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THE BEHAVIOR OF WATER IN JET FUELS AND THE CLOGGING OF MICRONIC FILTERS AT LOW TEMPERATURES

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NRL REPORT 3604

THE BEHAVIOR OF WATER IN JET FUELS AND THE CLOGGING OF MICRONIC FILTERS AT LOW TEMPERATURES

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January 11, 1950

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CONTENTS

ABSTRACT

A study of the behavior of water in fuels, and its effect on the clogging of micronic type filters, especially at low temperatures has been made.

A method for the determination of water in fuels using the Karl Fischer reagent has been developed and used in the determination of the solubility of water in several fuels and pure hydrocarbons from 32°F to 120°F. The effect of aromatic content, rates of saturation and disappearance of suspended water from fuels have been investigated.

A small scale apparatus was devised for the study of the clogging of micronic filters at low temperatures. The variables—temperature, water content of the fuel, fuel pressure, porosity and type of paper were studied for their effects on filter clogging. Mechanisms of clogging as a function of temperature are proposed.

A number of representative substances were tested as potential freezing point depressants for the prevention of clogging. In general, it was found that the more hydrophylic compounds are the more effective antifreezes. However, these compounds are the ones more readily leached from the fuel by contact with water. Methyl alcohol was found to have the best antifreeze action, but it is lost very readily from fuel solutions to water. In selecting a suitable antifreeze, due consideration must be given to the methods of handling the fuel and to the methods which may be used for the introduction of the additive.

PROBLEM STATUS

This is a final report on the problem and, unless otherwise notified by BuAer, the problem will be closed one month from the date of mailing the report.

AUTHORIZATION

NRL Problem No. C01-10D
BuAer Problem No. TED NRL-pp-502

THE BEHAVIOR OF WATER IN JET FUELS AND THE CLOGGING OF MICRONIC FILTERS AT LOW TEMPERATURES

STATEMENT OF PROBLEM

(1) To determine the solubility of water in aviation engine fuels conforming to specifications AN-F-48 and AN-F-58 at several different temperatures.

(2) To study the effect of aromatics on the solubility of water in an aliphatic hydrocarbon.

(3) To investigate factors influencing the clogging of micronic type filters at low temperatures.

(4) To study the effectiveness of various additives for the prevention of filter clogging at low temperatures.

BACKGROUND

Although the solubility of water in hydrocarbons is low, this solubility has a large temperature coefficient. In view of the normal methods of handling, most fuels contain dissolved water in amounts approaching the saturation values for the prevailing temperature. Therefore, when a fuel is cooled, water may separate either as a liquid or, at low temperatures, as an ice. Although the amount of water thus separated is small, it may cause considerable trouble due to the corrosion of metal parts by liquid water, or to the clogging of fuel filters by ice. The corrosive nature of such separated water has been demonstrated at this Laboratory and the results are presented in NRL Report No. P-1279. The clogging of filters by ice has been the subject of fairly extensive investigations at the Eglin Air Force Base, Florida,[1] at the Thornton Research Center of the Shell Aeronautical Laboratory, England,[2] at the Thompson Products, Inc. Laboratory, Inglewood, California, for the Coordinating Research Council (CRC),[3] and at the Lockheed Aircraft Corporation, Burbank, California.[4]

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[1] *"Engineering and Development Test (Climatic Hangar Cold) of Fuel System of P-80B Airplane." Letter Final Report on APG Project No. 4-48-5-CHC (Restricted), Air Proving Ground, Eglin Air Force Base, Florida, May 25, 1948.*

[2] *Williams, C. G., "Fuels and Lubricants for Aero Gas Turbines." Journal of the Institute of Petroleum, 33: 267-324, 1947.*

[3] *"Low Temperature Pumping Characteristics and Physical Properties of Aviation Gas Turbine Fuels." Coordinating Research Council Report (Restricted), revised June 24, 1949.*

[4] *Duffendack, J. C., "Cold Test on Low Pressure Micronic Filter for Model P-80B Fuel System." Lockheed Aircraft Corporation Report No. 6349, December 22, 1947.*

At Eglin Field, full scale low temperature studies using JP-1 fuel (AN-F-32) in a P-80B fuel system showed that ice formed in the fuel system and that under certain conditions, the fuel stoppage was such that there resulted a substantial loss of engine power. It was also found that the injection of AN-A-18 alcohol at the boost pump inlet screen was an effective method of clearing the fuel system.

In laboratory tests at Thornton, the clogging tendencies of a number of fuels were studied as a function of temperature. Under their experimental conditions, it was found that the addition of 0.5-1 percent of isopropyl alcohol was an effective antifreeze for temperatures as low as -58°F.

The results of the CRC pumping tests showed that a fair correlation exists between the temperature at which incipient filter plugging occurs and the temperature of initial precipitation as measured by the ASTM cloud point. It was also found that fuels containing suspended water will cause filter plugging by ice crystals at temperatures only slightly below 32°F.

At Lockheed it was found that the water in the fuel freezes and clogs a micronic type filter at approximately 15°F and that the addition of a small amount of alcohol will prevent this.

Due to the low solubility of water in hydrocarbons, the majority of existing methods for determining water are inadequate and special methods and techniques must be employed in order to obtain precise data. Such methods are discussed in NRL Reports, Nos. P-1279 and P-1573. The latter report also presents the results on the solubility of water in various hydrocarbon fuels as determined by the reaction of water with the acetyl chloride-pyridine reagent.

SOLUBILITY OF WATER IN HYDROCARBONS

Choice of Method

Of the various methods, reviewed in NRL Reports P-1279 and P-1573, for determining water in hydrocarbons, the method of Smith and Bryant[5] using the acetyl chloride-pyridine reagent appeared to offer the most promise. An investigation of this method showed that unless excessive precautions are employed, the precision of the results obtained is not entirely adequate. As a consequence, the method utilizing the Karl Fischer reagent[6] was investigated and a technique developed which proved to be more satisfactory.

Procedures

Determination of Water in Hydrocarbons

A detailed description of the procedure developed for the determination of water by means of the Karl Fischer reagent is given in Appendix I. In essence it consists of adding an excess of reagent to the sample and backtitrating with a standard water in methanol solution. The end point is determined potentiometrically. In order to ensure

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[5] *Smith, D. M., and Bryant, W. M. D., "Titrimetric Determination of Water in Organic Liquids Using Acetyl Chloride and Pyridine." J. Am. Chem. Soc., 57: 841-845, 1935.*

[6] *Mitchell, J. and Smith, D. M., "Aquametry." New York, Interscience Publishers, 1948.*

homogeneity throughout the titration, a toluene/methanol solvent is employed. The reproducibility of results from duplicate determinations, using this method, was found to average better than 0.0002 percent water for 50 gm samples of fuel.

The presence of tetraethyl lead interferes with this determination. Consequently, in studying the solubility of water in such fuels, the lead was removed by treating with hydrochloric acid prior to saturating the fuel with water. Although a fuel thus de-leaded may have slightly different solvent properties for water than the original fuel, it is believed that the difference is not significant. Details of the method used for lead removal are given in Appendix II.

Saturation of Fuels with Water

Fuels were saturated by allowing them to stand over water for at least 24 hours in a constant temperature bath. It was found necessary to start with a fuel containing less water than the saturation value in order to avoid the formation of cloud-like water suspensions.

Rate of Fuel Saturation with Water

In order to study the rate of saturation of AN-F-58 fuel under static conditions, approximately 1 gallon of preheated (90°F) fuel and 100 ml of water were brought together in a bottle (a 1 gallon bottle having a height of 10 in. at the shoulder and an i.d. of $5\frac{1}{2}$ in.) with a minimum of agitation and allowed to stand in a bath at 90° F. Samples were removed, by syphoning, from near the center of the fuel layer. In another test, preheated fuel and water were shaken together for one minute, allowed to stand for 15 minutes at 90° F and the fuel layer analyzed.

Disappearance of Suspended Water from Fuels

An experiment was conducted on the rate of disappearance of suspended water from AN-F-58 fuel. This was done by immersing a bottle (as above) of the fuel, saturated at 90° F, in a bath maintained at 32° F. Samples were removed periodically, by syphoning, from both near the top and bottom of the fuel layer and analyzed for water.

Results

Solubility

The solubility of water in three fuels and two pure hydrocarbons was determined at four temperatures. These results are given in Table 1 and shown graphically in Figure 1. In addition, a study was made of the effect of aromatic content on the solubility of water in a paraffinic hydrocarbon. Octane and toluene were chosen as a representative pair for this study. The solubility of water at 60° F was determined for this system and the results are given in Table 2 and shown graphically in Figure 2.

Rate of Fuel Saturation with Water

The static test showed that the fuel absorbed water at a moderate rate and was essentially saturated at the end of six hours. The data are presented in Table 3 and Figure 3.

TABLE 1
Solubility of Water in 3 Fuels and 2 Hydrocarbons

Fuel	Solubility of water (wt %) Temperature (°F) 32	60	90	120
AN-F-58	0.0024	0.0056	0.0093	0.0143
AN-F-48 (91/98 octane) (De-leaded)	0.0027	0.0068	0.0110	0.0193
AN-F-48 (115/145 octane) (De-leaded)	0.0025	0.0055	0.0102	0.0174
n-Octane	0.0020	0.0046	0.0076	0.0115
Toluene	0.0222	0.0407	0.0672	0.1055

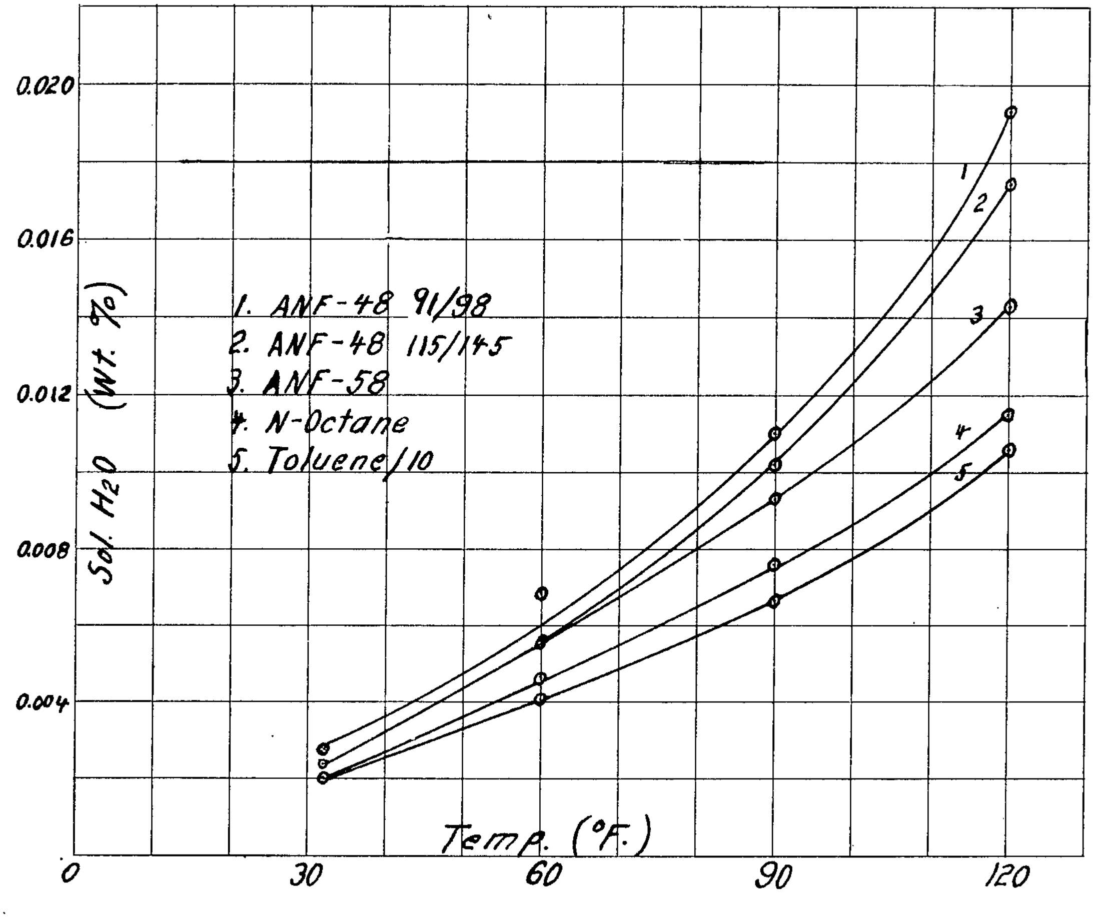

Figure 1 - Solubility of water in fuels

TABLE 2
Solubility of Water
in n-Octane/Toluene Mixtures at 60°F

Composition		Solubility of water (wt %)
Toluene (wt %)	n-Octane (wt %)	
0.0	100.0	0.0046
9.5	90.5	0.0059
19.7	80.3	0.0081
40.0	60.0	0.0123
60.3	39.7	0.0196
80.0	20.0	0.0285
100.0	0.0	0.0407

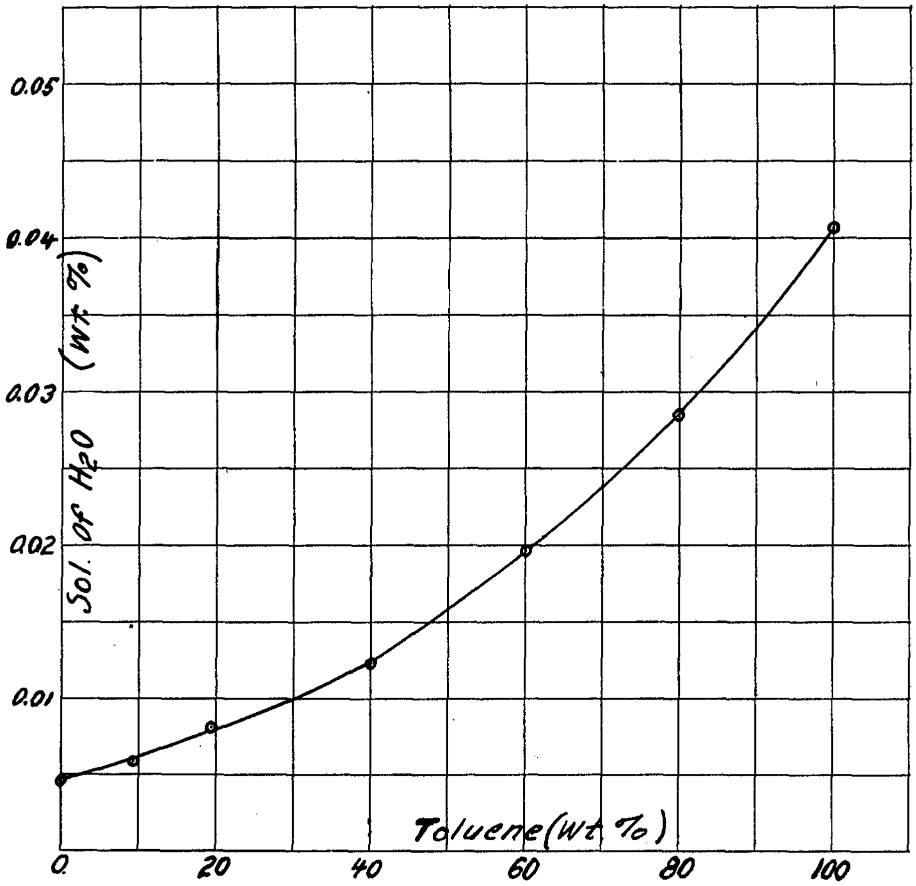

Figure 2 - Solubility of water in n-octane/toluene mixtures at 60° F

TABLE 3
Rate of Saturation of
AN-F-58 Fuel with Water at 90°F (Static)

Time (hrs)	Water Content (wt %)	Saturation (%)
0	0.0053	57
1	0.0068	73
2	0.0074	80
3	0.0082	88
4	0.0086	93
6	0.0092	99

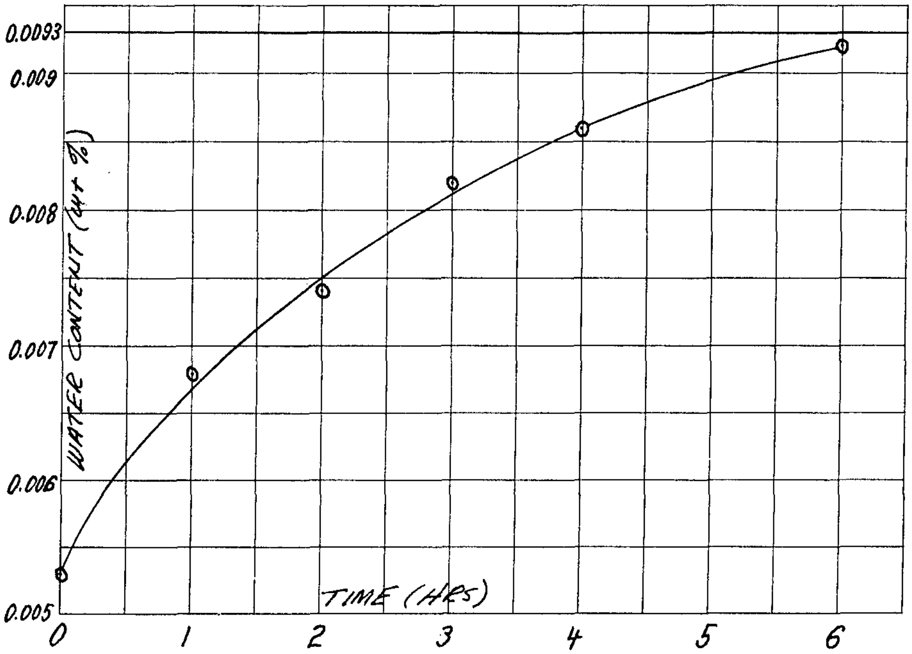

Figure 3

In the dynamic saturation test the initial water content of the AN-F-58 fuel was 0.0041 percent. Analysis of the fuel after the one minute shaking and 15 minute settling period showed it to contain 0.0090 percent water. This figure is essentially the saturation value for this fuel at 90° F, the temperature of the experiment.

Disappearance of Suspended Water from Fuels

In this test, it was found that due to the very small particle size of the water in the cloud-like suspension, the water settled slowly. Although approximately 50 percent of the suspended water had disappeared by the end of the first day, at the end of six days, the fuel still contained a small amount of suspended water. No significant differences were found in the analyses of the samples taken from near the top and bottom of the fuel layer. The results given in Table 4 and Figure 4 are the averaged values.

Discussion

Solubility

As may be seen from Table 1 and Figure 1, the solubility of water in hydrocarbons increases rapidly with increasing temperature. At 32° F, the solubility of water in the three fuels studied is essentially the same and is approximately 0.0025 percent by weight which corresponds to 0.0025 oz water/gallon of fuel. For these fuels, the solubility of water at 120°F is from 6.0 to 7.1 times that at 32° F.

From Table 2 and Figure 2, it may be seen that at 60° F, the solubility of water in toluene is approximately 9 times that in n-octane. For mixtures, the solubility of water increases with increasing aromatic content. This increase is not directly proportional to the aromatic content but rather falls along a smooth curve which lies lower than the straight line function. The compositions of the octane/toluene mixtures are given on a weight basis. When the water solubility data is plotted versus composition, expressed as either volume percentage or mol fraction, the curve given in Figure 2 retains the same general shape and is displaced only by a small amount. This data suggests that a similar behavior may be expected for the effect of aromatics on the solubility of water in other paraffinic fuels.

TABLE 4
Rate of Disappearance of
Suspended Water from AN-F-58 Fuel

Time (days)	Water Content (wt %)	Suspended Water Remaining (%)
0	0.0093	100
1	0.0057	48
4	0.0035	16
5	0.0033	13
6	0.0027	4

Of the materials investigated, toluene is the only one for which values for water solubility, as determined by several different methods, could be found in the literature. The effect of temperature on the solubility

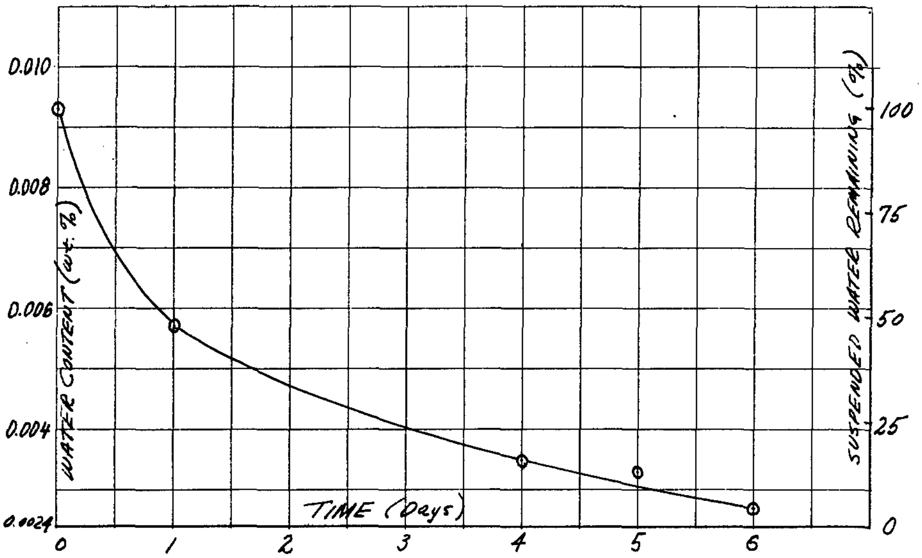

Figure 4

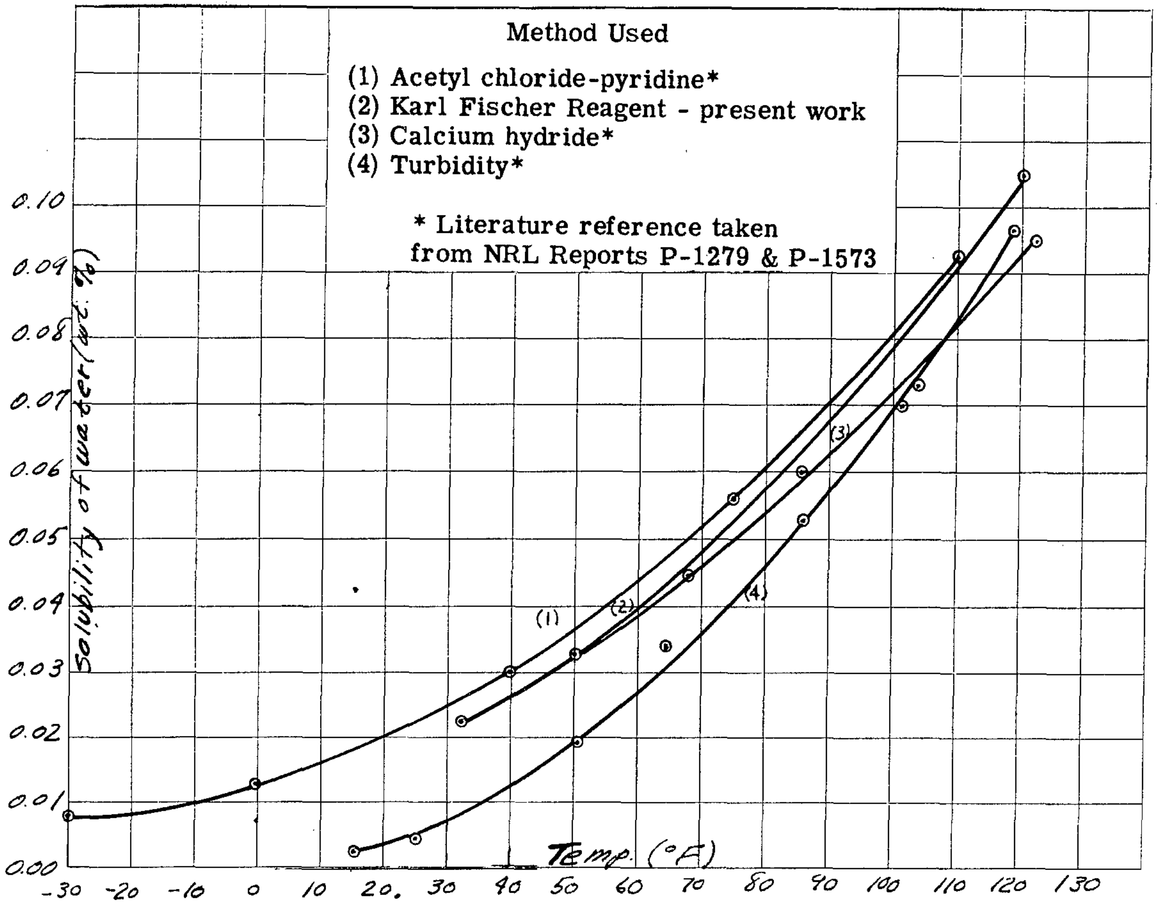

Figure 5 - Solubility of water in toluene

of water as determined by four different methods is shown in Figure 5. From this figure, it is seen that with the exception of the turbidity studies at the lower temperatures, there is reasonable agreement among the results obtained by the four methods. The best overall concordance in results is between those obtained by means of the acetyl chloride-pyridine and Karl Fischer reagents.

Rate of Fuel Saturation

The rate of fuel saturation experiments indicate that although the solubility of water is low, the rate with which the fuel becomes saturated is very rapid, especially when the fuel-water mixture is agitated. This is to be expected since it involves the solution of a liquid in a liquid.

In normal handling, fuels frequently come in contact with liquid water or with air of a high R.H. Because of this, fuels generally contain dissolved water in amounts approaching the saturation values and unless special precautions and equipment are used, it would be very difficult to service and maintain operational jet-fuel systems with dry fuel.

Disappearance of Suspended Water from Fuels

The experiment on the disappearance rate of water from fuels shows that when a fuel is cooled below the saturation temperature, part of the water separates in the form of a fine cloud which disappears very slowly. An examination of such a cloud under a microscope and a Tyndall beam indicated that the particle size of the water droplets is of the order of less than ten microns in diameter. Due to the very slow settling rates of such small particles, Brownian movement and convection currents play an important role in keeping the cloud in suspension. This would tend to keep the cloud homogeneous which is in line with the experimental finding that the water content at the top and bottom of the fuel layer was essentially the same. The disappearance of the cloud may be due not only to coalescence of the particles and settling, but may be due in part to a re-solution of the smaller droplets with deposition on surfaces such as the walls of the container and larger water drops. Evidence of such deposition is given in NRL Report P-1279.

Although the water content of AN-F-58 fuel can be reduced markedly by exposure to low temperatures, the time required may be considerable, especially in larger tanks and under conditions which favor convection. Inasmuch as the solubility of water in AN-F-58 fuel is low, the total quantity of water which separates on cooling is small and appears as a tenuous cloud which is not readily discernible. Thus, unless proper care is exercised, low temperature experiments using such fuels may give misleading results since the fuels can contain considerably more water than the saturation values.

Precautions in Handling "Equilibrated" Fuels

Three factors play an important part in the way fuel samples must be handled so that the water content is not altered. These are: the very small amounts of water present, the large differences in the polarities of fuel and water, and the vapor pressure of the water in the fuel. For example, a 50 gm sample (size ordinarily taken for analysis) of AN-F-58 saturated at 32°F contains only 1.2 mg of water (by comparison, an ordinary drop of water weighs 35-50 mg). In view of this, any slight contamination or loss can cause a large error in the results.

It is a well known fact that a glass surface has a strong affinity for water. This is explained by the highly polar nature of both water and glass. By contrast, most hydrocarbons are relatively nonpolar and are not as strongly adsorbed by glass. Therefore, when a sample of fuel containing dissolved water is placed in a dried flask, it may be expected that the glass surface will remove part of the water by adsorption. This was vividly demonstrated by the results of the following experiment.

Two 250 ml glass-stoppered Erlenmeyer flasks were dried overnight in an oven at 110°C and allowed to cool in a desiccator. The first flask was rinsed with three successive 25 ml portions of AN-F-58 fuel (saturated at 60°F) and the rinsings placed in the second flask. A fresh 75 ml portion of the original fuel was placed in the first flask and the water content of the fuels in both flasks was determined. A modification of the acetyl chloride-pyridine method was used.[7] The results found for three independent experiments averaged 0.0050 ± 0.0003 percent for the fresh sample in the rinsed flask and 0.0012 ± 0.0002 percent for the rinsings in the second flask. These results indicate that over 75 percent of the original dissolved water in the fuel had been removed by the walls of the two dried flasks.

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[7] *Smith, op. cit.*

In view of the above results, a practice was established of "equilibrating" the walls of any fresh container to the fuel to be stored or handled in it by thoroughly rinsing with at least three portions of that fuel prior to its use. Other experiments have shown that this procedure is adequate to ensure the obtaining of consistent results.

Another precaution which must be observed is that containers of fuel must be kept tightly stoppered to prevent loss of water to the atmosphere. The necessity for this was demonstrated by the following experiment.

Three 250 ml glass-stoppered Erlenmeyer flasks were "equilibrated" and filled with AN-F-48 91/98 octane fuel (saturated at 60° F). Approximately 80 ml samples were withdrawn from each flask and the flasks re-stoppered. These samples analyzed 0.0068, 0.0069 and 0.0068 percent water. After a time interval which varied from 1 - 3 hours, a second series of samples from the same flasks analyzed 0.0060, 0.0065 and 0.0063 percent water. This decrease in water content cannot be attributed to adsorption by glass sincethe three original samples had been saturated independently and were allowed to stand for different lengths of time before running the first analyses. A logical explanation for this significant decrease in water content is the loss of water to the air which displaced the first sample. This air had an initial R.H. of about 20 percent at 76°F. The average loss of water from the fuel was approximately 0.7 mg. This amount of water added to the 80 ml of free air in the flask would raise its R.H. to only about 60 percent.

CLOGGING OF MICRONIC FILTERS AT LOW TEMPERATURES

The facilities at this Laboratory did not permit the conducting of full scale tests on filter clogging. A small scale bench set-up was therefore devised in such a way that tests could be run under a variety of conditions. It is considered that although results obtained in this manner are not absolute, they are valid and can be extrapolated to apply reasonably well to full scale conditions. The effects of the following variables on filter clogging were studied: (1) temperature, (2) water content of fuel, (3) fuel pressure, (4) pore size and kind of filter paper. In addition, tests were run to determine the nature of the material causing the clogging.

Materials

The fuel used in the clogging experiments was AN-F-58 (inspection data given in Appendix III). The samples used were equilibrated to known water content by saturation at various temperatures using methods already described. The toluene used was of reagent grade. The n-octane used was purified by treatment with sulfuric acid and by distillation. The filters used were cut from the paper of low pressure filter elements such as are used in the Navy and Air Force jet aircraft. The 10 micron type papers (specification AN-6236-2) were manufactured by Skinner Purifiers Division of the Bendix Aviation Corporation and by Purolator Products Incorporated. In addition, a 25 micron type paper obtained from the Purolator Company was also tested (serial No. 710-1). Since the paper in the micronic filter elements is not homogeneous, test sections were selected with considerable care and tested for resistance to fuel flow at room temperature. Only those samples having comparable resistances were used in the clogging experiments.

Apparatus and Procedures

General

A detailed description of the apparatus and procedure used is given in Appendix IV. In essence it consisted of an enclosed filter holder having an effective filtration area of 1.0 cm^2. Part of this holder was made of glass to permit ready observation of the filter paper. The fuel was admitted to the filter element through a copper coil so constructed that the coil and filtration unit could be completely immersed in a cooling bath. The fuel was supplied by gravity from a reservoir system designed to ensure a constant head. The filtrate was warmed by passing through a copper tube immersed in a water bath maintained at approximate room temperature. The effluent was collected and measured in a graduated cylinder. The temperature of the fuel being filtered was measured with an iron-constantan thermocouple placed 2-3 mm directly above the filter paper.

Determination of Flow Rates and Clogging Points

In general, the majority of the experiments were conducted by maintaining a constant pressure drop across the filter equal to a 6 cm head of fuel (1 oz/in.^{2}). Fuel was passed through the system and flow rates were measured by timing each 10 ml increment of flow. The flow rate for a typical filtration is shown graphically in Figure 6. It is seen that the time required for a 10 ml increment of flow is reasonably constant for a considerable volume of total flow but toward the end, the time increases very rapidly.

Although Figure 6 is a good representation of the general shape of clogging curves, the exact rate of clogging was not always the same. For comparative purposes, therefore, it was necessary to choose an arbitrary point to represent a clogged filter. This point was taken as that total volume of flow at which the time/10 ml was 10 times that at the start.

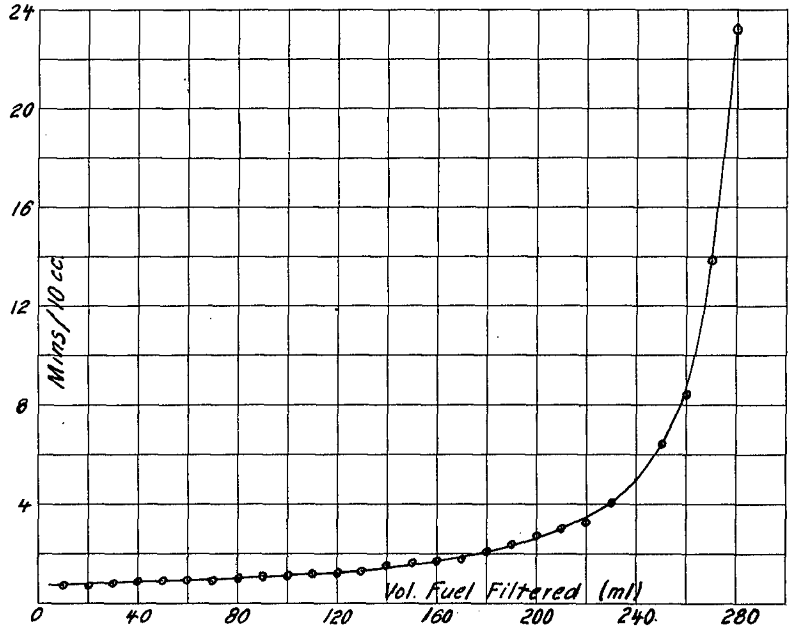

Figure 6 - Typical clogging of filter

TABLE 5
Effect of Fuel Temperature on Filter Clogging

Temp. (°F)	10 Micron Paper: 10x Pt (ml)	10 Micron Paper: Average Deviation (ml)	10 Micron Paper: No. of Determinations	25 Micron Paper: 10x Pt (ml)	25 Micron Paper: Average Deviation (ml)	25 Micron Paper: No. of Determinations
20	427	16	3	1260	100	2
10	243	34	4	860	10	2
0	229	18	7	700	60	2
-10	35	13	4	240	47	3
-20	31	4	4	70	10	2
-40	353	79	6	160	20	2
-60	345	60	4	260	53	3

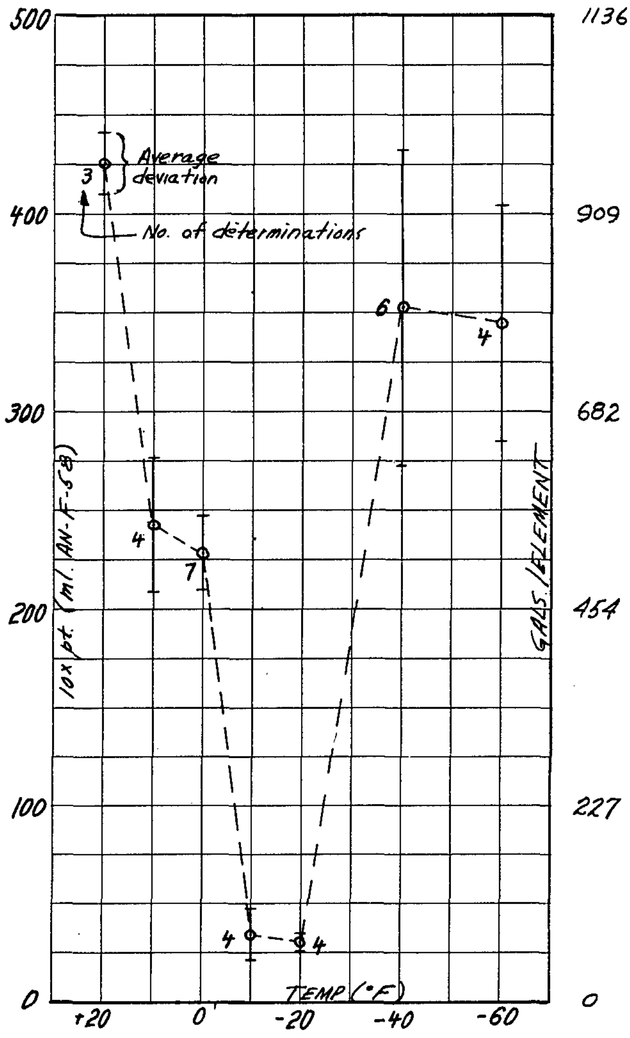

Figure 7 - Effect of fuel temperature on filter clogging (10 micron paper)

In every case in which clogging occurred, this 10x point was on the steep portion of the curve and thereby gave a clearly defined value which is indicative of the clogging characteristics for the particular experiment.

Nature of the Material Causing Clogging

It was desirable to obtain some confirmatory evidence that the material which clogged the filters at low temperatures was ice or snow. To accomplish this, experiments were conducted in which clogged filters were allowed to warm up slowly and the flow rates were measured as a function of temperature. A number of such warm-up tests were carried out following the clogging tests with AN-F-58 fuel under various conditions. In addition, similar tests were also made using toluene and n-octane.

Results

Effect of Temperature on Filter Clogging

In experiments, using 10 micron paper, variables were controlled as follows:

Fuel - AN-F-58 saturated at 60° F(0.0056% water)

Pressure drop across filter - 1 oz/in.^{2}

Paper - 10 micron type (Skinner)

Resistance of paper - such that 0.35 to 0.45 min required to pass 10 ml of fuel/cm^2 at room temperature and 1 oz/in.^{2} fuel pressure

Temperature - For a given experiment maintained ±1°F. Tests conducted at +20°F, +10°F, 0°F, -10°F, -20°F, -40°F, and -60°F. In each of these experiments the fuel was pre-cooled for at least 15 min.

The results obtained are summarized in Table 5 and shown graphically in Figure 7. Detailed data are given in Table 9 (Appendix V).

Another series of experiments similar to those given above, but using 25 micron paper were carried out under the following conditions:

Fuel - same as above

Pressure drop across filter - 0.73 oz/in.^{2}

Paper - 25 micron type (Purolator)

Resistance of paper - such that 0.35 and 0.41 min required to pass 10 ml of fuel/cm^2 at room temperature and 0.73 oz/in.^{2} fuel pressure

Temperature - same as above

The results of these tests are summarized in Table 5 and Figure 8. Detailed data are given in Table 9 (Appendix V).

Effect of Water Content of Fuel on Filter Clogging

In studying the effect of water content of fuel on filter clogging, the conditions used were as follows:

Fuels - AN-F-58 having water contents of 0.0050%, 0.0056%, 0.0074%, and 0.0093%.

Pressure drop across filter - 1 oz/in.^{2}

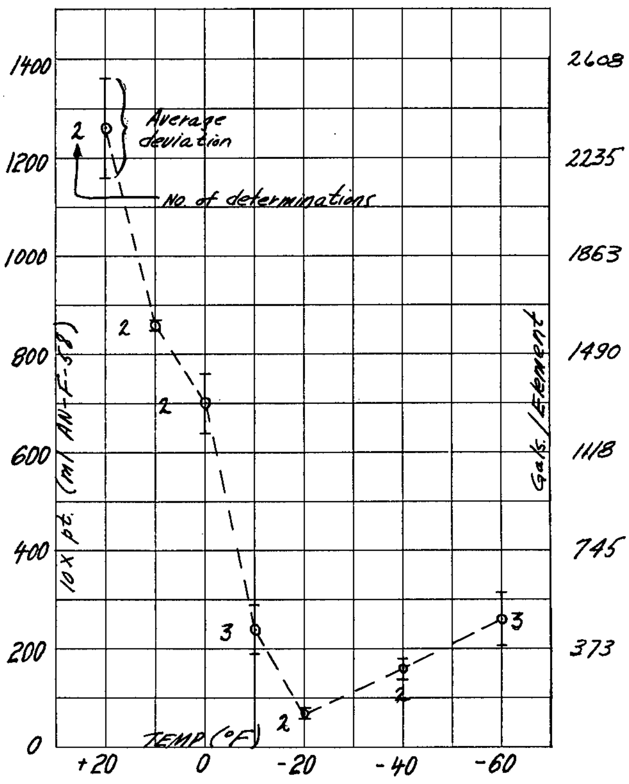

Figure 8 - Effect of fuel temperature on filter clogging (25 micron paper)

TABLE 6
Effect of Water Content of Fuel on Filter Clogging

Water Content (wt %)	10x Pt (ml)	Average Deviation (ml)	No. of Determinations
0.0050	250	13	3
0.0056	229	18	7
0.0074	173	11	3
0.0093	68	4	3

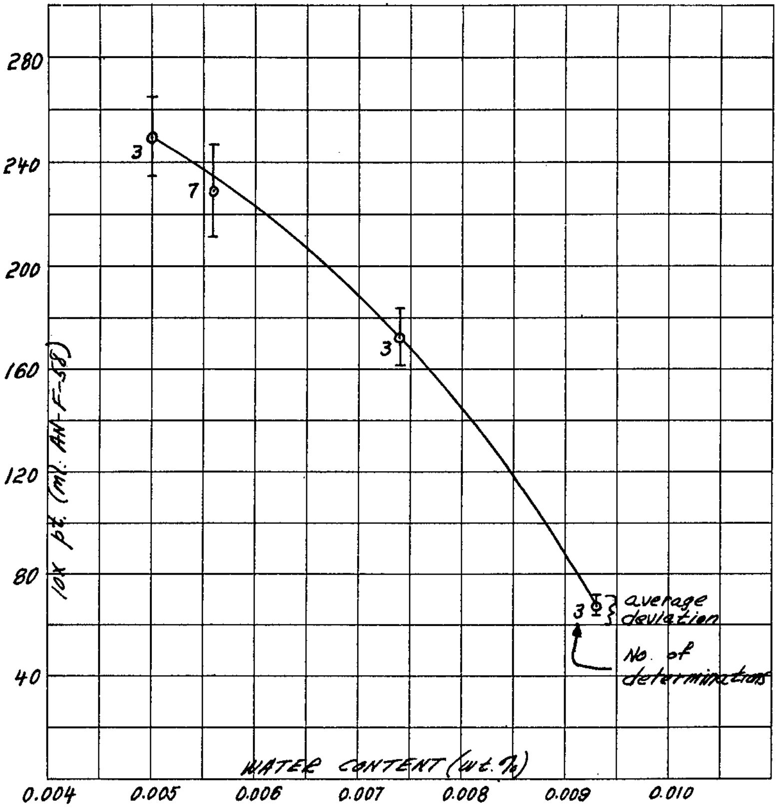

Figure 9 - Effect of water content of fuel on filter clogging

Paper - 10 micron type (Skinner)

Resistance of paper - such that 0.37 to 0.40 min required to pass 10 ml of fuel/cm^2 at room temperature and 1 oz/in.^{2} fuel pressure

Temperature - 0° ± 1°F

The results of these tests are summarized in Table 6 and Figure 9. Detailed data are given in Table 10 (Appendix V).

Effect of Fuel Pressure on Filter Clogging

In order to determine the effect of fuel pressure on filter clogging, an experiment was conducted in which the flow rate was maintained constant by varying the pressure drop across the filter.

Fuel - AN-F-58 saturated at 60°F(0.0056% water)

Pressure drop across filter - varied from 1 oz to 3 lb/in.^{2}

Paper - 10 micron type (Skinner)

Resistance of paper - such that 0.40 min required to pass 10 ml of fuel/cm^2 at room temperature and 1 oz/in.^{2} fuel pressure.

Temperature - 0° ± 1°F

Flow Rate - 4.5 - 5.1 ml/min/cm^2

The results for this experiment are given in Table 7 and Figure 10.

Effect of Pore Size and Type of Filter Paper on Clogging

The results on the effect of pore size for the 10 and 25 micron papers are given in Table 5 and Figures 7 and 8. Two types of 10 micron paper (Skinner and Purolator) were compared at 0°F, 1 oz/in.^{2} fuel pressure using AN-F-58 fuel (saturated at 60°F). Seven determinations of the 10x point using the Skinner paper gave an average value of 229±18 ml. Using the Purolator paper, three determinations gave an average of 247±4 ml. Detailed data for these experiments are given in Table 9 (Appendix V).

Nature of the Material Causing Clogging

The results of typical flow rates during the warm-up of clogged filters using AN-F-58 fuel, n-octane and toluene are presented graphically in Figure 11. Detailed data for these experiments are given in Table 11 (Appendix V).

Discussion

Nature of the Material Causing Clogging

Possible materials which may cause clogging of or hinder flow through a filter at low temperatures are ice, wax, hydrates, foreign matter and immiscible liquids. An examination of Figure 11 shows that as the temperature rises, the flow is not a function of the viscosity change but rather there is a sharp break-through at 32°F. It was observed that the solid which had collected on the filter melted rapidly at this temperature and the melting was coincident with the break-through, thereby indicating that this solid was probably ice.

In these experiments, it is unlikely that hydrocarbon hydrates were the clogging agents, since the three different materials studied (AN-F-58 fuel, n-octane and toluene) all showed the same break-through temperature of 32°F. In view of the known properties

TABLE 7
Effect of Fuel Pressure on Filter Clogging at 0°F

Fuel Passed (ml)	Pressure Drop (oz/in.^{2})	Fuel Passed (ml)	Pressure Drop (oz/in.^{2})
110	1	290	6.0
130	1.25	300	6.75
170	1.50	310	9.0
180	1.75	320	11.0
200	2.0	330	14.0
220	2.25	340	18.25
230	2.50	350	23.0
240	2.75	360	26.75
250	3.00	370	35.0
260	3.50	380	38.75
270	4.0	390	44.5
280	5.0		

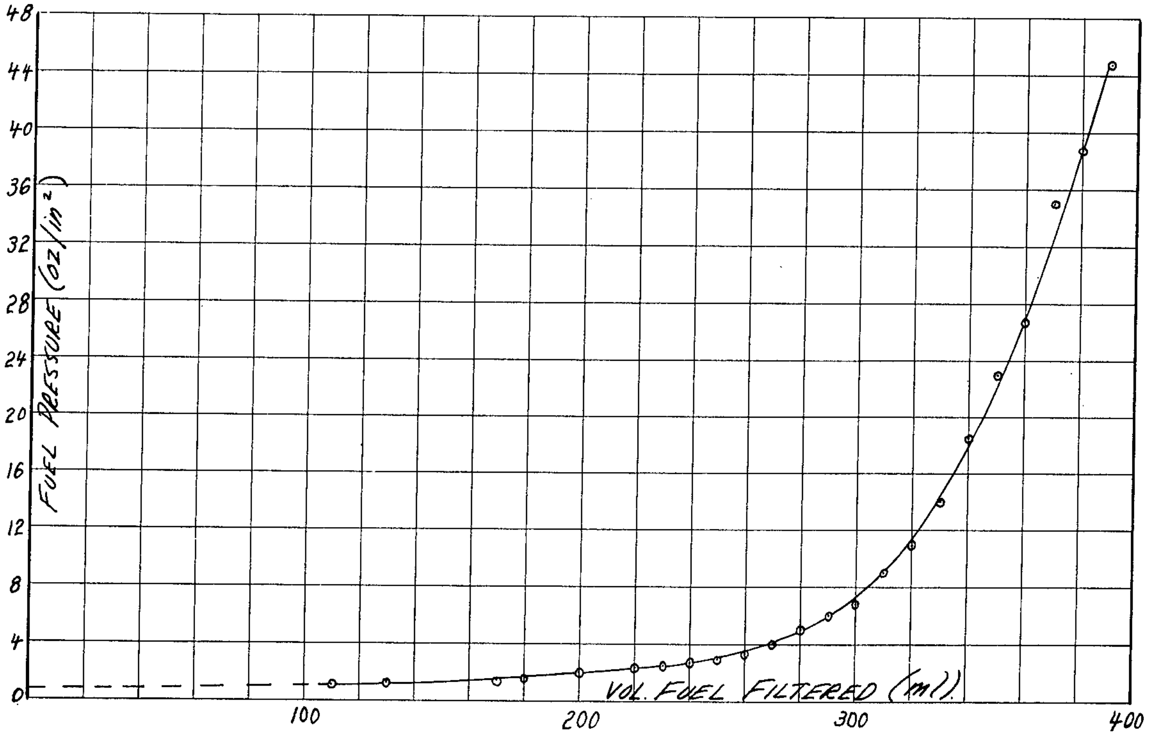

Figure 10 - Effect of fuel pressure on filter clogging at 0° F

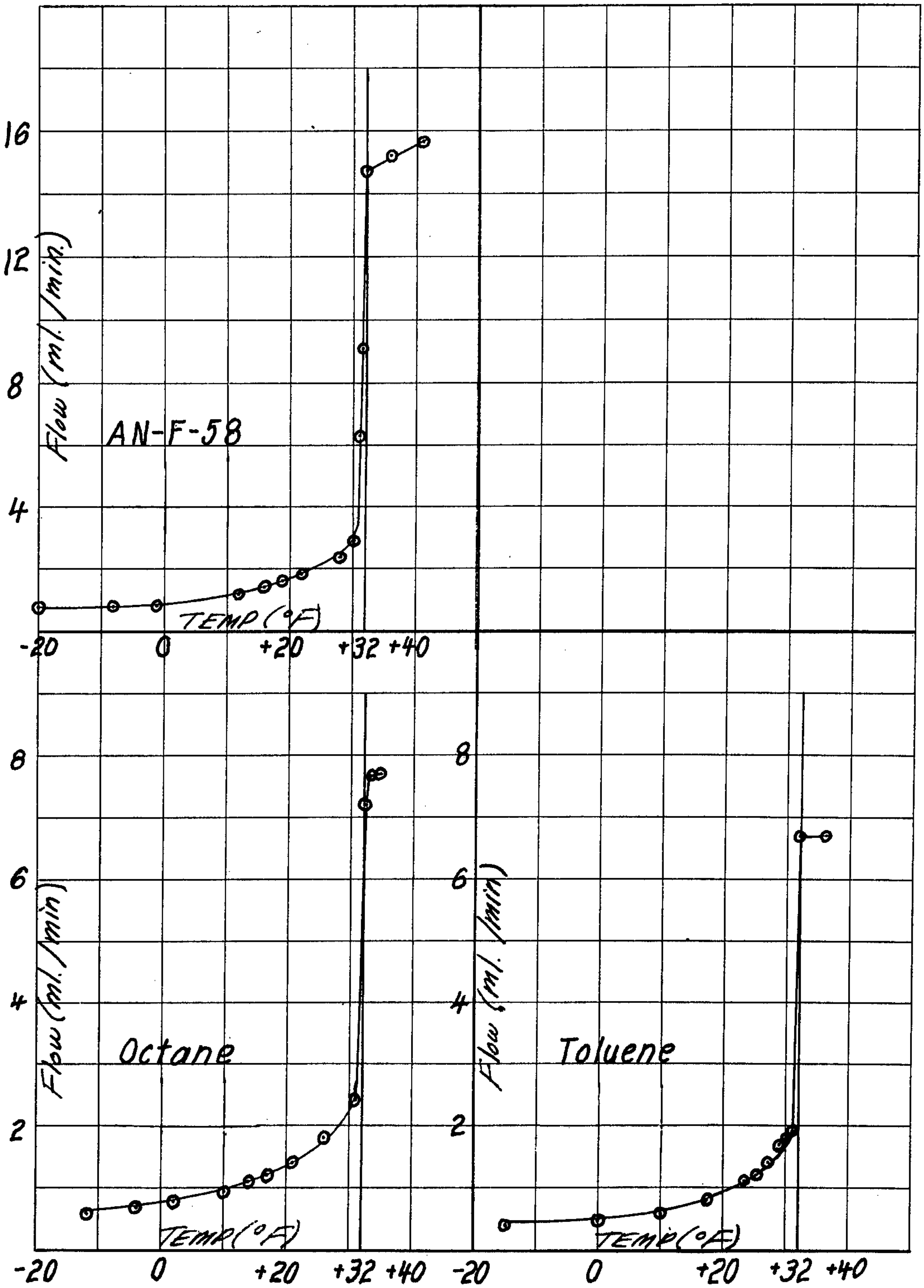

Figure 11 - Typical flow rates through clogged filters on warming

of such hydrates,[8] it is also highly improbable that they would be formed at all under the conditions of these tests. Furthermore, were they formed, it would be unlikely that all three would melt sharply at the same temperature. The separation of wax could not be responsible for the clogging since, in the AN-F-58 fuel used, wax separation was not observed at temperatures above -67°F and the n-octane and toluene used had been purified so that no waxes were present. Foreign matter (dust, rust, etc.) and immiscible liquids are excluded as clogging agents, in these tests, because such materials would not give consistent sharp break-throughs at 32°F.

Effect of Temperature on Filter Clogging

From Figures 7 and 8, it is seen that as the temperature is decreased there is a very marked increase in the rate of clogging. This was true for both the 10 and 25 micron papers. In both cases, the maximum clogging occurred at -20° F. Below this temperature clogging was not as rapid especially with the 10 micron paper.

The fuel used throughout these experiments was saturated at 60° F and contained a total of 0.0056 percent water. At 20°F the solubility of water is approximately 0.0014 percent (extrapolated value), therefore on cooling this fuel to 20°, approximately 75 percent of the water is separated. That portion of the remaining water which separates on further cooling could not be wholly responsible for the sharp drop in the curves (to -20°F) given in Figures 7 and 8. It appears, therefore, that there must be more than one method through which clogging occurs. This is further demonstrated by the rise in the curves at temperatures below -20°F. In the experiments at temperatures down to -20°F, it was observed that the clogged filter papers had much the same appearance as fresh paper. On the other hand, at the lower temperatures (i.e. -40° and -60°F), clogged filters were coated with a white crystalline material. In the first instance, clogging was probably due to glaze-ice formed on or within the paper whereas in the latter case, clogging was probably due to the surface loading of the paper with a bed of snow-ice. The very small volumes required for clogging at -20°F indicate that clogging is due to the closing of the pores of the paper rather than the formation of a filter bed. This would occur if part of the water in suspension remained supercooled in liquid form until it came in contact with the paper or ice crystals on the paper. Upon contacting these, this supercooled water would freeze to seal the pores of the paper with glaze-ice. Such a mechanism would require very small amounts of water. The steepness of the first portions of the curves may be due to either the ratio of the supercooled water and ice crystals present in the fuel or to the passage of supercooled water through the filter. In the experimental procedure used, -20°F presented the optimum condition for maximum clogging for both the 10 and 25 micron papers. However, the temperature for maximum clogging may differ as a function of the variables—rate and manner of cooling, time at low temperatures, agitation, etc.

The existence of liquid water in the supercooled state in the form of fine droplets suspended in air or deposited on polished surfaces at temperatures of -20°F and lower has been demonstrated at other laboratories.[9] Examination of fuels cooled to 0° to 10°F at this Laboratory and viewed with a microscope and in a Tyndall beam revealed that much of the suspended water was in the liquid state. On the other hand, when fuels cooled to

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[8] *Deaton, W. M. and Frost, E. M., "Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipe Lines." Bureau of Mines Monograph 8, 1946.*

[9] *Schaefer, V. J., "The Formation of Ice Crystals in the Laboratory and the Atmosphere." Chem Reviews, 44: 291-320, 1949.*

-40° to -60° F were viewed in a Tyndall beam, the presence of snowlike crystalline material was evidenced by the scintillating nature of the particles. These observations support the mechanism given above.

Throughout these experiments, filter paper test sections having effective filtration areas of 1 cm^2 were used. The total filtration area of the 10 micron type Skinner filtration element was found to be approximately 8600 cm^2. Therefore 1 ml of flow through a test section is equivalent to approximately 2.3 gallons of flow through the entire element. For example: at 0° F, it was found that 229 ml of fuel was necessary to clog the test section. In order to clog an entire element to an equivalent degree it would require 229 x 2.3 or approximately 525 gallons of fuel. In a like manner, the total filtration area of the 25 micron Purolator element was found to be approximately 7050 cm^2. Therefore 1 ml of flow through a test section of this paper is equivalent to approximately 1.9 gallons of flow per element. (The right hand ordinates in Figures 7 and 8 are the calculated clogging values in gallons per element.)

Effect of Water Content of Fuel on Filter Clogging

An examination of Figure 9 shows that at 0° F the water content of the fuel has a pronounced effect on the rate with which ice will clog a filter. Furthermore, this clogging is not directly proportional to the amount of water present, but as the water content increases, the fuel which passes through the filter before clogging occurs becomes relatively less and less. This data also shows the importance of controlling closely the water content of a fuel in the quantitative study of filter clogging since a relatively small difference in the water content makes a large difference in the clogging rate. Although these experiments were carried out at 0° F, it is to be expected that a similar behavior exists at the other temperatures.

Effect of Fuel Pressure on Filter Clogging

In the experiment at 0° F a constant flow rate of 4.5-5.1 ml/min/cm^2 was maintained by varying the pressure drop across the filter from 1 oz. to 3 lb/$in.^2$ Since 10 micron type Skinner paper was used, this flow rate corresponds to approximately 10.2 to 11.5 gallons/min/filter element which is of the order of that used in full scale fuel systems. The pressure drop was varied up to 3 lb/$in.^2$ since that pressure represents the lower limit at which the relief by-pass valves of the fuel filters open.

The results of this experiment show that, with a constant flow rate, the pressure drop across the filter is a function of the total volume of fuel filtered. From the curve given in Figure 10, it is seen that, at first, the pressure drop is low and rises slowly. However, there is a break point after which comparatively small volumes of total flow produce large increases in the pressure drop necessary to maintain the flow rate. Thus at 240 ml, the pressure drop had risen to only $2\frac{1}{2}$ oz/$in.^2$ while at 390 ml, the pressure drop was approximately 3 lb/$in.^2$ A similar experiment at -20°F required only 145 ml of total flow before a pressure drop of 3 lb/$in.^2$ was reached. This is in keeping with the previous 10x point clogging results. It was observed at both 0°F and -20°F that when the 3 lb pressure drop was reached and maintained constant, the decrease in flow rate was comparatively slow and it appeared that a granular filter bed of ice was being formed.

It is interesting to point out the similarity between the type curve obtained in these experiments and that given for typical clogging in Figure 6. Both are of the same general shape and exhibit break points. It is also interesting to note that the break point of the curve given in Figure 10 (approximately 240 ml), corresponds rather closely to the average 0° F 10x point obtained previously (229 ± 18 ml). Since the temperature of this experiment was also 0° F and the paper and fuel were the same, it follows that the break point obtained by this method is related to the 10x point and both are representative of moderately clogged filter elements.

Effect of Pore Size and Kind of Filter Paper on Clogging

An examination of a filter paper under a microscope shows that, at best, the pore size is far from being uniform. A paper designation of 10 microns does not mean that all of the pores are 10 microns in diameter but rather that this paper will retain most of the particles down to 10 microns in size. Of course, some of the smaller particles are also retained and some of the larger ones pass. Because of this lack of homogeneity, the test papers used in this work were chosen with care. As described earlier, only those papers which had a comparable initial resistance to fuel flow were used.

In studying the effect of pore size, the 10 micron type Skinner and 25 micron type Purolator papers were used. From the results given in Table 5 and Figures 7 and 8, it is seen that through the temperature range of +20° to -20° F (with the exception of the -10° F figure), the 25 micron paper passes from 2.3 to 3.5 times as much fuel as does the 10 micron paper before clogging. At the lower temperatures the 10 micron paper actually passes slightly more fuel than the 25 micron paper. As described previously, clogging at temperatures down to -20° F is probably due to the formation of glaze-ice which seals the pores of the paper. Since the 25 micron paper has a greater "open" area than the 10 micron paper, a larger volume of fuel is required to seal these pores with ice. At the lower temperatures, clogging is probably due to the surface loading of the paper with a bed of snow-ice. In such cases, the "open" area of the paper is not as important in determining the quantity of fuel required to clog the paper but rather the "relative packing" of the crystals of snow-ice and the pressure drop across the filters are the governing factors.

The two 10 micron type papers compared were those produced by the Skinner and Purolator Companies. The results of these experiments showed that the papers tested were quite close in performance with perhaps the Purolator paper passing slightly more fuel/cm^2. The sample of the latter paper also appeared to be somewhat more homogeneous both from visual inspection and the fact that the average deviation of the 10x point was smaller. For the samples received at this Laboratory the total area of the Purolator filtration element was less than that for the Skinner unit (7125 cm^2 vs. 8600 cm^2). Based on these samples, the Skinner element should pass slightly more fuel than the one supplied by Purolator (525 gal. vs. 470 gal., under the conditions tested).

USE OF ADDITIVES FOR THE PREVENTION OF FILTER CLOGGING AT LOW TEMPERATURES

Four principal methods have been suggested for the prevention of filter clogging by ice. They are: (1) mechanical methods such as heating the fuel upstream of the filters or the mechanical removal of ice from the filter surface, (2) use of pre-dried fuels in a "water-free" system, (3) use of physical or chemical agents which remove water by adsorption, hydrate formation or reaction and (4) use of additives as freezing point depressants. Since this study is concerned with the last method only, the others will not be considered further.

In order for a substance to be a satisfactory antifreeze, it must give a suitable freezing point depression, be noncorrosive, have no serious effect on the burning qualities of the fuel, be soluble in both fuel and water, have a partition coefficient between fuel and water such that a high concentration of the material appears in the separated aqueous phase and this phase must have a low relative viscosity. Other desirable properties include low cost, ready availability, nontoxicity and prolonged stability in the fuel system. In view of these requirements, the number of compounds which can be considered is limited. The compounds which were investigated for their effectiveness in preventing clogging are methyl alcohol (AN-M-32), denatured ethyl alcohol (AN-A-18), isopropyl alcohol, diacetone alcohol (O-A-393), acetone (O-A-51b) ethylene glycol, and dioxane. Although other compounds could have been included, it was felt that the results obtained with these would be representative of antifreezes. In addition, miscibility studies were carried out with AN-F-58 fuel (saturated with water at 60°F) and methyl, ethyl and isopropyl alcohols and with AN-F-48 91/98 octane fuel (containing TEL and saturated with water at 60°F) and ethyl alcohol. Cursory studies also were made on the melting points of the frozen aqueous phases separating from some of the above mixtures.

Procedures

Clogging Studies

In general, clogging tests were carried out at -20° F in the apparatus described earlier, using AN-F-58 fuel saturated with water at 90° F (0.0093 percent water) and to which 1 percent of the antifreeze had been added. The filter paper used was the Skinner 10 micron type. The pressure drop across the filter was varied depending on the progress of each individual run.

Miscibility Studies

Miscibility studies were made by determining the temperature at which the first visual indication of phase separation occurred when a known fuel-alcohol-water mixture was cooled slowly. Methyl, ethyl and isopropyl alcohols were used in these studies.

Melting Point Studies

Some of the mixtures used above were cooled strongly so as to freeze the separated aqueous phase. These were allowed to warm slowly and the temperature was noted at which melting of the solid phase occurred.

Results

Clogging Studies

The results of the effectiveness of antifreeze additives on the prevention of clogging are given in Table 8.

In addition, a study was carried out to determine the effect of temperature on restriction to flow using ethyl and isopropyl alcohols as additives. In these experiments, the pressure drop across the filter was maintained constant at 1 oz/in^2. With this pressure drop, using fuel containing 1 percent of 99 percent isopropyl alcohol, it was found that a 10x point could be obtained at temperatures up to 25° F. It was found that, qualitatively, the higher the temperature, the greater the volume of fuel required for the 10x point.

TABLE 8
Effect of Additives on Clogging

Additive	Additive Added to Fuel (%)	Temp. (°F)	Max. Press. Drop Applied (oz/in.^{2})	Total Flow at Max. Press. (ml)	Flow Rate at Total Flow (min/10 ml)
Methyl Alcohol (AN-M-32)	1.0	-20	2.5	1750*	1.1
	0.1	-20	6	1780*	1.0
	0.1	0	6	1600*	1.0
Ethyl Alcohol (AN-A-18)	1.0	-20	3	1600*	1.0
	0.2	-20	6	1600*	1.0
	0.1	-20	21	1750*	1.2
Isopropyl Alcohol (99%)	1.0	-20	4	1820*	1.6
	0.3	-20	48	880	4.0
	0.1	-20	48	475	3.0
Diacetone Alcohol (O-A-393)	1.0	-20	4	1800*	0.6
Ethylene Glycol	1.0	-20	7	1450*	1.0
Acetone (O-A-51b)	1.0	-20	48	785	2.9
Dioxane	1.0	-20	48	270	clogged
None	--	-20	48	145	1.4
	--	0	48	390	2.1

*No indication of a tendency to clog. Runs stopped arbitrarily at the total flows listed.

When fuel containing 1 percent of 99 percent ethyl alcohol was used, a 10x point was not obtained at temperatures as low as -60°F. In these low temperature runs, however, the initial rate of flow was considerably less than for fuel without the additive under the same conditions. This is caused by the formation of a liquid barrier of higher viscosity.

Miscibility Studies

The results of these studies are presented graphically in Figures 12, 13, 14, and 15. It is to be emphasized that the curves given in these figures represent the limits for complete miscibility and that miscibility may still be considerable in the areas below the curves. Detailed data for these tests are given in Tables 12, 13, 14, and 15 (Appendix V).

Melting Point Studies

The melting point results are presented graphically in Figure 16. Detailed data are given in Table 16 (Appendix V). For fuels containing 0.13 volume percent of 97-100 percent methyl alcohol, the separated phase appeared to be liquid at -40°F. A melting point could not be obtained on this material.

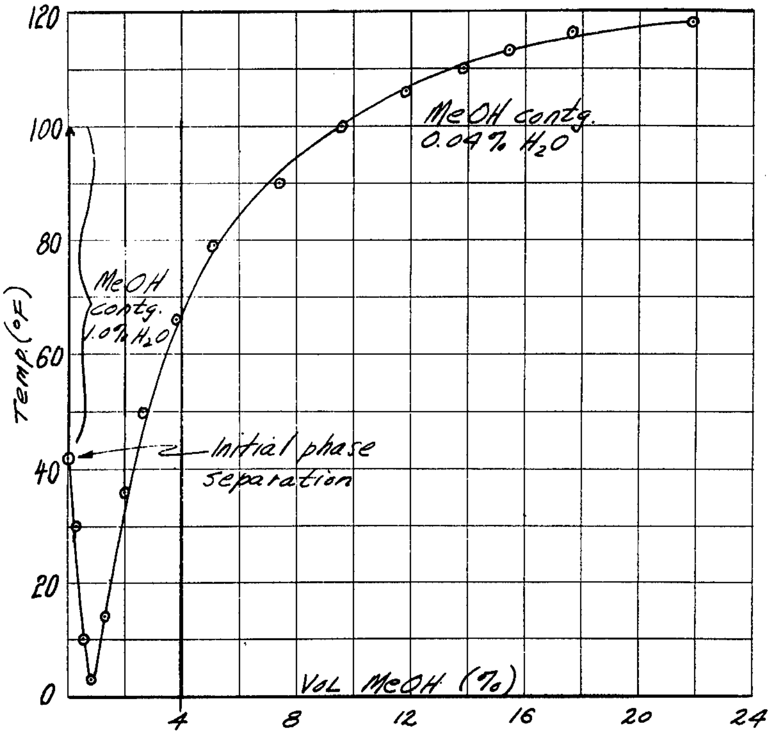

Figure 12 - Complete miscibility limits for methyl alcohol in AN-F-58

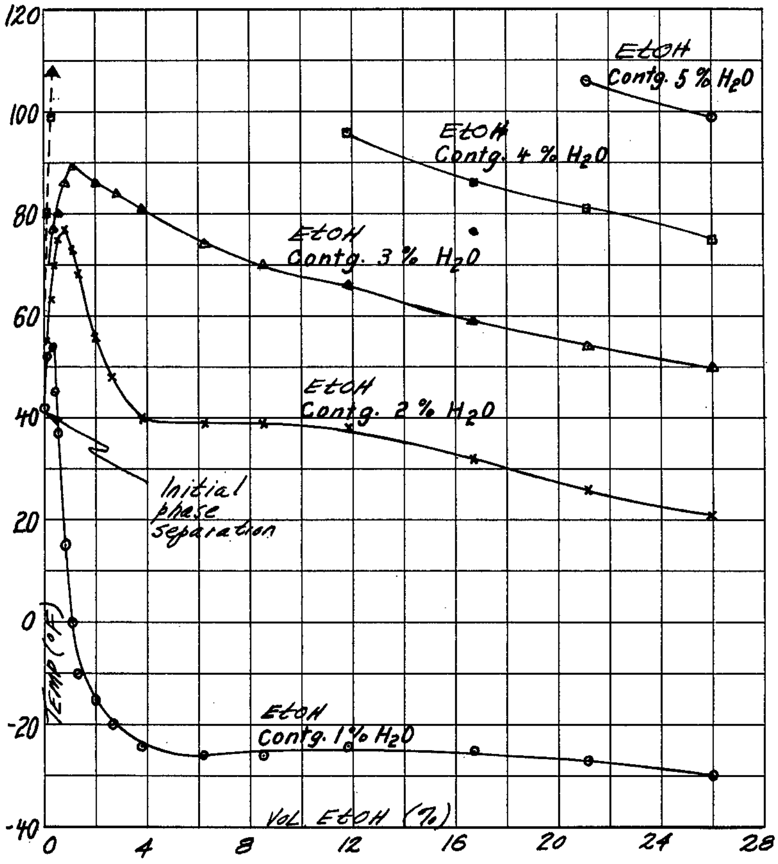

Figure 13 - Complete miscibility limits for ethyl alcohol in AN-F-58

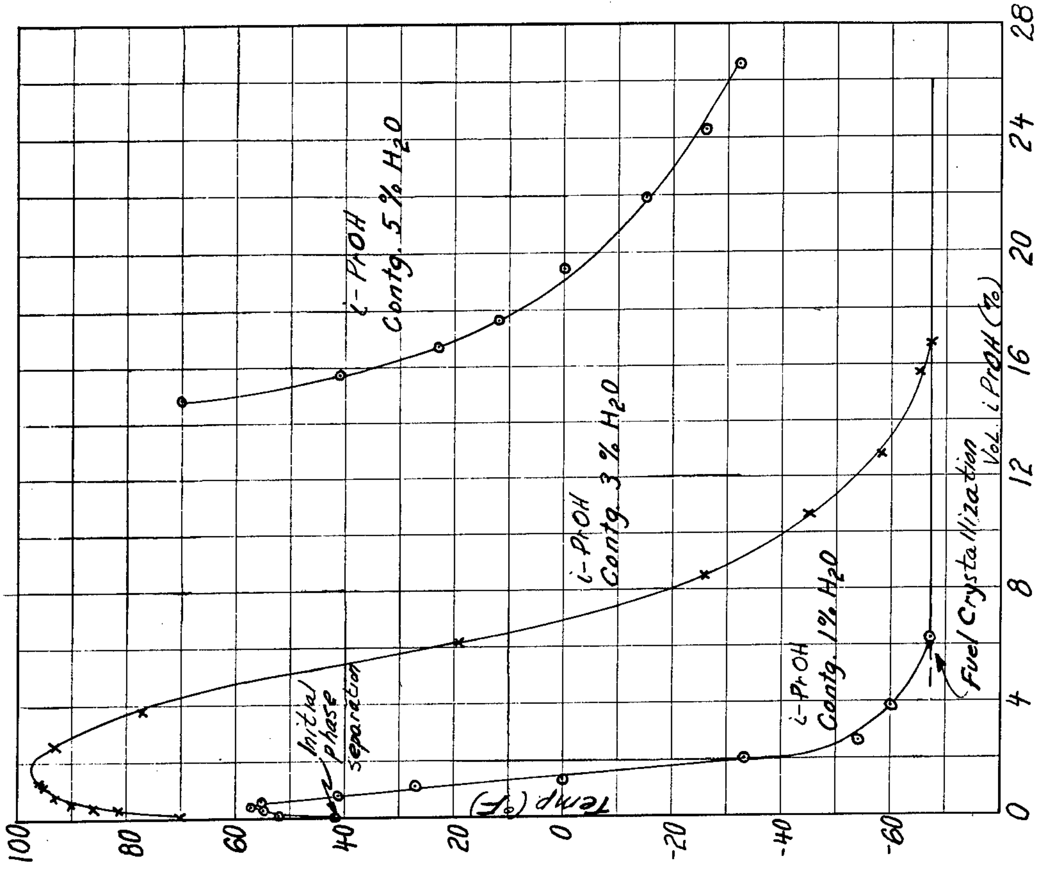

Figure 14 - Complete miscibility limits for isopropyl alcohol in AN-F-58

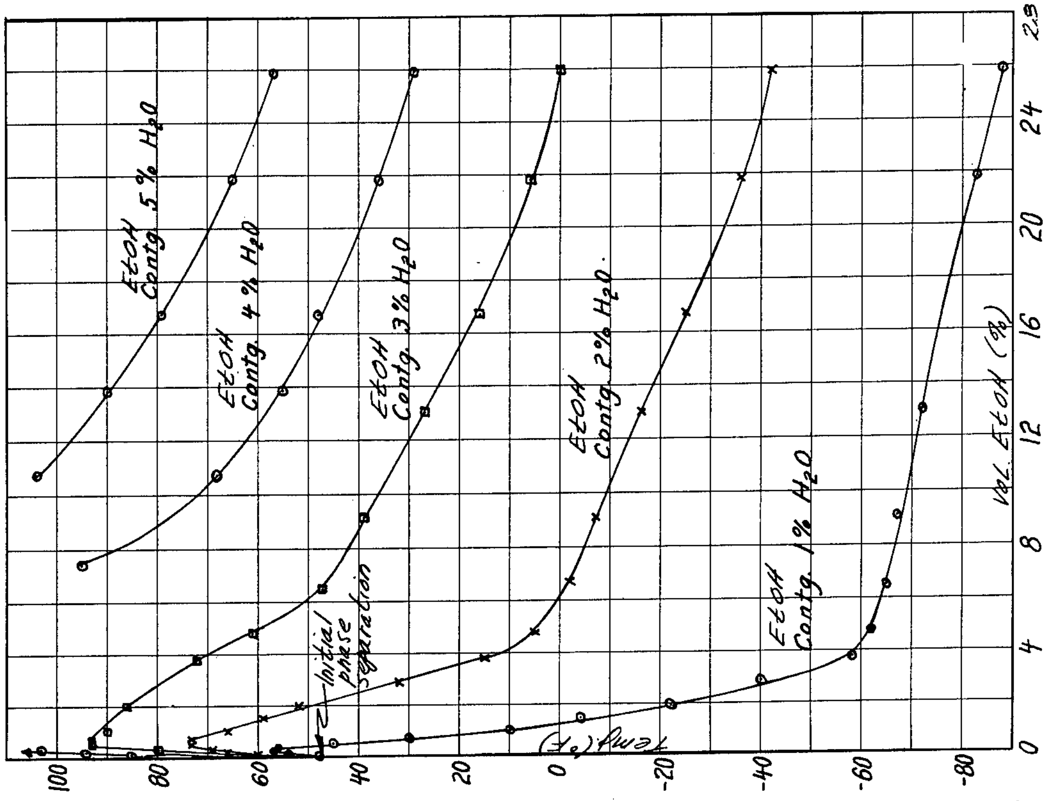

Figure 15 - Complete miscibility limits for ethyl alcohol in AN-F-48 91/98 octane

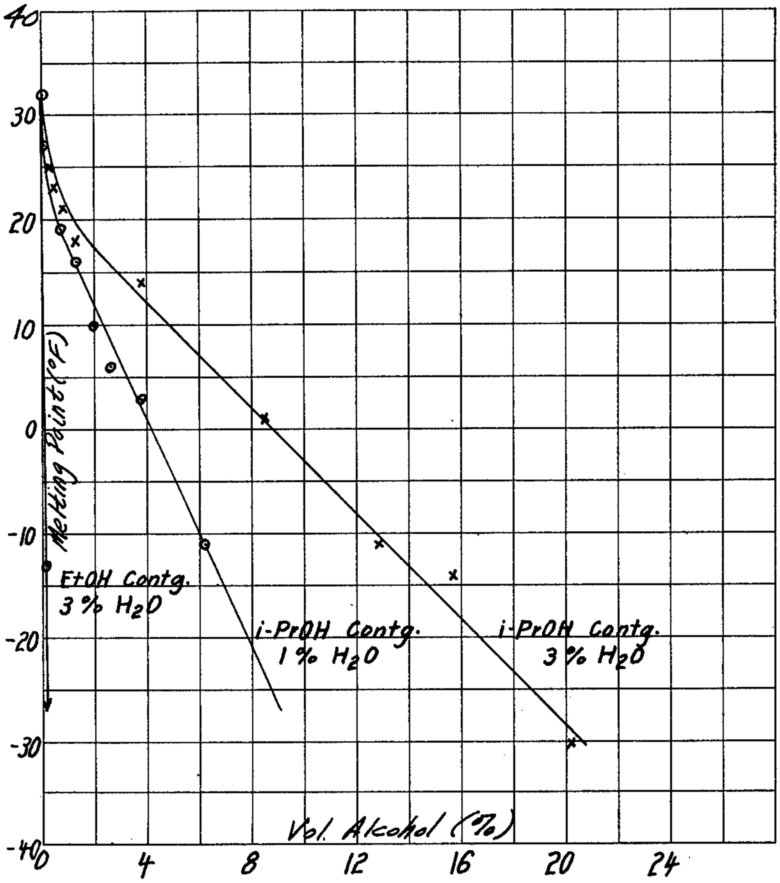

Figure 16 - Melting point of solid phase from AN-F-58/alcohol mixtures

Discussion

Clogging Studies

From Table 8 it is seen that when 1 percent of additive was used, five of the seven compounds tested were effective in preventing clogging. However, the pressure drop across the filter required to maintain a reasonable flow varied from 2.5 oz/in.^{2} in the case of methyl alcohol to 7 oz/in.^{2} in the case of ethylene glycol. The reason for this difference is attributed to the relative viscosities and quantities of the separating aqueous phases. Such a phase collects on the filter surface to form a partial liquid barrier which hinders the flow of fuel. The higher the viscosity of the aqueous phase, the greater the pressure required to maintain fuel flow. Although clogging did not occur when acetone was used, the pressure drop required to maintain flow was excessive. In this particular case, it was noted that a white deposit collected on the filter which on warming coalesced into a single clear immiscible globule. This behavior was not noticed for the other additives.

Of the compounds tested, only isopropyl alcohol, acetone and dioxane were completely soluble in the fuel at room temperature. It is conceivable that part of the antifreeze action of the other compounds was due to the partial extraction of water into the phase which collected at the bottom of the reservoir. This may be true particularly in the cases of ethylene glycol and diacetone alcohol which are hygroscopic in nature and for which a relatively large second phase was observed.

From Table 8 it may be seen further that methyl alcohol had good antifreeze action even when only 0.1 percent was added to the fuel. Ethyl alcohol was also effective at this concentration but required a somewhat greater fuel pressure to maintain flow. When present to the extent of 0.2 percent, ethyl alcohol gave results comparable to those obtained with 0.1 percent methyl alcohol. Isopropyl alcohol was not effective at 0.3 percent.

Miscibility Studies

The results given in Figures 12, 13, 14 and 15 show the very pronounced effect that small amounts of water have on the complete miscibility of the alcohols with fuel. For example, it may be seen that methyl alcohol containing 1.0 percent water is not completely miscible at 100 °F when 0.1 percent of this alcohol is added to the fuel whereas methyl alcohol containing 0.04 percent water is completely miscible at 3°F when 0.8 percent of this alcohol is added to the fuel. This same type of behavior is also true for the other alcohols but to a somewhat lesser degree. It may be noted also that there is a progressive increase in the solubility of the alcohol as the molecular weight increases. In the case of isopropyl alcohol the study could be carried only to -67°F because a flocculent crystalline solid separates out at this temperature. A comparison of Figures 13 and 15 shows that ethyl alcohol has a somewhat better compatibility with AN-F-48 91/98 octane fuel than with AN-F-58.

Melting Point Studies

The method employed in these cursory determinations was such that true equilibrium conditions were not attained. As a consequence, the results obtained are not strictly reproducible and can be used only in a qualitative way. The results show that only very small amounts of methyl and ethyl alcohols are necessary to prevent the formation of ice. On the other hand, using isopropyl alcohol it was possible to have a solid phase present at fairly high temperatures and at high concentrations of the alcohol. A comparison of the results in Figures 14 and 16 shows that under the conditions of the experiment, the ice formed by strong cooling did not remelt nor redissolve at certain concentrations and temperatures at which only one phase would exist under equilibrium conditions. In view of the slowness with which equilibrium is attained, a similar behavior could be expected under certain unusual and extreme operating conditions.

General

One of the most important properties that an effective antifreeze additive must possess is a proper partition coefficient between fuel and water so that the separated aqueous phase contains a high concentration of the additive. Of necessity, such a compound must be highly hydrophylic. In general this type of compound cannot be expected to have a high solubility in fuel. The results of both the clogging and melting point tests show that methyl alcohol was the most effective antifreeze agent. On the other hand, the results of the miscibility studies showed that methyl alcohol had the poorest solubility in the fuel. This behavior is to be expected on the basis of the structures of the compounds involved in that methyl alcohol most closely resembles water and has the lowest molecular weight. By virtue of the fact that a good antifreeze agent must of necessity be highly hydrophylic, it follows that it will be leached the more readily from fuels by water. Thus, while these studies indicate that methyl alcohol is the best antifreeze agent, it will also be lost very readily from the fuel solution to any water present. In choosing the most suitable additive, due consideration must be given to the methods of handling which affect the quantities of water that might contact the fuel. This includes water that may be suspended or entrained in the fuel or that may be present in the sumps of the fuel system. One method by which this leaching problem may be overcome is to keep the additive separate from the fuel until such time as it is needed. One way in which this may be accomplished is the method developed at Eglin Air Force Base[10] in which the additive is injected directly into the fuel line when the pressure drop across the filter indicates icing.

SUMMARY AND CONCLUSIONS

1. A method for the determination of water in fuels using the Karl Fischer reagent has been developed.

2. The solubility of water in several fuels and pure hydrocarbons has been determined over the temperature range of 32° F to 120° F.

3. Addition of an aromatic to an aliphatic hydrocarbon increases the solubility of water. This increase is less than would be expected from the proportional amount of aromatic added.

4. Fuels on contact with water saturate rapidly, especially on agitation.

5. On cooling a fuel below its saturation temperature, water separates as a fine cloud which disappears very slowly.

6. A laboratory apparatus for the study of filter clogging at low temperatures has been devised. Using this apparatus, the effects on filter clogging of a number of variables were determined under controlled conditions.

7. It has been demonstrated that at low temperatures micronic filters are clogged by ice. Clogging may result either from the surface loading of the filter by snow-ice or by the formation of glaze-ice on or within the filter from supercooled water.

8. A very marked increase in the rate of clogging was found as the temperature was lowered. A maximum of clogging occurred at -20°F. Below this, clogging was not as severe.

9. As the water content of the fuel is increased, the rate with which clogging occurs is increased. This increase is greater than the proportional amount of water present.

10. At constant flow rate, the pressure drop across the filter rises as the volume of fuel passed increases. At first, the pressure drop increases slowly, but as the filter becomes clogged, it rises rapidly.

11. Relatively small differences in performances were found for the two different makes of 10 micron paper tested. The 25 micron paper passed approximately three times as much fuel as the 10 micron paper down to -20°F.

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[10] *APG Letter Final Report, op. cit.*

12. A number of representative substances were tested as potential freezing point depressants for the prevention of low temperature clogging.

13. In general, it was found that the more hydrophylic compounds are the more effective antifreezes. However, these compounds are the more readily lost from the fuel through leaching by water.

14. Of the compounds tested, methyl alcohol was found to be the best antifreeze, being effective when only 0.1 percent was added to the fuel. On the other hand, it becomes lost very readily from fuel solutions to any water present.

15. In selecting a suitable antifreeze, due consideration must be given to the methods of handling and storage which affect the quantities of water that might contact the fuel and to the methods which may be used for the introduction of the additive.

* * *

APPENDIX I
DETERMINATION OF WATER IN HYDROCARBONS

REAGENTS

Methanol – C.P., preferably having a water content of 0.03 to 0.1 percent.

Toluene – purified grade, dried over calcium sulfate.

Karl Fischer (K. F.) Reagent – Dissolve 42.3 gm of iodine in a mixture of 835 ml methanol and 135 ml of C.P. pyridine (dried over KOH). Cool this mixture in a water-bath and bubble in 32 gm of sulfur dioxide (dried by passing through sulfuric acid). The addition of sulfur dioxide should require approximately 1 to 1½ hours. The initial strength of this reagent varies somewhat and depends on the water content of the pyridine and methanol used. With the materials used at this Laboratory, 1 ml of freshly prepared reagent has been found to be equivalent to approximately 1.6 mg of water.

APPARATUS

A diagram of the apparatus used is given in Figure 17. The reaction flask is a 3-necked Woulff bottle having a capacity of 500 ml. K.F. reagent is metered into the flask from an automatic 10 ml burette (A) through capillary (B). Capillary (B) is 9 inches long and of such diameter that it allows a reagent flow of approximately 1.5 ml/min. Methanol is added from a 5 ml automatic burette (C) through capillary (D). Capillary (D) is 36 inches long and of a diameter such that the methanol flows through it at a rate of approximately 0.2 ml/min. The electrodes are platinum vs. platinum + 10 percent rhodium. These are sealed through glass and connected through shielded copper leads to a Brown Electronik Precision Indicator having a range of 10 mv. The electrode leads are so connected that a positive E.M.F. is indicated when an excess of water is present and a zero reading is given by excess K.F. reagent. Stirring is effected by a magnetic stirring bar. Samples and solvents are added through the port which is normally protected by the drying tube.

PROCEDURE

Bringing Solvents and Solutions to the End Point – The stirrer is started and a slight excess of K.F. reagent is added to the solution present in, or solvent (100 ml toluene +55 ml methanol) added to the flask. This excess is indicated by a reading on the potentiometer of 0.00 mv which is stable for at least 3 minutes. Methanol is then allowed to flow in from burette (C), without stopping, to an arbitrary end point reading of 0.04 mv.

Standardization of Methanol – Approximately 0.50 ml of K.F. reagent is metered into a solution "end-pointed" as above, and the mixture is again brought to the end point with methanol from burette (C). The strength of the methanol reagent (actually the water present in the methanol) is calculated in terms of equivalence of K.F. reagent from the ratio of the quantities of reagent and methanol used.

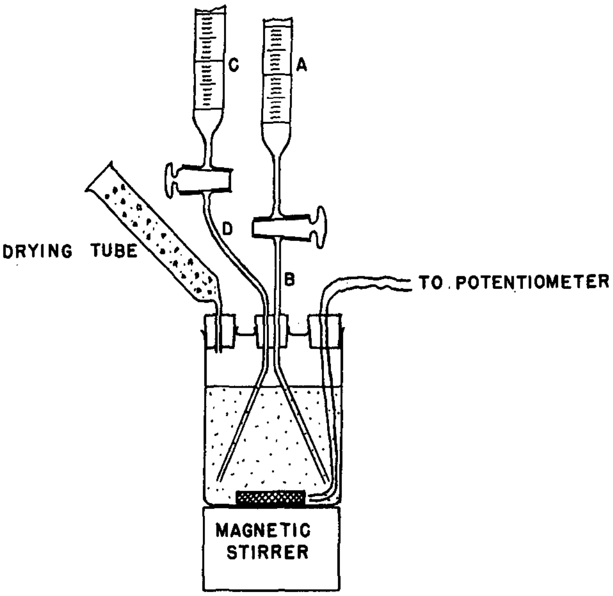

Figure 17 - Apparatus for determination of water

Standardization of K.F. Reagent — Approximately 10.0 to 18.0 mg of water is added to an "end-pointed" solution from a weighed 0.25 ml tuberculin syringe (2-3 drops). The mixture is again brought to the end-point with K.F. reagent and methanol. The water equivalence (N) of the reagent is calculated in terms of mg water/ml reagent.

$$N = \frac{\text{wt water (mg)}}{\text{ml K.F. - methanol (calc. as equiv. ml K.F.)}}$$

Since the K.F. reagent is not entirely stable on storage, it must be standardized before use at least once each day.

Determination of Water in Samples — A weighed sample of the material under investigation is added to an "end-pointed" solution and titrated with K.F. reagent and methanol as described. The water content is calculated on a wt % basis as follows:

$$\text{wt \% water} = \frac{N[\text{ml K.F. - methanol (calc. as equiv. ml K.F.)}]}{\text{wt sample} \times 10}$$

The size of the sample taken is governed by its water content. Since most hydrocarbons contain very little water, a sample weight of approximately 50.0 gm is generally used. For materials having high water contents, much smaller samples are used.

* * *

APPENDIX II
REMOVAL OF TETRAETHYL LEAD FROM FUELS

Place 250 ml of fuel and 50 ml of concentrated hydrochloric acid in the extraction apparatus (described in the ASTM Standard Method of Test for Tetraethyl Lead in Gasoline, D526-42). Heat this mixture and reflux for 30 minutes. Allow to cool and replace the acid with 50 ml of water. Reflux for 10 min. Allow to cool and repeat the extraction with a fresh 50 ml portion of water. After cooling, transfer the fuel to a separatory funnel and wash with successive portions of water until the washings give a negative test for chloride with silver nitrate solution.

* * *

APPENDIX III
INSPECTION DATA FOR AN-F-58 USED IN THIS STUDY

Gravity, Specific 60/60°F	0.7339
Gravity, °API	61.3
Distillation, IBP °F	101
5% over, °F	126
10% over, °F	142
20% over, °F	169
30% over, °F	212
40% over, °F	260
50% over, °F	269
60% over, °F	276
70% over, °F	285
80% over, °F	302
90% over, °F	384
95% over, °F	469
End Point, °F	495
Recovery, % vol.	98.0
Residue, % vol.	1.0
Distillation Loss, % vol.	1.0
Gum Accelerated, mg/100 ml	2.3
Sulfur, % wt	0.436
Aromatic Content, % vol.	8.5
Heat of Combustion, BTU/lb.	18,865
Viscosity at 100° F, Centistokes	0.68
Viscosity at -40° F, Centistokes	1.91

Fuel obtained from Naval Air Material Center, U. S. Naval Base Station, Philadelphia, Pa., from Phillips Petroleum Co., in November 1948.

* * *

APPENDIX IV
CLOGGING OF MICRONIC FILTERS AT LOW TEMPERATURES

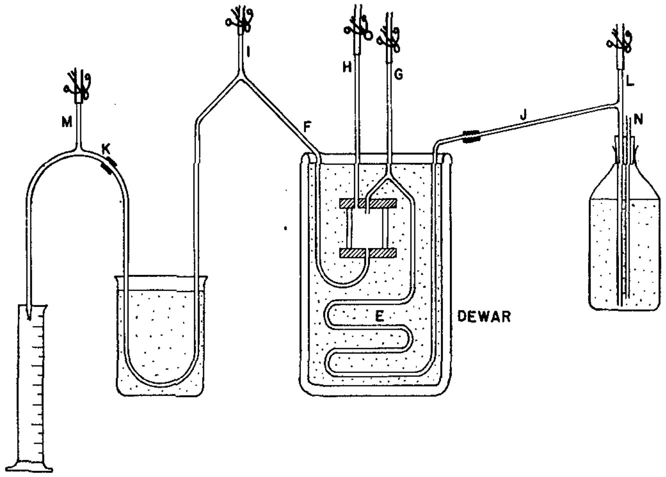

Figure 18 - Filter clogging apparatus

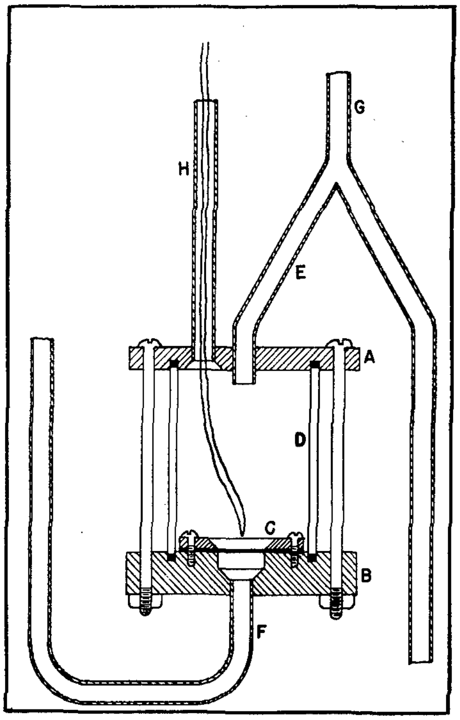

Figure 19 - Detail of filtration cell

APPARATUS

A diagram of the apparatus used is given in Figures 18 and 19. End plates (A) and (B) are made of brass and carry both the inlet and outlet tubes (E and F) which are of 1/4 in. o-d copper tubing. Thrust plate (C) has a center hole having an area of 1.0 cm^2. This hole matches a like one in the bottom end plate (B). Test sections of the filter paper are held in place by the thrust plate which is fastened to the bottom end plate by 4 No. 6 brass screws. The filtration cell is completed by the sight glass (D) which is of Pyrex tubing 2 in. long x 40 mm o.d. The ends are cut square and fire polished. The cell is held together by 4 No. 8 brass bolts. Rubber gaskets are used between the end plates and the sight glass to effect a tight seal. Inlet tube (E) carries a vertical section (G) which acts as a bubble trap. The inlet tube is joined to the fuel reservoir tube (J) by a short length of rubber tubing. In addition to the inlet tube, the top plate carries another vertical section of copper tubing (H) which serves to act as a bubble trap and also as the entrance for the thermocouple. Outlet tube (F) also carries a vertical bubble trap (I) and is connected to the efflux tip (K) by a short piece of rubber tubing. The fuel reservoir tube (J) and efflux tip (K) are both made of glass and carry bubble traps (L and M). A constant fuel head from the reservoir is assured by means of air inlet tube (N). Bubble traps (L, G, H, I and M) all carry short lengths of rubber tubing which are closed by pinch clamps. The pressure drop across the filter is governed by the vertical distance between the bottom of air inlet tube (N) and the efflux tip (K).

PROCEDURE

A test section of filter paper is fitted into place and the apparatus is assembled. The vertical distance between the bottom of air inlet tube (N) and the efflux tip (K) is adjusted, with the aid of a cathetometer, to the desired fuel head. A short length of rubber tubing closed by a pinch clamp is attached to the efflux tip and the system is filled with the fuel. All bubbles in the lines and under the paper are worked out by manipulating the fuel reservoir and also by "squeezing" the rubber tube attached to the efflux tip (K). The Dewar flask containing acetone cooled with dry ice is then placed around the filtration cell and cooling spiral. After standing for 15 minutes at the desired temperature, the rubber tube is removed from the efflux tip. The flow is received in a graduated cylinder and rates are determined by timing measured increments. For experiments in which the pressure drop across the filter is increased during a run, a controlled compressed air supply of the desired pressure is attached to air inlet tube (N) of the fuel reservoir.

* * *

APPENDIX V
TABLES OF EXPERIMENTAL DATA

TABLE 9
Effect of Temperature and Type of Paper on Filter Clogging

Temp. (°F)	10 Micron (Skinner)		25 Micron (Purolator)		10 Micron (Purolator)	
	Porosity*	10x Pt.	Porosity*	10x Pt.	Porosity*	10x Pt.
20	0.37	410	0.37	1360		
	0.35	420	0.40	1160		
	0.35	450				
		Av. 427 ± 16		Av. 1260 ± 100		
10	0.35	310	0.35	870		
	0.37	240	0.38	850		
	0.38	240				
	0.42	180				
		Av. 243 ± 34		Av. 860 ± 10		
0	0.37	260	0.37	760	0.35	250
	0.38	260	0.38	640	0.37	240
	0.40	220			0.33	250
	0.38	210				
	0.37	200				
	0.40	220				
	0.40	230				
		Av. 229 ± 18		Av. 700 ± 60		Av. 247 ± 4
-10	0.42	30	0.39	170		
	0.44	60	0.40	260		
	0.38	30	0.40	290		
	0.38	20				
		Av. 35 ± 13		Av. 240 ± 47		
-20	0.41	40	0.38	80		
	0.38	25	0.37	60		
	0.38	30				
	0.43	30				
		Av. 31 ± 4		Av. 70 ± 10		
-40	0.45	360	0.41	180		
	0.37	240	0.37	140		
	0.40	230				
	0.35	450				
	0.38	480				
	0.35	360				
		Av. 353 ± 79		Av. 160 ± 20		
-60	0.35	400	0.39	230		
	0.39	310	0.40	340		
	0.39	260	0.39	210		
	0.40	410				
		Av. 345 ± 60		Av. 260 ± 53		

* Porosity is minutes required to pass 10 ml of fuel at room temperature for a pressure drop across the paper of 1.0 oz/in.^{2} for the 10 micron papers and 0.73 oz/in.^{2} for the 25 micron papers.

TABLE 10
Effect of Water Content of Fuel on Filter Clogging

Water Content (wt %)	Porosity*	10x Pt.	Average
0.0050	--	270	
	0.37	240	
	0.38	240	250 ± 13
0.0056	0.37	260	
	0.38	260	
	0.40	220	
	0.38	210	
	0.37	200	
	0.40	220	
	0.40	230	229 ± 18
0.0074	0.34	190	
	0.39	160	
	0.40	170	173 ± 11
0.0093	0.39	65	
	0.39	65	
	0.38	75	68 ± 4

* Porosity is minutes required to pass 10 ml of fuel at room temperature for a pressure drop across the paper of 1.0 oz/in.^{2}

TABLE 11
Typical Flow Rates Through Clogged Filters on Warming

AN-F-58		n-Octane		Toluene	
Temp. (°F)	Rate (ml/min)	Temp. (°F)	Rate (ml/min)	Temp. (°F)	Rate (ml/min)
-35	1.0	-34	0.9	-36	0.4
-26	0.9	-23	0.6	-29	0.5
-20	0.8	-12	0.6	-15	0.4
- 8	0.8	- 4	0.7	0	0.5
- 1	0.8	+ 2	0.8	+10	0.6
+12	1.2	10	0.95	17	0.8
16	1.4	14	1.1	23	1.1
19	1.6	17	1.2	25	1.2
22	1.8	21	1.4	27	1.4
28	2.4	26	1.8	29	1.7
30	2.9	31	2.4	30	1.8
31	6.3	32	7.2	31	1.9
31.6	9.1	33	7.7	32	6.7
32	14.7	34	7.7	36	6.7
32.4	14.7				
36	15.2				
41	15.6				
53	16.7				

TABLE 12
Complete Miscibility Limits for Methyl Alcohol in AN-F-58

MeOH with 0.04% H_2O		MeOH with 1.0% H_2O	
Vol. %	Temp. (°F)	Vol. %	Temp. (°F)
0.0	42*	0.0	42*
0.3	30	0.1	>100
0.5	10	27.9	>100
0.8	3		
1.3	14		
2.0	36		
2.6	50		
3.8	66		
5.1	79		
7.4	90		
9.6	100		
11.8	106		
13.8	110		
15.7	113		
17.6	116		
21.9	118		
28.6	120		
40.0	125		

*Initial phase separation

TABLE 13
Lowest Temperature for Complete Miscibility of Ethyl Alcohol in AN-F-58

Vol. Alcohol Added (%)	Water Content of Alcohol				
	1.0%	2.0%	3.0%	4.0%	5.0%
0.0	42°F*	42°F*	42°F*	42°F*	42°F*
0.1	52	55	61	80	>110
0.3	54	63	71	99	
0.4	45	70	77	>110	
0.5	37	75	80		
0.8	15	77	86		
1.1	0	73	89		
1.3	-10	68	91		
2.0	-15	56	86		
2.6	-20	48	84		
3.8	-24	40	81		
6.2	-26	39	74		
8.5	-26	39	70		
11.8	-24	38	66	96	
16.7	-25	32	59	86	
21.1	-28	26	54	81	106
25.0	-30	21	50	75	99
28.6	-32	17	46	70	95

*Initial phase separation

TABLE 14
Lowest Temperature for Complete Miscibility of
Isopropyl Alcohol in AN-F-58

Vol. Alcohol Added (%)	Water Content of Alcohol			
	1.0%	3.0%	5.0%	10.0%
0.0	42°F*	42°F*	42°F*	42°F*
0.1	52	70	>104	>106
0.3	55	81		
0.4	57	86		
0.5	55	90		
0.8	41	93		
1.1	27	95		
1.3	0	96		
2.0	-33	93		
2.6	-54	93		
3.8	-60	77		
6.2	-67 (wax)	19		
8.5		-26		
10.7		-45		
12.8		-58	>110	
14.8			70	
15.7		-65	41	
16.7		-67 (wax)	23	
17.6			12	
19.4			0	
21.9			-15	
24.2			-26	
26.5			-32	>106

*Initial phase separation

TABLE 15
Lowest Temperature for Complete Miscibility of Ethyl Alcohol in AN-F-48 (91/98 Octane)

Vol. Alcohol Added (%)	Water Content of Alcohol				
	1.0%	2.0%	3.0%	4.0%	5.0%
0.0	48°F*	48°F*	48°F*	48°F*	48°F*
0.1	54	60	61		85
0.2	57	66	73		94
0.3	56	69	81		103
0.5	45	73	93		
0.7	30	73	93		
1.0	10	66	90		
1.5	- 4	59			
2.0	-22	52	86		
2.9	-40	32	84		
3.8	-58	15	72		
4.8	-62	5	61		
6.5	-65	- 2	47		
7.4				95	
9.1	-67	- 7	39		
10.7				68	104
13.0	-72	-16	27		
13.8				55	90
16.7		-25	16	48	79
21.8	-83	-36	6	36	65
25.9	-88	-42	0	29	57

*Initial phase separation

TABLE 16
Melting Point of Solid Phase From AN-F-58 Alcohol Mixtures

Vol. (%)	i-PrOH Containing 1% H_2O	i-PrOH Containing 3% H_2O	EtOH Containing 3% H_2O
0.0	32°F*	32°F*	32°F*
0.1	27		-13
0.3		25	no ice
0.5		23	
0.7	19		
0.8		21	
1.3	16	18	
2.0	10		
2.6	7		
3.8	3	14	
6.2	-11		
8.5		1	
12.8		-11	
15.7		-14	
20.2		ca. -30	

*Initial phase melting point

NAVY-DPPO PRNC. WASH., D.C.

UNITED STATES GOVERNMENT

memorandum

6180-550:HWC:mls

DATE: 21 August 1991

REPLY TO ATTN OF: Code 6180

SUBJECT: CLASSIFICATION OF NRL REPORT 3604

TO: Code 4827.1 (Mary Templeman)

Ref: (a) Telcon, Mary Templeman and H. Carhart, 19 August 1991

1. As a follow-up to reference (a), I see no reason why NRL Report 3604 "The Behavior of Water in Jet Fuels and the Clogging of Micronic Filters at Low Temperatures" dated January 11, 1950, should not be Unclassified - Unlimited Distribution.

Homer W. Carhart

HOMER W. CARHART, Director
Navy Technology Center for
Safety and Survivability
Code 6180

Completed 1-11-00 ac

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