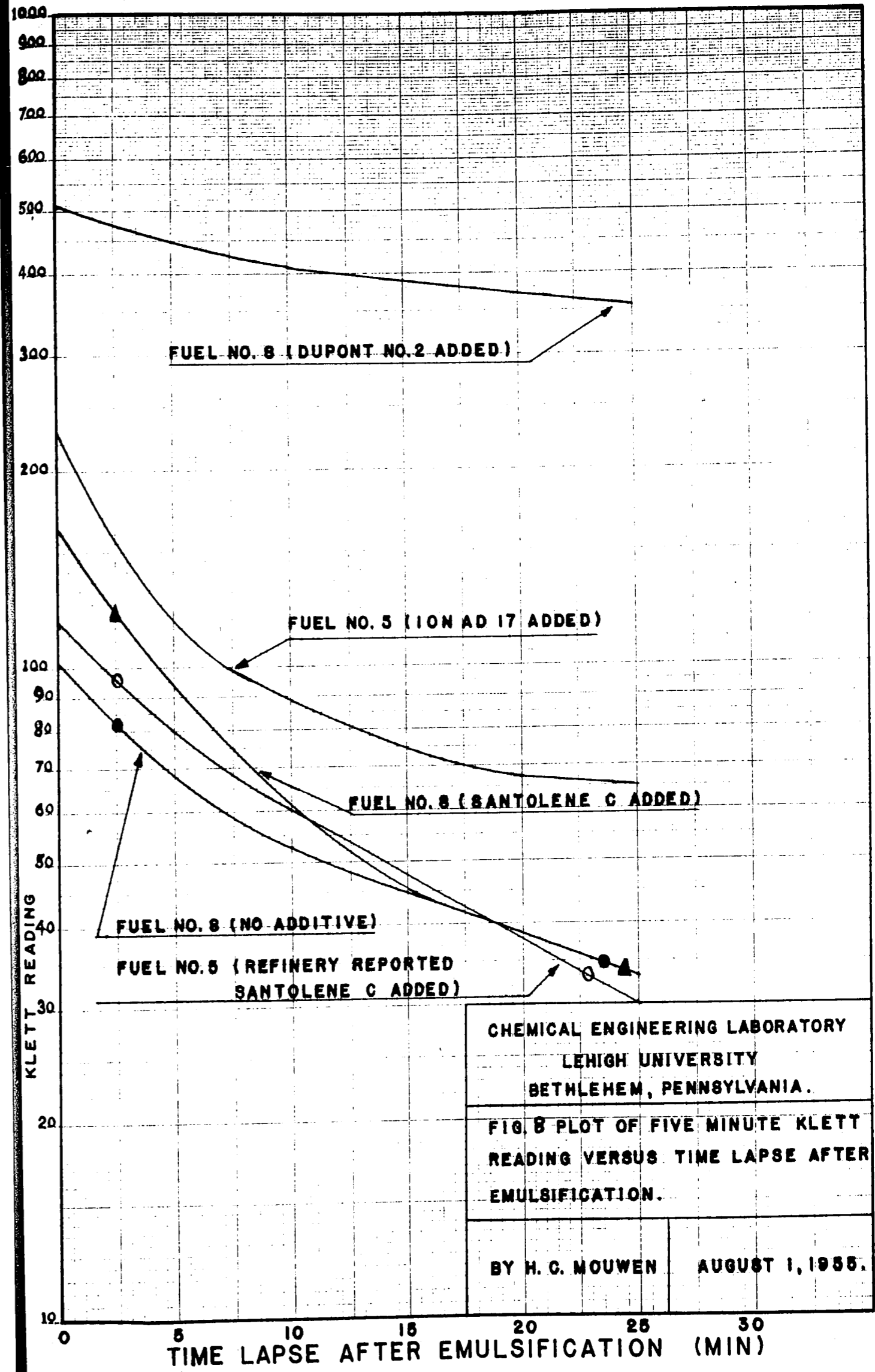
Again the Phillips Petroleum Company blends, Samples No. 9 through No. 18, Table I, also show no definite relationship between viscosity and the fuel's tendency to emulsify with water.

During each fuel analysis the existent gum content was carefully considered as an important variable. The gum content is now realized as being very important but it seems that a large excess must be present before its effects are noted. Fuel Sample No. 17 contains 20.3 mg/100 ml of existent gum and this fuel produced a very dense emulsion with water. Very little water was left in the bottom of the mixing jar after the emulsification. When the gum content of fuel Sample No. 17 and No. 13 is considered, a wide spread is realized and hence the emulsifying tendencies of the fuels and water are also widely spread. But when fuel Sample No. 13 is compared to No. 11 the emulsifying spread is lost although these two fuels do vary in existent gum content.

Another property which was considered was the density of the fuels. Since the bulk of the investigations was concerned with jet turbine fuels this property did not have a sufficient spread so that its effects can be formalized. It is granted that there is a spread in density between gasoline and diesel fuel but it is believed that density effects will be realized in the settling rate of water particles and not in the emulsifying tendencies of the fuel and water.

The next consideration and perhaps most important of all to be mentioned is the effect of additives on the fuel and water emulsions. The additives studied included: Santolene "C" (Monsanto Chemical Co.); Dupont Fuel Oil Additive No. 2; Ionad-17 (Shell Oil Co.). It is believed that the additives mentioned above are completely typical, and are important ones. Since the recommended amount of additive to be used usually consists of 6 lbs. of additive per 1000 barrels of fuel, it was difficult to produce these proportions on a laboratory scale. It was decided that all the additives would be evaluated by adding one drop of additive per 500 cc of fuel. Figure 8 shows the type of displacement noted for the Klett reading versus time lapse after emulsification plot for representative samples.

A knowledge of the various additives and their specific abilities coupled with their effects on fuel and water emulsifications shown in Figure 8 indicate that the rust preventive or metal deactivator type do not particularly enhance the emulsification process; whereas the solutizer and dispersant type greatly enhances the ability of the fuel to hold the water in suspension. When ION-17 was added to fuel Sample No. 5 the



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FIG. 8 PLOT OF FIVE MINUTE KLETT
READING VERSUS TIME LAPSE AFTER
EMULSIFICATION.

BY H. C. MOUWEN AUGUST 1, 1955.

value of the interfacial surface tension was decreased almost 30%, from 34.7 dynes/cm to 24.7 dynes/cm. This clearly exhibits the correlation that as the interfacial surface tension decreases the emulsifying tendencies of the fuel increase. Again the value of (γ) for fuel Sample No. 8 changed from 21.7 dynes/cm to 10.5 dynes/cm when Dupont No. 2 additive was added to the fuel. Santolene "C" only changed the interfacial surface tension value from 21.7 dynes/cm to 17.2 dynes/cm. Both ION-17 and Dupont No. 2 additives are solutizer and dispersant type additives while Santolene "C" is a metal corrosion inhibitor type additive. The most important point to observe is that the stability of the emulsion is greatly effected. It is only natural to expect this group of solutizer and dispersant type additives to affect the fuel and water emulsions as shown. The additives certainly can be the most important single variable.

CONCLUSION

Testing of the emulsification tendency of a representative sample of available fuels in the range of JP-3 and 4, and a few fuels outside this range indicates a wide variation in tendency to form emulsions of varying stability. Inspection of the data indicates that one of the major variables which can be easily measured is the interfacial tension of the fuel mixture with water. Another major variable is the volume average boiling temperature of the fuel.

For fuels having less than specification quantity of existent gum, there appears no particular problem of emulsification due to the presence of gum. If the amount of gum exceeds the specification significantly, it very rapidly becomes a major emulsifying agent, and will probably result in the formation of extremely vicious emulsions.

Presence of naturally occurring or intentionally added surface active compounds can exert more profound influences on enhanced emulsification tendency than any other factor measured. Fuel additives do enhance the emulsifying tendencies of a fuel with water; but the extent of this effect varies with the type of additive in question. Any practical application of demulsification equipment must be considered in the light of the probably increasing use of surface active additives in these fuels.

Consideration of the viscosity of the fuels leads to the conclusion that it is a significant factor in the rate of the breaking of an emulsion under the influence of gravity, but that it does not appear to be a primary factor in or cause of

formation of emulsion from the point of view of interfacial forces.

Chemical type of the hydrocarbons appears to have a significant influence on the stability of the water in oil emulsion. The branched-chain type of molecular structure of any stabilizing compounds in the fuels will result in more stable emulsions than a straight-chain type molecular structure.

Emulsions of an arbitrary small amount of water in oil can be characterized as to the degree of emulsification in terms of its light transmission characteristics. A Klett-Summerson Colorimeter was employed to measure this transmission. The Klett reading (K) was related to the Emulsifying Factor by:

$$\text{LOG K} = .00397 \text{ E}$$

where K - is the Klett reading
E - is the Emulsifying Factor and equal to
($T + 217 - 2.99\delta$)
T - is the volume average boiling temperature
of the fuel ($^{\circ}\text{F}$)
 δ - is the interfacial surface tension between
the fuel and water (dynes/cm) (30.0°C)

The above relationship allows a dependable prediction to be made with respect to the emulsifying tendencies of a fuel with water. This prediction can be further employed in the consideration of fuel demulsification equipment.

APPENDIX

TABLE VI

N-PRIMARY AMINES (RNH ₂)	CARBON CHAIN LENGTH	ARMEEN				
		10D	12D	16D	2C	2T
P E R C E N T						
Octyl	8	4				
Decyl	10	90	2			
Dodecyl	12	6	95			
Tetradecyl	14		3			
Hexadecyl	16			92		
Octadecyl	18			7		
Octadecenyl	18			1		
Mol. Combination Wt.		166	195	250		
N-ALKYL RADICALS (R ₂ NH)						
Octyl	8				8	
Decyl	10				9	
Dodecyl	12				47	
Tetradecyl	14				18	
Hexadecyl	16				8	30
Octadecyl	18				10	25
Octadecenyl	18					45
Mol. Combining Wt. (Approx.)					450	530

TABLE VII

CALCULATED DATA

FUEL	(A)	(B) .00597T	(A-B)		LOG K _{CAL}	K _{EXP}	K _{CAL}
SAMPLE NO.	LOG K _{EXP}	+ 0.517					
1	1.9638	2.2069	-.2431	41.1	2.06284	92	116
2	1.8573	1.8340	+.0233	27.1	1.8567	72	72
3	2.0531	1.9491	+.1040	21.6	2.0351	113	108
4	1.7243	1.7150	+.0093	35.9	1.6344	53	43
5	1.9085	1.7706	+.1379	34.7	1.7018	81	51
6	1.6721	1.7150	-.0429	31.6	1.6860	47	49
7	1.6021	1.7111	-.1090	31.7	1.6780	40	46
8	1.8389	1.7785	+.0604	21.7	1.8645	69	73
9	2.2406	2.0046	+.2360	22.6	2.0787	174	120
10	1.7559	1.6000	+.1559	20.6	1.6979	57	50
11	2.0086	1.9015	+.1071	21.0	1.9954	102	99
12	1.9085	1.9015	+.0070	22.0	1.9835	81	96
13	1.9494	1.9055	+.0439	22.3	1.9835	89	96
14	2.0569	1.9491	+.1078	15.5	2.1105	114	129
15	1.4150	1.5088	-.0938	35.1	1.4361	26	27
16	1.5441	1.7388	-.1947	35.2	1.6661	35	46
17	EXCESS	GUM					
18	1.8808	1.8856	-.0048	32.2	1.8486	76	71
19	1.5315	1.4651	+.0664	28.3	1.4718	34	30
20	2.6042	2.5124	+.0918	21.1	2.6063	402	404
21	1.9912	2.2109	-.2197	39.5	2.0866	98	122
22	2.2504	2.2109	-.0395	24.7	2.2612	178	183
23	1.4472	1.3699	+.0773	35.1	1.2972	23	20
24	1.4472	1.4016	+.0456	35.4	1.3250	23	22
25	2.4183	2.4172	+.0011	34.3	2.3524	262	224
26	2.0128	2.1831	-.1703	39.6	2.0589	103	114
27	2.3874	2.4212	-.0338	28.3	2.4278	244	267
28	2.0453	2.1593	-.1140	39.6	2.0351	111	108
29	1.2041	1.3501	-.1460	37.0	1.2536	16	18
30	2.3856	2.4212	-.0356	23.2	2.4913	299	310
31	2.3010	2.2149	+.0861	25.8	2.2533	200	180
32	1.8751	1.8658	+.0093	33.1	1.8169	75	67

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