10 October 1939 NRL Report No. P-1563

FR-1563

NAVY DEPARTMENT

Report

on

The Examination of Experimental

Alcohol-Gasoline Blends.

FR-1563

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

Number of Pages: Text - 8 Appendices - 3

Authorization: BuAer.ltr. Aer-E-46/MN JJ7G1 of 30 September 1936.

Date of Test: June and July 1939.

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Distribution: BuEng. (2)
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ABSTRACT

(1) The examination of six experimental fuels submitted to this Laboratory for test on 13 July 1939 yielded the following results: The experimental fuels appear to be compounded from a gasoline base stock containing some aromatic hydrocarbons, from ethyl alcohol, possibly denatured with methanol, and from fusel oil. The latter probably functions as a blending agent. All the blends carry some water ranging in concentration from 1 to 10 per cent. The concentrations of alcohols vary from 25-60 per cent and of hydrocarbons from 70-35 per cent in the six samples. The distillation curves are roughly comparable and are characterized by a short but definite plateau in the boiling range of amyl alcohol. The gum content is abnormally high but the material appearing as gum seems to be an oil rather than a typical gum deposit. The water tolerance of all the samples is good compared with simple ethanol-gasoline blends but separation into two phases will occur if an excess of water be added. The cloud point in no case is sufficiently low to pass Naval specifications but is lower than might be anticipated in view of the water content. There is no apparent correlation between the determined water content, cloud point, and water tolerance; nor was such expected since the ratio of hydrocarbon to alcohol and of ethanol to amyl alcohol varies from sample to sample as does the actual water content.

(2) A digest of expert technical opinion of competent authorities on the subject of alcohol-gasoline blends is included in Appendix B of the attached report.

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INTRODUCTION

(a) Authorization

1. This study was authorized by Bureau of Aeronautics letter Aer-E-46/MN JJ7G1 of 30 September 1936.

(b) Statement of Problem

2. This report deals with the study of certain special engine fuels which were recently forwarded to this Laboratory for test. The investigation was designed to determine the constitution of those fuels and to ascertain what peculiarities they might possess that would explain the claims of the inventor. Attention is directed to a copy of a letter (Appendix A) wherein these claims for the unusual properties of the fuels were set forth.

3. It will be shown that the fuels submitted for examination are mixtures of gasoline and alcohols. They differ from the usually encountered blends of ethanol and gasoline in that each specimen contains a considerable percentage of an alcoholic fraction boiling higher than ethanol of which the main constituent appeared to be isoamyl alcohol. The presence of this material seems to have a stabilizing effect on the water tolerance of the blends so that each specimen can contain several per cent of water without separating into two phases. It is on the ability of these experimental fuels to carry amounts of water far in excess of what may be contained in a straight ethanol-gasoline blend and on the presence of this water that the inventor bases his assertations of improved engine performance. It will be shown in this report that the statements of the inventor as to the water content of the blends are essentially correct, but because the claims of engine performance are of such a nature that verification of them depends on engine tests and determination of octane numbers, this Laboratory reserves comment on their validity pending the outcome of the octane number determinations which are being conducted at the Langley Field laboratory of the National Council for Aeronautics.

(c) Known Facts Bearing on the Problem

4. In Appendix B will be found a digest of known facts relating to alcohol-gasoline blends. This information is believed to be of interest in connection with the usability of alcohol fuel blends but is withheld from the body of the report to avoid complicating the immediate purpose of presenting the analytical results on the particular samples submitted for study.

(d) Theoretical Considerations

5. Several methods have been developed for the determination of ethanol and water in ethanol-gasoline blends. Most of these resort to the device of treating the blends with a definite amount

of water, measuring the volumes of the separated phases, and estimating the percentage composition from curves constructed from gasoline-alcohol blends of known composition. In the present instance such methods fail because the presence of higher alcohols introduces another variable, the effect of which is unknown. Precipitation of the hydrocarbon fraction with water and isolation of the alcohol from the aqueous phase by salting and steam stripping is not entirely satisfactory because of the solubility of hydrocarbons in aqueous alcohol and the partition of alcohols between the water and the hydrocarbon phases. Volume changes coincident with the mixing of hydrocarbons and alcohols and alcohols and water together with inevitable operating losses affect the accuracy of the results. The separation of such blends by straightforward distillation and fractionation is virtually impossible. It is well known, for example, that the individual constituent hydrocarbons of natural gasoline are practically inseparable by distillation methods. Such success as has been attained was achieved only by working with large quantities of material, employing highly efficient columns, and months or years of tedious labor.

6. In alcohol-gasoline blends the problem is enormously complicated because of the formation of binary and ternary azetropes and constant boiling mixtures between water, gasoline hydrocarbons, and alcohols. Benzene, water and ethanol, for instance, form a minimum boiling mixture distilling at 64.8°C., while the constituents boil at 80° and 100° and 78°C., respectively. An azetrope of benzene and ethanol boils at 68.2°C.; one of isopropyl alcohol and n-hexane at 61°C.; isopropanol and cyclo-hexane at 68.6°C.; isoamyl alcohol with the three xylenes boiling between 126.8°C. and 128°C.; ethanol and toluene at 76.6°C., water and isoamyl alcohol at 95.1°C.; water and toluene at 84.1°C.; ethanol and heptane at 74°C. These are only a few of the many such or similar mixtures which are to be anticipated in a gasoline blended with ethanol and higher alcohols and water. It is obvious from the complexity of such mixtures that a precise analysis of the quantitative composition of these blends in terms of hydrocarbon, alcoholic and water content is no simple task and that the problem of isolating and positively identifying the several components of these fractions is still more difficult. It was not believed that the present investigation warranted more than approximate analysis of the samples submitted for water, alcohol and gasoline. Allowing the reasonable assumption (based on the general similarity of physical properties) that the several samples differed from each other only in variant proportions of the three principal constituents, it was deemed unnecessary to examine more than one specimen for specific chemical compounds. In this way a great saving of time was effected without greatly impairing the validity of the results. The analytical methods employed are given in detail below.

METHODS AND DATA OBTAINED

(a) Description of Materials

7. On 13 June 1939 were received at this Laboratory six samples of experimental gasoline in glass bottles bearing the following identifying marks: numbers .775, .780, .803, .806, .810, .820. From samples .775 and .780 were removed 500 cc for test at this Laboratory and the remaining portions (3/4 gallon each) were returned to the Navy Department for octane ratings. The last four samples were retained for analysis since the quantity available was insufficient for the determination of octane numbers. All samples were clear with a slight yellow cast, somewhat less fluid than ordinary gasoline, and were strong with the odor of fusel oil.

(b) Resume' of Analytic Methods

8. The study of the specimens included a qualitative and quantitative analysis of the six samples followed by a detailed examination of one selected sample with the purpose of isolating and definitely identifying the specific chemical compounds present therein. Analysis as applied to all the specimens embraced the determination of gravity, gum, cloud point, water tolerance, distillation characteristics, and qualitative and semi-quantitative estimation of the type of compounds present in the fuels.

9. Determination of Physical Constants. The specific gravity was taken at prevailing room temperature (26°C.) with a hydrometer in the usual fashion. The methods for gum and Engler distillation followed the standard ASTM procedures. Water tolerance, or break point, was estimated by carefully adding a measured quantity of water drop-wise to 50 cc of the fuel at 25°C. and noting the point of appearance of a definite cloud permanent on stirring. The cloud point, or the temperature to which the specimen lost homogeneity through the separation of an insoluble phase, was found by chilling a test portion in an appropriate cooling bath and observing the point at which a definite turbidity appeared. Methods for detecting and identifying the chemical compounds present are to be found in Naval Research Laboratory reports numbers P-1394 and P-1499. Gum and distillation characteristics were determined by standard ASTM procedures. Embodied in the table below are the results of gravity, cloud point, water tolerance, Engler distillation, and gum determinations. A plot of the distillation curves of three typical samples is also included. It will be noted in the data under Engler distillation in Table I that additional information is given in a column headed "cc in the Lower Immiscible Layer." During these distillations it was observed that the distillate collecting in the receiving graduate was not homogeneous but consisted of a lower aqueous alcoholic phase overlaid with an insoluble phase predominantly hydrocarbon in composition. As the distillation proceeded the lower phase increased in volume much more rapidly than the upper until between the 60 per cent and 90 per cent point a substance distilled which, by virtue of mutual

solubility in the two phases, restored homogeneity to the distillate. This substance, most of which appeared to boil in the neighborhood of 130°C. (about 266°F.), appeared to be mainly isoamyl alcohol. The gum content of the samples exceeded the permissible amounts of preformed gum. However, the material remaining after evaporation of the gasoline was not the hard or sticky type of gum usually encountered. Instead it had the characteristics of an oil, probably vegetable since it was saponifiable with caustic alkali, unsaturated toward bromine, and yielded acrolein on fusion with potassium bisulfate. The possibility exists that it is maize oil since fusel oil obtained by the fermentation of corn frequently carries 1/2 to 1 per cent of this kernel oil together with oily products derived from the decomposition of proteins. If so, the presence of it may be accidental and can be ascribed to the adventitious occurrence of corn oil in the fusel oil used in blending. It is unlikely that the material was added intentionally as a stabilizing agent because 0.5 gram of the residues remaining after the gum tests fail to increase the water tolerance of 50 cc of a synthetic blend prepared at this Laboratory. The synthetic blend containing 35 per cent 73 octane gasoline, 40 per cent anhydrous ethanol, 20 per cent isoamyl alcohol, and 5 per cent water had a residual water tolerance of 10.75 cc per 100 cc. After addition of 1 per cent of oily matter recovered from the experimental fuels, the water tolerance was 11.0 cc, an insignificant increase.

(c) Semi-quantitative Analysis

10. An attempt was made to estimate the relative proportions of alcohol, hydrocarbon and water present in the various samples. This was done by measuring 50 cubic centimeters of the specimen into a 100 cc glass-stoppered graduated cylinder and adding distilled water to the 100 cc mark. After a thorough shaking the phases were allowed to separate and the volume of each read. From the known solubility behavior of hydrocarbons and alcohols it is apparent that the upper water-insoluble phase consists mainly of hydrocarbons and high boiling alcohols, while the aqueous phase contains most of the water present in the gasoline plus a considerable fraction of the lower boiling alcohols together with some of the high boiling ones, and a small amount of hydrocarbon. After separation of the hydrocarbon layer the water solution was saturated with solid potassium carbonate and, allowing the now insoluble alcohol to separate, the volume of that material salted out was read. Ignoring volume changes that are known to occur on mixing alcohol and water or alcohol and hydrocarbon, the partition of alcohol, water and hydrocarbon between the upper and lower phase after dilution to 100 cc, and the small though perceptible solubility of alcohol in saturated carbonate solutions, it is evident that the volume of the upper insoluble phase is a rough measure of the hydrocarbon content of the samples and the volume of the material salted out of the lower phase is a similar measure of the alcohol content. Likewise, the sum of the hydrocarbon and alcoholic fraction deducted from the volume of the samples used should indicate the water content of the original material.

Table I

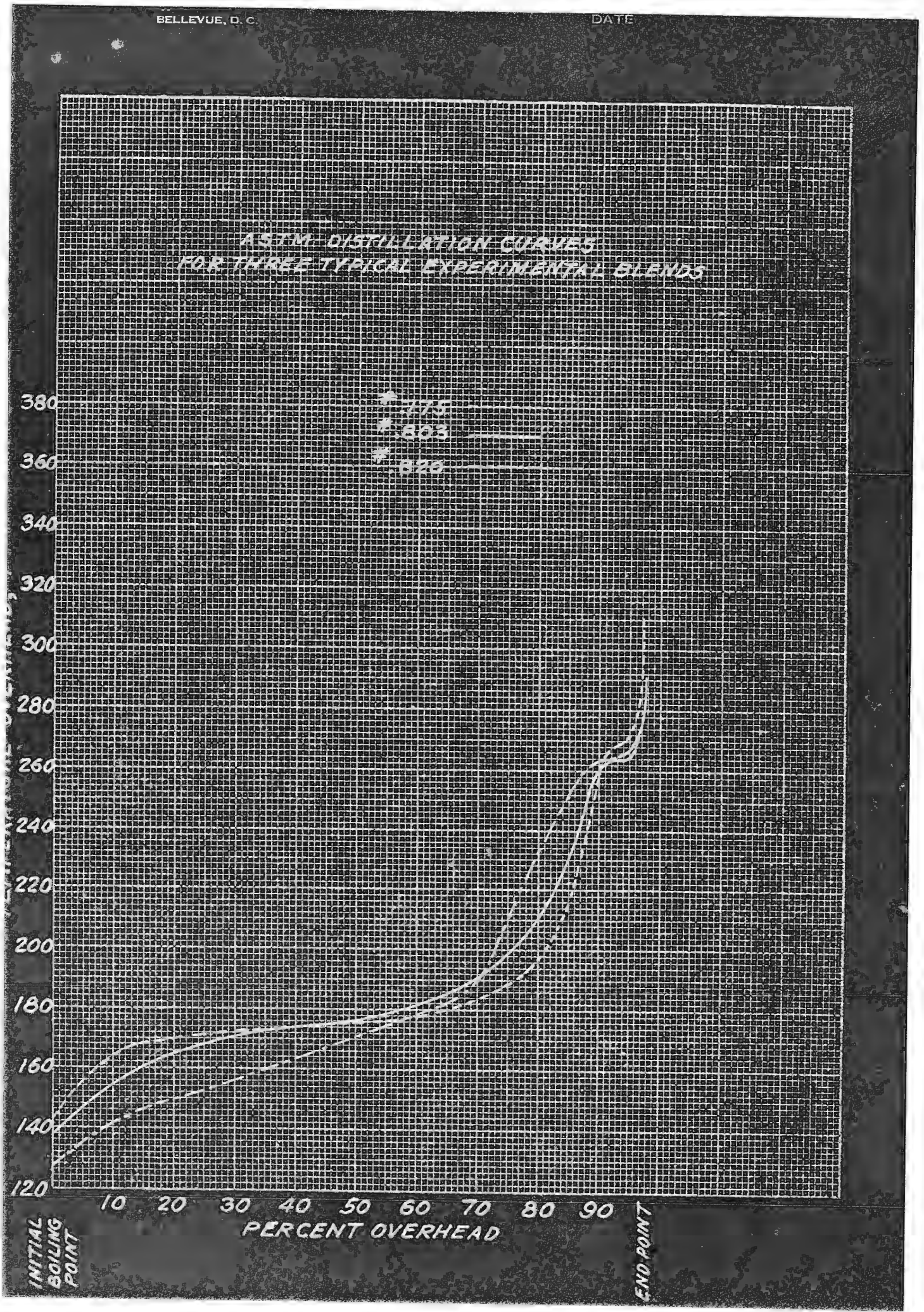
Physical Characteristics of Experimental Blends.

	Gasoline #.775		Gasoline #.780		Gasoline #.803		Gasoline #.810		Gasoline #.806		Gasoline #.820	
Specific gravity at 26°C.	0.785		0.788		0.809		0.805		0.815		0.817	
Engler Distillation	Temperature Overhead, °F.	cc in Lower Immiscible Layer	Temperature Overhead, °F.	cc in Lower Immiscible Layer	Temperature Overhead, °F.	cc in Lower Immiscible Layer	Temperature Overhead, °F.	cc in Lower Immiscible Layer	Temperature Overhead, °F.	cc in Lower Immiscible Layer	Temperature Overhead, °F.	cc in Lower Immiscible Layer
Initial boiling point	127	-	134	-	138	-	138	-	138	-	142	-
10%	142	1	148	2	156	4	161	5	159	4	165	6
20%	150	4	155	6	165	10	167	12	168	11	170	15
30%	156	7	162	12	171	12	170	22	172	20	172	24
40%	163	11	168	18	174	28	172	32	174	30	174	34
50%	171	16	175	24	176	38	176	41	177	40	176	44
60%	178	23	188	32	180	48	178	52	180	50	178	54
70%	189	34	228	*	185	58	184	62	184	60	184	64
80%	234	41	260	*	210	*	208	*	194	70	198	74
90%	263	*	268	*	264	*	264	*	262	*	264	*
95%	266	*	290	*	264	*	270	*	264	*	270	*
End point	290	*	382	*	290	*	307	*	290	*	312	*
Recovery, %	97.5		96		97.5		97.5		97.5		97	
Residue, %	1.5		2		1.5		1.5		2.0		2	
Loss, %	1.0		2		1.0		1.0		0.5		1.0	
ASTM gum in milligrams per 100 cc	434.2		894.4		1254.6		279.4		562.6		1020.0	
Water tolerance cc/100 cc	3.5		2.0		10.5		7.0		10.5		-	
Cloud point, °C.	-15		-1		-26		-22		-25		-1	

* Homogeneous.

BELLEVUE, D. C.

DATE



It is felt, however, that the values so found for water are more grossly in error than for hydrocarbon or alcohol, not only for the reasons mentioned above but because the result suffers the accumulated error of volume readings. Table II represents the composition of the experimental blends as determined above.

Table II

Percentage Composition of Experimental Blends.

Principal Constituents	.775	.780	.803	.806	.810	.820
Hydrocarbons	66%	70%	40%	35%	40%	35%
Alcohols	28	25	53	55	59	60
Water (by difference)	6	5	7	10	1	5

(d) Qualitative Analysis

11. Six hundred cc of one sample, #.820, was distilled through an efficient column and the distillation interrupted when the temperature of the overhead reached 81°C. The distillate and the still residue so obtained were respectively treated with an equal volume of water, the separated hydrocarbons removed, and the aqueous layer salted with potassium carbonate to recover alcohols. Thus, the sample was split into four fractions: (I) low boiling hydrocarbons, (II) low boiling alcohols, (III) high boiling hydrocarbons, and (IV) high boiling alcohols. The fractions were individually redistilled and the distillates collected were examined for specific chemical compounds. The presence of aromatic and aliphatic hydrocarbons was proved. Ethyl alcohol and isoamyl alcohol were definitely shown to be present and strong indications of the presence of methanol and alcohols intermediate between ethyl alcohol and amyl alcohol obtained. The details of the procedure followed in this separation and analysis are given in Appendix C.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

12. A careful analysis of one of the submitted samples demonstrated that it contained three principal ingredients, namely, the hydrocarbon or gasoline base, ethyl alcohol, and an amyl alcohol. It also carried a few per cent of water. Due to the formation of azetropes and constant boiling mixtures in hydrocarbon — water-alcohol combinations, complete separation and positive identification of the components of such mixtures is extremely difficult. Therefore gasoline hydrocarbons, amyl alcohol and ethanol are not necessarily present to the exclusion of other substances; but these compounds do

appear to comprise the major portion of the blend. On a basis of the general similarily of physical properties (odor, distillation range, and behavior on dilution with water) it seems that all six specimens were compounded correspondingly and that they differ among themselves mainly in a differing ratio of the mentioned constituents. Approximate analyses indicate an alcoholic content varying between 25 and 60 per cent and a hydrocarbon concentration of 35 to 70 per cent in the several samples. As alcohol-gasoline blends they appear novel only in view of the water content though amyl alcohol is not ordinarily used as a blending agent in the usually encountered ethanol gasoline fuels. Moreover, most alcohol-gasoline blends rarely carry more than 20 per cent alcohol, while some of the specimens examined in the present instance appeared to be compounded with several times that quantity.

13. The submitted specimens failed to pass Naval specifications in two important respects. First, the cloud point is too high; and second, the gum content as determined by the standard ASTM procedure exceeds the permitted quantity. While the material which deposited as gum on evaporation of a test sample was not "gum" in the usual sense of the word, but appeared to be a vegetable oil, the presence of which should be looked upon with suspicion since the behavior of it in an engine is unknown.

14. The water tolerance of the fuels is of such an order as to exclude storage in water displacement systems, though the possibility of separation in dry storage equipment is slight if the tanks are guarded against the ingress of water.

15. The superficial physical characteristics of the blends are good. In appearance all are clear with a slight yellow cast and quite fluid, though less so than ordinary aviation gasoline. It is not believed that the slight increase in viscosity will interfere with liquid flow in fuel systems now in use. However, the odor of all the samples is unpleasant and characteristic of fusel oil.

16. There appeared to be nothing extraordinary in the nature of the original gasoline base stock used in preparing the blends. Indications are that its hydrocarbon content is predominantly aliphatic, with some unsaturates and about 20 per cent aromatics boiling in the xylene range. The dominant alcohol in the blends is ethyl alcohol, isoamyl alcohol being present in about one-fifth the quantity of the other. Strong evidences of the presence of secondary alcohols evinces the opinion that the isoamyl alcohol was added in the form of fusel oil.

(b) Recommendations

17. On the basis of these findings the Laboratory withholds recommendation of the experimental blends for Naval use on the following grounds:

(1) Though it is known that the addition of alcohol to a given gasoline usually results in improved octane rating,

lowered engine operating temperatures, increased volumetric efficiency, and somewhat cleaner combustion, the resulting blend is deficient in available heat energy as compared with the base gasoline. For example, the heats of combustion (determined at constant pressure) for a homologous series of alcohols range from 328,700 calories per mol for ethyl alcohol to 795,000 calories per mol for n-amyl alcohol. The same values for the aliphatic hydrocarbons in the aviation gasoline range are 833,100 for n-pentane to 1,303,400 for "isooctane." It is doubtful that the advantages which may accrue through alcohol blending will off-set this deficiency, especially in view of the excellent performances of isooctane-hydrocarbon blends in which the total heat content is unimpaired and available for useful work.

(2) In those fuels which contain amounts of alcohol in excess of 20 per cent, it is anticipated that changes in the carburetor setting and possibly redesign of the carburetor mechanism will be necessary to insure the proper air-fuel ratio.

(3) The high cloud points of the blends may give trouble when the fuel is subjected to low temperatures during altitude flying through separation of the various constituents.

(4) The fact that the blends separate on the addition of excessive amounts of water excludes the storage and handling of them in water displacement systems.

(5) Several minor drawbacks are to be expected in the practical use of alcohol blends of the compositions approximating those submitted for tests. Spillage of fuels containing more than 20 per cent alcohol, especially those in which the amount of amyl alcohol is high, is likely to result in injury to lacquered and painted surfaces. Again, alcohol blends when introduced into installations that have long been used for the storage of gasoline loosen and dissolve the precipitated gum frequently found on the walls of such systems so that a possibility exists of accidentally introduced dangerous quantities of gum into a motor when the blend is withdrawn for use. Moreover, it is suggested that amyl alcohol-ethanol-gasoline mixtures may possess a more pronounced solvent action on the linings of supply hoses and gasketing materials than does gasoline alone. No data are available on the corrosiveness of such blends toward metals. It is probable that the water content of the blends will tend to promote corrosion processes. Finally, isoamyl alcohol has a characteristic, quite unpleasant and pervasive odor. In some persons, the prolonged breathing of these vapors produces headaches and symptoms of nausea. Recorded data on the rate of absorption through the skin and the toxicity of amyl alcohol are scant, though the best reported data indicate that the substance is eight times as toxic as ethanol.

APPENDIX A

C o p y

B. WOULBROUN
Ingenieur A.i.Lg.
Bruxelles

June 17th 1939

United States Navy
Washington, D.C.

For the attention of the
Bureau of Engineering

Dear Sirs:

I am writing you herewith for the purpose of requesting you to permit me to carry out in your Laboratory at Annapolis a test on a carburant which is able to withstand a much higher compression ratio than is now known or believed to exist.

This carburant is characterized by the fact that water is introduced into it in mixture with the gasoline and other agents; the liquid obtained is perfectly homogenious and because of the introduction of water, the temperature in the cylinders is lowered and compression ratio increased.

As the proportion of water introduced is variable, a rather wide range of compression ratio can be reached; therefore, what is known as the octaine point, can be adjusted to wish. The prevailing maximum compression ratio of 7:1, may be increased to 10 or more.

All of the ingredients needed by me for the before-mentioned purposes are obtainable here and my product can be produced at a cost of about 20¢ per gallon.

I firmly believe that my process may be of interest to you, especially in the field of aeronautics. Inasmuch as I have definitely established the efficiency and usefulness of my discovery, I am prepared to demonstrate it before your representatives - on a variable compression ratio motor, which I understand you possess.

In the anticipation of the receipt of your early advices, I remain,

Very sincerely yours,

/s/ B. WOULBROUN
Temporary address:
Room 1748
120 Broadway
New York, N. Y.

C O P Y

APPENDIX B

Information of General Interest Concerning the Properties and Usability of Alcohol-Gasoline Blends.
(See Page 3, Paragraph c of report.)

Although reported work is scant on gasoline-alcohol blends of the particular composition of those herein examined, the scientific literature of the past few years is replete with data on straight ethanol-hydrocarbon mixtures. Since interest in alcohol-gasoline blends is beginning to assume some importance in this country and because special fuels of this nature will in all probability appear from time to time, it is thought germane to the purposes of this report to review briefly the opinions of the more eminent investigators in this field. The following is a digest of these opinions as presented before the American Chemical Society in 1936 in the Symposium on Motor Fuels. For complete details the original publications and more recent papers on the subject should be consulted. Egloff and Morrell believe that "Alcohol gasoline has no overall technical advantages compared to gasoline. The increased fuel consumption of the 10 per cent alcohol-gasoline blend is approximately 4 per cent higher than gasoline alone based on road and block tests. The improvement in anti-knock value and consequent efficiency when alcohol is added to gasoline (employing suitable design and operating conditions) is less than the decrease in efficiency as measured by fuel consumption. The overall effect is an increased fuel consumption. The use of alcohol introduces operating difficulties especially in starting, acceleration, and vapor locking. The handling and shipment of alcohol gasoline are difficult because of the ease with which these components separate when traces of water are introduced. It is difficult to keep water out of bulk storage tanks, . . ."

Holding essentially the same view, Bridgeman of the Bureau of Standards finds that "Blends containing ethyl alcohol have no advantage over gasoline as motor fuels though they can be used satisfactorily if full advantage is taken of available technical information. Small percentages of ethyl alcohol in the blend are more advantageous than large percentages from the standpoints of maximum power and acceleration for minimum fuel consumption and ease of engine starting and warming. The reverse is true from the standpoints of vapor locking and water tolerance. The alcohol used for blending should be essentially anhydrous in order to prevent separation of the alcohol in service. By employing a suitable blending agent the water tolerance of the blend can be markedly increased though the ethyl alcohol used must be practically anhydrous unless very large percentages of the blending agent are employed."

In their comparative examination of the engine performances of a standard motor gasoline and 190 proof ethanol, Lichty and Ziurys of Yale University state "Theoretical analysis shows ideal possibilities ranging from 2 per cent increase in power with gasoline compared

to pure alcohol to 6.8 per cent increase with pure alcohol compared to gasoline, depending on mixture conditions. The water in 190 proof ethyl alcohol has a negligible effect on power but increases the specific fuel consumption about 6.6 per cent owing to the lowered heating value per given quantity of fuel compared to pure alcohol."

They found in working with single and multi-cylinder engines under various conditions that there is " . . . a small average increase in power (not much more than the experimental error involved) in favor of 190 proof alcohol. However, the specific fuel consumption with 190 proof alcohol is about 60 per cent higher on a weight basis and about 50 per cent higher on a volume basis than with gasoline."

Finally, Christensen of the Chemical Foundation of Kansas Company, differing somewhat from the above opinions, summarizes his views as follows: "Various types of alcohol blends are in common use in practically every country, the usual distributed commercially containing 5 to 25 per cent of ethanol or of methanol and ethanol. Anhydrous ethanol is miscible with gasoline in all proportions; methanol ordinarily requires the addition of a stabilizer, ethanol being entirely satisfactory for this purpose. Properly prepared alcohol blends containing not more than about 25 per cent alcohol by volume may be used interchangeably with gasoline of equal anti-knock rating. Such blends may be safely stored and distributed in modern commercial equipment. Used in this type of blend alcohols are not substitutes for gasoline but serve the purpose of increasing the anti-knock value and otherwise improving the fuel. It is on this basis that the value of these alcohols must be determined . . ."

Considering these and other opinions, proponents of alcohol-gasoline blending apparently regard alcohol not as a substitute for gasoline but as an anti-detonating agent. Its anti-detonating properties generally permit the use of higher compression ratios than is possible with the given gasoline base stock so that a more efficient utilization of the theoretical energy content of the fuel is achieved. The use of alcohol-gasoline blends, in addition to improved knock rating, is claimed to result in lowered engine operating temperatures, increased volumetric efficiency, somewhat cleaner combustion, and a yield of carbon monoxide in the exhaust gases lower than is obtained with the base gasoline. The addition of alcohol to the base gasoline affects the volatility characteristics in a direction that tends to flatten the middle portion of the ASTM distillation curve; the most important effect is a more even distribution of the fuel charge to the cylinders.

Objections have been raised to alcohol blends because of the increased cost as compared with gasoline, poor engine performance, increased fuel consumption, difficulties of storage, and corrosion problems. The cost of alcohol-gasoline blends must necessarily be higher than that of gasoline alone since tax-exempt ethanol currently sells at about 30 cents per gallon. The price of isoamyl alcohol is in the same range though fusel oil is probably

lower. But, the quantity of fusel oil available in this country is limited and already well allocated for other industrial uses so that the ultimate source of higher alcohols, should such blending become general, will most likely be petroleum pentane. The more reliable tests indicate that alcohol blended fuels show harder starting, deficient acceleration, and a somewhat enhanced tendency to vapor locking. Lubrication troubles arising from oil dilution and varnish formation have been reported. An increase in fuel consumption is to be expected from theoretical reasons. Alcohols may be looked upon as hydrocarbons which have undergone partial oxidation. Hence, the heats of combustions of alcohols are lower than those of the parent hydrocarbons. This deficiency in energy content may be off-set somewhat by an increase in octane number and the increase in efficiency which follows the utilization of higher compression ratios. But the second effect does not overcome the first as shown in the work of Brown tabulated below.

Absolute Alcohol in Blend, %	Increase in Octane Number, %	Increase in H.U.C.R., %	Possible Increase in Efficiency due to Increase in H.U.C.R., %	Increase in Fuel Consumption due to the Addition of Alcohol, %
5	3	2	1.0	2.5
10	7	5	3.0	5.0
15	12	9	4.5	7.5
20	15	15	6.2	10.0

Storage troubles arise through the intolerance of alcohol blends to even small amounts of water. It has been shown that straight 10 per cent blends of anhydrous ethanol in gasoline separate on the addition of as little as 0.2 per cent of water. However, the water tolerances may be greatly increased by the addition of aromatics, certain amines, phenols, fatty acids and higher alcohols. This function of higher alcohols is indicated by Bridgeman, who finds the affects tabulated below.

Increase in Water Tolerance Produced by the Addition of 5% Higher Alcohols to a 10% Ethanol-Gasoline Blend.

Temp. °F.	No Blending Agent	Water Tolerance, Volume %				
		n-Propyl	iso-Propyl	n-Butyl	iso-Butyl	ter-Butyl
104	0.48	0.90	0.85	0.92	0.90	0.86
68	0.38	0.75	0.72	0.80	0.77	0.73
32	0.29	0.61	0.58	0.67	0.64	0.60
-4	0.21	0.47	0.43	0.55	0.51	0.50
-40	0.14	0.35	0.30	0.43	0.39	0.39

The corrosiveness of gasoline-alcohol mixtures has been demonstrated by Zdarsky who noticed in long-time storage tests that iron became pitted and rusty, zinc suffered both uniform and penetrating corrosion, and lead and copper were extensively attacked. The anhydrous blend did not affect aluminum but did corrode that metal and some of its alloys when water was present. No corroborated instances of engine corrosion under operating conditions appear to have been reported.

APPENDIX C

A Detailed Description and Discussion of the Methods and Results of the Qualitative Analysis of the Blends.
(See Page 10 of Report.)

(a) The Detection of Aromatic Hydrocarbons and Functional Groups.

The hydrocarbon fraction from two of the samples (.775 and .803) were obtained by "breaking" the blend with water. These fractions were exhaustively extracted with water to remove residual alcohol, dried four hours over anhydrous chloride, and aniline point determined. The aniline point of the hydrocarbon fraction from .775 was 20°C.; from .803 below 0°C. This denotes the presence of aromatics in a concentration probably exceeding 20 per cent of the hydrocarbon fraction. Whether these aromatics were added intentionally or were component hydrocarbons of the gasoline base stock used in preparing the blends is unknown. At any rate, qualitative tests for aromatics on the whole specimen were positive for all the blends. The results of the qualitative examination of these blends for various functional groups are given below.

Table A

Qualitative Tests for Functional Groups.

	.775	.780	.803	.805	.810	.820
(1) Peroxides	Faint traces	++	-	Traces	++	+
(2) Carbonyl compounds	Trace	+	Trace	Traces	Traces	+
(3) Aldehydes	-	-	-	Traces	Traces	+
(4) Acetyl ($CH_3C=O$) or potential acetyl groups	Trace	+	+	+	+	Trace
(5) Acids	-	-	Trace	Trace	Trace	+
(6) Unsaturates	+	++	+	+	++	+++
(7) Aromatics	+	+	+	+	+	+

The detailed explanation of the method for conducting these tests is found in Naval Research Laboratory Report No. P-1499.

In brief, however, the procedure and the significance of the results in the present instance, are as follows:

(1) Peroxides. Positive: Appearance of a red color on treating with thiocyanate-ferrous sulfate reagent. Positive peroxides indicate that the sample examined is reacting with atmospheric oxygen or has at some time been subjected to some oxidizing influence. The presence of peroxides is a danger signal warning of incipient deterioration and anticipating deleterious effects on the octane rating, gum content, and corrosive properties of the fuel.

(2) Carbonyl Compounds. Positive: Yellow precipitate with 2,4-dinitrophenylhydrazine reagent. In traces carbonyl compounds are merely indicative of oxidation. In the present case the carbonyl compounds found were probably present in the alcohols used for blending. Heavier carbonyl tests in conjunction with heavy positive reaction in Test 4 would indicate a blending agent of the methyl ketonic type.

(3) Aldehydes. Positive: Red color with magenta solution bleached with sulfurous anhydride. The significance of the positive aldehydes is about the same as the carbonyl compounds.

(4) The iodoform reaction for CH_3CO- or potential CH_3CO- in groups. Positive: The formation of iodoform with hypo-iodite. Methyl ketones and substances which contain groupings that are easily oxidized to CH_3CO- under the experimental conditions give positive tests. Hence, in the abs ence of methyl ketones the presence of secondary alcohols may be suspected.

(5) Acids. Positive: Reddening of litmus paper. Traces of acids in the present case mean little more than the occurrence of a slight amount of oxidation.

(6) Unsaturates (alkaline potassium permanganate).
(7) Aromatics (coloration with chloroform - aluminum chloride reagent).

These tests give information as to the type of hydrocarbons present.

Examination of the data in Table A shows that in general the condition of the samples is excellent since absorption of atmospheric oxygen has assumed no more than negligible proportions. The aldehyde and acid tests are not significant but the light indications of carbonyl compounds in conjunction with the heavier test for potential CH_3CO- groups seems to indicate the possible presence of secondary alcohols.

(b) Isolation and Identification of Specific Chemical Compounds Present in the Blends.

It was thought desirable to isolate in a relatively pure condition for purposes of identification some of the chemical compounds present in the fuel blends. The difficulties of effecting complete separation of all the substances in alcohol-gasoline mixtures has been outlined in the attached report (see page 4). However, it was hoped that at least the nature of the blending alcohols could be determined. Accordingly, 600 cc of sample #.820 was slowly distilled through a 5-foot column. The distillation was stopped when the temperature of the distilling vapors reached 81°C. The condensate and the residue remaining in the flask were each treated with equal volumes of water and the immiscible upper layer separated. The water layer was then saturated with anhydrous potassium carbonate which forced the dissolved alcohols out of solution. In this manner four fractions were obtained in which the components of the blend were largely segretated as indicated below:

I. Water insoluble layer boiling up to 81°C.
Total volume, 70 cc. Approximate composition: low boiling hydrocarbons.

II. Water soluble layer boiling up to 81°C.
Total volume, 285 cc. Approximate composition: low boiling alcohols.

III. Water insoluble layer boiling above 81°C.
Total volume, 110 cc. Approximate composition: high boiling hydrocarbons.

IV. Water soluble layer boiling above 81°C.
Total volume, 84 cc. Approximate composition: high boiling alcohols.

After drying with appropriate desiccating agents, Fractions I, II, III and IV were individually distilled through a 5-foot vacuum-jacketed, silvered column packed with Fenske rings. Results of the analysis of the sub-fractions so obtained are presented in Tables B and C.

Table B

Detailed Examination of Experimental Fuel #.820. Data on Fractions I and III (Hydrocarbons).

(a) FRACTION I. Consisting of the water insoluble portion of the distillate boiling up to 81°C. (177.8°F.). Total volume, 70 cc.

SUB-FRACTION	1	2	3	4	5	6	7	8	9	10	11	12
Distillation range, °C.	33-80	80-85	85-109	109-112	112-135	135-145	145-152	152-153	153-164	164-165	165-175	175-178
Distillation range, °F.	91-176	176-185	185-228	228-233	233-275	275-293	293-305	305-307	307-327	327-329	329-347	347-352
Volume distillate, cc	6.4	0.3	7	1.2	2.8	2.0	5.5	1.5	2	1	3	0.3
Qualitative tests -												
Aromatics	+	+	+	+	++	+	++	++	++	++	++	++
Alcohols	+	-	+	-	-	-	-	-	-	-	-	-
Carbonyl compounds	-	-	-	Trace	Trace	-	-	Trace	Trace	Trace		

(b) FRACTION III. Consisting of the water insoluble portion of the still residue boiling above 81°C. (177.8°F.). Total volume, 110 cc.

SUB-FRACTION	1	2	3	4	5	6	7	8 (Residue)

The distillation and qualitative examination of fractions I and III which should be rich in hydrocarbons reveal that these fractions are contaminated with alcohols, fraction III being relatively richer in alcoholic bodies than fraction I. This is to be expected on the basis of decreased solubility of the higher alcohols in water and increased solubility in hydrocarbons. For the reverse reason, the sub-fractions of fraction I give practically negative tests for alcohols. The low initial boiling point of fraction I and the boiling range of fractions I and III, coupled with only moderate test for aromatic compounds until the distillation temperature reaches the neighborhood of 120°C., indicates the presence of aliphatic hydrocarbons and largely excludes the simpler aromatics such as benzene and toluene. The maximum concentration of aromatic hydrocarbons seems to occur in the boiling range of the xylenes (130 to 140°C.). It is interesting to note the spread of fraction I, which it is remembered, was derived from the distillate of the initial fractionation boiling up to 81°. Its range of 33° to 178° demonstrates the presence of minimum boiling mixtures of alcohol and hydrocarbon in the original material. No derivatives of any aromatic hydrocarbon which would admit the definite characterization of a specific chemical individual could be prepared.

Table C

Detailed Examination of Experimental Fuel #.820. Data on Fractions II and IV (Alcohols).

(a) FRACTION II, Consisting of water soluble-saturated K_2CO_3 insoluble portion of distillate boiling up to 81°C. (177.8°F.). Total volume, 285 cc.

SUB-FRACTION	1	2	3	4	5	6	7	8	9
Distillation range, °C.	63-70	70-73	73-75	75-77	77-80	80-87	87-94	94-97	Residue
Distillation range, °F.	145-158	158-163	163-167	167-170	170-176	176-188	188-201	201-206	
Volume distillate, cc	8	40	89	34	62	11	3	8	6.5
Qualitative tests -									
Aromatics	+	Trace	Trace	-	-	-	-	-	-
Alcohols	++	++	++	++	+	+			
Carbonyl compounds	+	Trace	Trace	-	-	-			
Aldehydes	+	Trace	Trace	-	-	-			
Acetyl or potential acetyl groups	+	+	++	+	-	-			
Resorcinol - H_2SO_4 for HCHO*	+		+						
Na-nitroprusside test**	-								
∝-Naphthyl urethane melting point	117°C.***			79°C.***					

* After oxidation in the hot copper oxide.
** For acetone.
*** The ∝-naphthyl urethane of methyl alcohol melts at 124°C.; of ethyl alcohol, at 79°C.

(Continued)

Table C (Continued)

(b) FRACTION IV. Consisting of the water soluble-K_2CO_3 insoluble portion of still residue boiling above 81°C. (177.8°F.). Total volume, 84 cc.

SUB-FRACTION	1	2	3	4	5	6	7	8
Distillation range, °C.	73-78	78	78-82	82-90	90-105	105-109	109-128	128-133
Distillation range, °F.	163-172	172	172-179	179-194	194-221	221-228	228-262	262-271
Volume distillate, cc	12	4	4	0.6	0.4	2.5	4	6
Qualitative tests -								
Aromatics	-	-	-	-	-	-	Trace	+
Alcohols	++	++	+	+	+	+	+	+
Carbonyl compounds	-	-	-	-	-	-	+	-
∝-Naphthyl urethane, melting point		78°C.*						
3,5-Dinitrobenzoate, melting point						61°C.*		

* Ethyl ∝-naphthyl urethane melts at 79°C.; the 3,5-dinitrobenzoate of isoamyl alcohol melts at 61.5°C.

The salient feature of the distillations of fractions II and IV is the volume of fraction II (285 cc) and the predominance of material boiling in the lower ranges (63 to 80°C.) with the greatest segregation of material in the range between 70 and 80°C. It is apparent that the dominant alcoholic compound in the original sample is ethyl alcohol. From sub-fraction 4 of fraction II was isolated a derivative of ethanol, the α-naphthyl urethane, which had a melting point agreeing with that recorded in the literature for known ethyl α-naphthyl urethane. Furthermore, a mixed melting point with an authentic sample of ethyl α-naphthyl urethane showed no lowering. A similar derivative was isolated from sub-fraction 2 of fraction IV. An examination of sub-fraction 1 of fraction II was made for methyl alcohol. A few drops of the suspected material, when oxidized with a hot copper spiral, gave a strong positive test for formaldehyde with resorcinol-sulfuric acid reagent which is specific for this compound. Since ethanol does not yield formic aldehyde under the conditions of the test and because certain of the higher branched chain secondary and tertiary alcohols which might do so may be excluded because of the low boiling range of the sub-fraction examined, the presence of at least a small amount of methyl alcohol in the original blend is strongly indicated. Characterization through the α-naphthyl urethane was unsuccessful due to contamination with the simultaneously formed ethyl derivative. However, it should be noted that the melting point of the product obtained was 117°C. against 124°C. for pure methyl α-naphthyl urethane. The urethanes of all other possible alcohols in this boiling range melt well under 100°C. This again is contributory evidence for the presence of methanol. Upon oxidizing a cubic centimeter of the fraction with copper oxide and preparing the 2,4-dinitrophenyl-hydrazone from the aldehydes formed, the material was found to melt at 149°C. which is 6° low for the recorded known compound from formaldehyde. But, here again contamination with the hydrazone of acetaldehyde may explain the discrepancy. While the presence of methyl alcohol cannot be considered as conclusively proved, it is difficult to explain the results obtained if it be considered absent. The quantity is undoubtedly small and could have been introduced fortuitously if a denatured alcohol were used in the preparation of the blend. The iodoform tests on the first four sub-fractions of fraction II are of some significance. Since methanol does not give the iodoform reaction and since ethanol also is non-reactive under the conditions of the test, the positive results obtained are tentatively ascribed to the presence of secondary alcohols. Secondary alcohols are known to occur in fusel oil which suggests that the isoamyl alcohol found in sub-fraction 6 of fraction IV was added as fusel oil rather than as the pure compound. The identification of isoamyl alcohol in this sub-fraction was accomplished by the preparation of the 3,5-dinitrobenzoate. After three crystallizations form dilute alcohol, the derivative was found to melt at 61°. The melting point of a known sample prepared from pure isoamyl alcohol was 61.5°. Characterization through the α-naphthyl urethane was unsuccessful. After repeated recrystallizations, the material still melts 8° to 10° low. This lowering of the melting point is probably caused by the presence of the urethanes of other alcohols isomeric with isoamyl. This is another indication that the isoamyl alcohol was introduced as fusel oil which contains a variety of isomeric and homologous alcohols.

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