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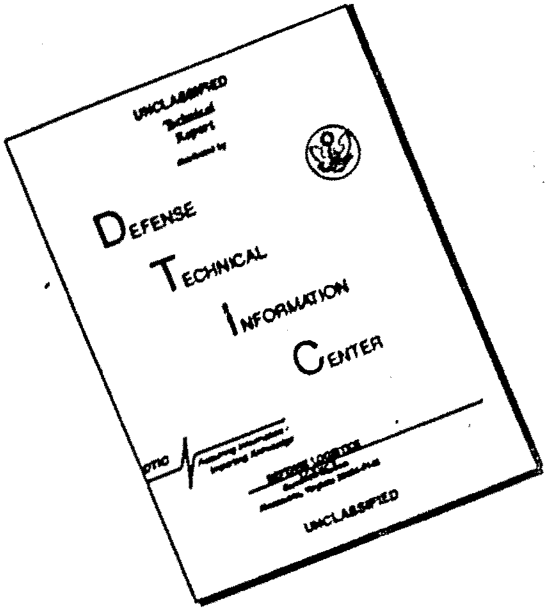

WADD TECHNICAL REPORT 61-40

INVESTIGATION OF WATER-REACTIVE CHEMICALS FOR ANTI-ICING ADDITIVES IN AVIATION FUELS

CONTRACT NR AF 33(616)-7006

MARCH, 1961

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MATERIALS CENTRAL
WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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INVESTIGATION OF WATER-REACTIVE CHEMICALS FOR ANTI-ICING ADDITIVES IN AVIATION FUELS

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Materials Central

Contract Nr AF 33(616)-7006
Project Nr 3048
Task Nr 30178

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

FOREWORD

This report was prepared by Arthur D. Little, Inc., Cambridge, Massachusetts, on Air Force Contract AF 33(616)-7006, under Task Nr 30178 of Project Nr 3048--Investigation of Water-Reactive Chemicals for Anti-Icing Additives in Aviation Fuels. The work was administered under the direction of Materials Central, Wright Air Development Division. Lt. John A. Hager was the Project Engineer for WADD. This work began in February, 1960 and was concluded in December, 1960.

Many of the compounds tested were not developed or intended by the manufacturer for the conditions to which they have been subjected. Any failure or poor performance of a material is therefore not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

ABSTRACT

A study has been made of water-reactive chemicals for use as anti-icing additives in aviation fuels. Four compounds have been found effective in preventing filter icing when fuel temperatures are reduced to -65°F, including 2,2-dimethoxypropane, trimethyl orthoformate, trimethyl orthoacetate, and trimethyl orthovalerate. Additive concentrations as low as 0.1% are sufficient to prevent icing when 500 mg/l of water is present in the fuel.

Each of the possible additives requires acid catalysis to initiate reaction with water. Several acid systems have been found effective including hydrogen chloride, phosphoric acid, and boron trifluoride. Acid concentrations in the range of 0.015 to 0.040 milliequivalents per ml of additive are sufficient.

Acid concentrations in the fuel are so low that corrosion effects are minimized. If necessary, however, certain corrosion inhibitors approved for use in military aviation fuels may be incorporated in the additive-catalyst system. Compatibility of the additive system with the topcoating material used on integral fuel tanks of certain aircraft appears to be satisfactory.

The reactive additive systems are soluble in the fuel and will react with any water or ice present to form soluble and combustible reaction products. Thus water in the fuel system is chemically destroyed and removed from the aircraft.

We recommend that the Air Force give serious consideration to utilization of a chemically reactive anti-icing additive for aviation fuels.

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I. INTRODUCTION

In recent years, as long-range jet aircraft have come to assume a major role in Air Force operations, numerous problems associated with fuel contamination have arisen. Perhaps the most serious situation concerns the presence of water in the fuel and in the aircraft fuel system. During extended flights at high altitudes, fuel temperatures may fall to very low levels, causing any water present to freeze. The ice thus formed may clog fuel filters and strainers or may lodge in fuel controls, resulting in engine malfunction or flameout. The crash of at least one B-52 has been definitely attributed to fuel starvation as a result of icing. Numerous other incidents, where icing was suspected, have also been recorded.

A number of possibilities exist for eliminating the hazards associated with airborne water. Perhaps the first prerequisite is to improve ground fuel-handling procedures. Some progress has already been made in that fuel cleanliness is now being routinely monitored at all SAC bases. The development of improved filter/separation equipment, together with instrumentation for monitoring fuel cleanliness, would insure that all fuel serviced to an aircraft contains neither particulates nor free water.

Even complete elimination of free water from aircraft fuels will not solve the icing problem, however, in that up to 150 ppm of water may be dissolved in the fuel. Since solubility decreases with decreasing temperature, a dispersion of free water may form as the fuel cools. Such a situation can lead directly to icing at critical areas within the fuel system.

Dissolved water may be eliminated from hydrocarbons by a number of fairly straightforward techniques, including desiccant adsorption, distillation, or dry gas stripping. Each of these methods requires considerable investment in capital equipment, however, and increases maintenance and operational costs. Moreover, icing might still occur as a result of water accumulating in the aircraft tanks due to condensation and breathing.

During the past two years the Air Force has encouraged industry to submit for evaluation any materials which might be added to fuels to control or eliminate icing. The obvious advantage of such a system is that it would be necessary to meter only a small quantity of the additive into the fuel to provide trouble-free operation.

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A large number of candidate materials have been screened by the Air Force. While many materials are effective anti-freeze agents, most of them have been eliminated because of their incompatibility with fuel system components. However, at the present time one effective candidate looks very promising and is being flight tested in a SAC wing at WPAFB. This material is identified as Phillips 55MB and is supplied by the Phillips Petroleum Co. A concentration of approximately 0.1% has been found effective in preventing icing.

Almost all of the candidate additives screened by the Air Force function by physical means. That is, their anti-icing action occurs as a result of freeze-point depression, dispersant characteristics, or other surface phenomena. Thus the physical form of the water may be modified, but in general no means is provided for removing the water.

This report concerns an alternate additive mechanism for controlling fuel icing. We propose to inject a chemical compound which will react with any water present, thus eliminating the possibility of ice formation. The ideal additive of this type would:

1. be soluble in the fuel;
2. react rapidly with water in fuel (either free or dissolved);
3. react over a wide temperature range;
4. yield soluble and combustible reaction products;
5. be noncorrosive and compatible with all fuel system components both before and after reaction.

Such an ideal additive would have certain advantages over the physically-acting type, including:

1. water in fuel would be destroyed and removed from the system;
2. pockets of free water in the system would be consumed;
3. even bulk ice would be destroyed and removed.

We feel that we have nearly reached the objectives of this contract. It now appears that a chemically reactive additive for removal of water and ice from fuel is completely feasible. In this report we present the results of our research and an analysis of requirements for additive utilization in Air Force facilities. We recommend that the Air Force give serious consideration to this method of control.

II. DISCUSSION

A. THEORY OF WATER REACTIVITY

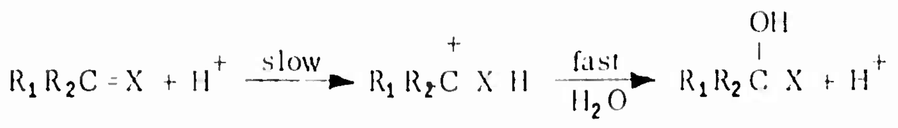
Water always behaves as a weak nucleophile in reactions with organic compounds. Since most of the water-reactive chemicals with which we are concerned are either partially or entirely organic, the theory of their reactivity stems from the physical organic realm of nucleophilic reactions.

Nucleophilic reactions are highly dependent upon a number of factors. In an investigation of water-reactive chemicals some of these factors are clearly defined whereas the others must be altered to obtain optimum water reactivity. Those factors which are clearly defined by the nature of the investigation are the nucleophile (water) and the solvent system (JP-4). Implicitly and less rigidly defined are the reaction rate (complete reaction within several hours), the reaction temperature (32°-80°F), and the physical and chemical properties of the organic reactants and products. In the initial investigations the problems of solid reactants and products, as well as corrosion and elastomer compatibility, were not a major concern. Those factors which were altered to optimize the reactivity of the water reactant were the site of nucleophilic attack, steric properties of the molecule, and the acidic properties of the medium.

Nucleophilic attack on a molecule is known to proceed by several mechanisms, and often the attack is not by one discrete mechanism but by a combination of two or more. The bulk of the reactants studied in this investigation fit into three mechanistic categories: (1) nucleophilic attack of a carbonium ion; (2) nucleophilic attack on a carbonyl carbon atom; (3) nucleophilic attack on tetrahedral carbon and silicon atoms, and organometallic compounds. The operation of the above mechanisms is dependent in varying degrees upon the fixed and variable factors that were previously mentioned. It is now possible to discuss all the reactions with water that were investigated in terms of the above mechanisms and the effects of the fixed and variable factors in the operation of the mechanism.

1. Nucleophilic Attack on a Carbonium Ion

The carbonium ion approach was attempted because of the well-known reactivity of carbonium ions for all nucleophiles irrespective of their nucleophilicity. It was thought that the low nucleophilicity of water would be overshadowed by the high reactivity of the carbonium ion. The formation of a carbonium ion in a solvent of low dielectric constant, such as JP-4, is the major drawback to this mechanistic approach and is probably responsible for the low water reactivity of the compounds that are postulated to react by this mechanism. The mechanism may be generalized by the following equation.

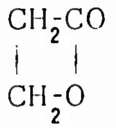


$$R_1R_2C=X + H^+ \xrightarrow{slow} R_1R_2\overset{+}{C}XH \xrightarrow[H_2O]{fast} R_1R_2\overset{OH}{\overset{|}{C}}X + H^+$$

where R_1 and R_2 may be aryl, alkyl, or hydrogen substituents and =X represents unsaturation susceptible to proton addition. It should be observed that the proton employed to generate the carbonium ion is subsequently reformed on a later step and is, therefore, an acidic catalyst. The reactions that were investigated are as follows:

$$n\text{-}CH_3(CH_2)_3\text{-}OCH=CH_2 + H_2O \xrightarrow{H^+} n\text{-}CH_3(CH_2)_3OH + CH_3CHO$$

n-butyl vinyl ether — n-butyl alcohol — acetaldehyde



$$\begin{matrix} CH_2\text{-}CO \\ | \quad\;\; | \\ CH_2\text{-}O \end{matrix} + H_2O \xrightarrow{H^+} HOCH_2CH_2COOH$$

2-propiolactone — 2-hydroxy propionic acid

$$(CH_3CO)_2O + H_2O \xrightarrow{H^+} 2CH_3COOH$$

acetic anhydride — acetic acid

$$C_6H_{11}NCNC_6H_{11} + H_2O \xrightarrow{H^+} C_6H_{11}NHCONHC_6H_{11}$$

dicyclohexyl carbodiimide — N, N'dicyclohexyl urea

2. Nucleophilic Attack on Carbonyl Group

The carbonyl group is made susceptible to nucleophilic attack at the carbon by virtue of the resonance hybrid which places a partial positive charge on the carbon and a partial negative charge on the oxygen. If a leaving group is bonded to the carbonyl carbon atom, nucleophilic attack by water in a non-polar medium will result in a concerted displacement of the leaving group. It should be noted that such a concerted displacement does not require charge separation in the transition state and is, therefore, favorable in JP-4 medium of low dielectric constant. The trigonal bonding of the carbonyl group greatly diminishes the steric effects observed in nucleophilic attack on tetrahedral carbon atoms and, thus, enhances the reactivity. The hydrolysis of acyl and aryl halides are typical examples of this type of reaction. Although thionyl chloride does not contain a carbonyl group, the sulfone group, substituted with two chloride leaving groups, behaves analogously in its hydrolysis and is included in this mechanistic group. The specific reactions that were investigated are:

$$CH_3COX \quad + \quad H_2O \quad \longrightarrow \quad CH_3COOH \; + \; HX$$

Acetyl chloride (X=Cl) — Acetic acid

Acetyl bromide (X=Br)

$$C_6H_5COCl \quad + \quad H_2O \quad \longrightarrow \quad C_6H_5COOH \; + \; HCl$$

Benzoyl chloride — Benzoic acid

$$C_{10}H_7COCl \quad + \quad H_2O \quad \longrightarrow \quad C_{10}H_7COOH \; + \; HCl$$

1-Naphthoyl chloride — 1-Naphthoic acid

$$ClSOCl \quad + \quad H_2O \quad \longrightarrow \quad SO_2 \; + \; 2HCl$$

Thionyl chloride — Sulfur dioxide

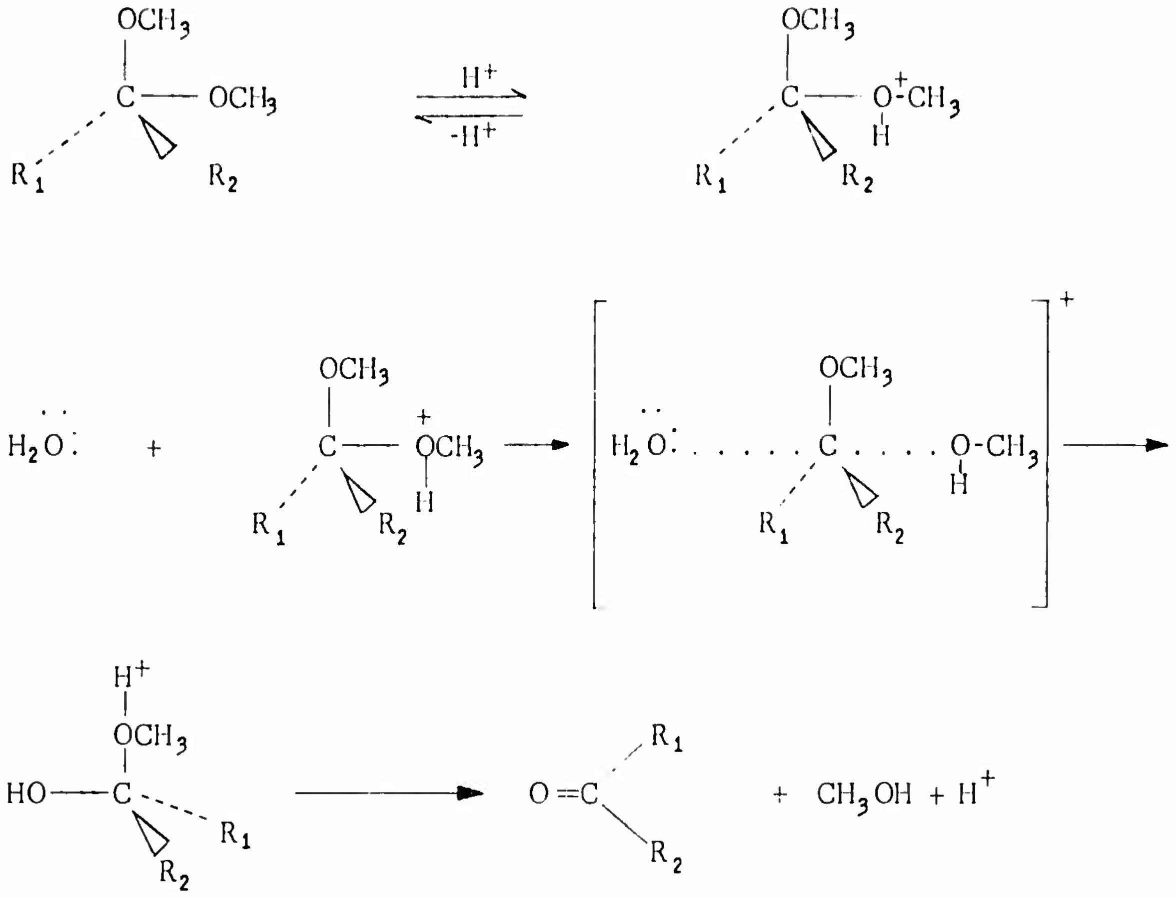
Nucleophilic attack on carbonyl carbons that are not bonded to a leaving group results in the formation of a charged intermediate. Since the formation of a charged intermediate in JP-4 is very unfavorable, the reactivity of these compounds would be greatly diminished in comparison to the above carbonyl reactions. Indeed, in the following examples reaction did not readily take place in JP-4.

C_6H_5NCO phenyl-isocyanate	$\xrightarrow{H_2O}$	$C_6H_5NHCOOH$ phenyl carbamic acid	$\xrightarrow[C_6H_5NCO]{-CO_2}$	$[(C_6H_5)NH]_2CO$ N, N'diphenyl urea
$N\text{-}C_4H_9NCO$ n-butyl isocyanate	$\xrightarrow{H_2O}$	$n\text{-}C_4H_9NHCOOH$ n-butyl carbamic acid	$\xrightarrow[n\text{-}C_4H_9NCO]{-CO_2}$	$[(n\text{-}C_4H_9)NH]_2CO$ N, N'-di-n-butyl urea
$p\text{-}NO_2C_6H_4NCO$ p-nitrophenyl isocyanate	$\xrightarrow{H_2O}$	$pNO_2C_6H_4NHCOOH$ p-nitrophenyl carbamic acid	$\xrightarrow[pNO_2C_6H_4NCO]{-CO_2}$	$[(pNO_2C_6H_4)NH]_2CO$ N, N'di-p-nitro phenyl urea
$1\text{-}C_{10}H_7NCO$ 1-naphthyl isocyanate	$\xrightarrow{H_2O}$	$1\text{-}C_{10}H_7NHCOOH$ 1-naphthyl carbamic acid	$\xrightarrow[1\text{-}C_{10}H_7NCO]{-CO_2}$	$[(1\text{-}C_{10}H_7)NH]_2CO$ N, N'dinaphthyl urea
$H_2C{=}C{=}O$ ketene	$\xrightarrow{H_2O}$	CH_3COOH acetic acid		

3. Nucleophilic Attack on Tetrahedral Carbon and Silicon Atoms, and Organometallic Compounds

The mechanism of nucleophilic attack of water on a tetrahedral carbon atom with displacement of a leaving group is usually concerted. Since any charge formation in the transition state is distributed throughout the activated complex, this reaction is favored in JP-4. The reaction rate is highly dependent upon steric and electronic effects resulting from substituents. The nature of the leaving group also plays a significant role in the substitution reaction.

Previously all reported mechanisms for acetal, ketal, and orthoester hydrolysis involved a carbonium ion intermediate. The difference between the hydrolysis in aqueous medium and that in JP-4 is significant, however, and a different mechanism is probably in effect for each medium. The most reasonable mechanism for acetal, ketal, and orthoester hydrolysis in JP-4 containing trace amounts of mineral acid is the following:



The fact that most of the methyl acetals (R_1 = alkyl; R_2 = H) show little reactivity, while methyl ketals (R_1 = R_2 = CH_3) and methyl orthoesters (R_1 = alkyl; R_2 = OCH_3) are very reactive, indicates that the steric effects of alkyl and methoxyl groups are offset by their electronic effects. The inductive and resonance effects resulting from alkyl and methoxyl substituents increase the electron density around the central carbon atom and thus facilitate bond-breaking in the transition state. The only acetal in this investigation, 1,3,3-trimethoxypropene, that hydrolyzes rapidly is in essence a "vinylogous orthoester," since the electronic effects of the 1-methoxyl group are transmitted via the olefinic double bond to the site of nucleophilic attack. The decrease in reactivity of ethyl ketals and orthoesters from that of methyl ketals and orthoesters is probably a result of steric blocking of the reaction site.

As might be expected, the function of the acid in the above mechanism is different from its function in the hydrolysis of the same compounds in aqueous media. The function of the acid catalyst in aqueous media, as in the discussion of the first mechanistic group, is to generate a carbonium ion. In the above mechanism, the proton forms an oxonium ion, which unlike the methoxyl, is an excellent leaving group. The formation of the oxonium ion helps to explain why only specific acid catalysis was observed in the following orthoester hydrolysis, whereas general acid catalysis was reported for the same reaction in aqueous medium.

a. Acetals

$RCH(OR')_2 + H_2O$	$\xrightarrow{H^+}$	$RCHO$ +	$2R'OH$
Dimethoxymethane $(R=H, R'=CH_3)$		Formaldehyde	Methanol
1, 1-Dimethoxyethane $(R=R'=CH_3)$		Acetaldehyde	Methanol
1, 1-Diethoxyethane $(R=CH_3\ R'=C_2H_5)$		Acetaldehyde	Ethanol
$CH_3OCH = CHCH(OCH_3)_2 + H_2O$	$\xrightarrow{H^+}$	$CH_3OCH = CHCHO$ +	$2CH_3OH$
1, 3, 3-Trimethoxypropene		β-methoxy acrolein	Methanol
$CH(OR)_2CH_2CH(OR)_2 + 2H_2O$	$\xrightarrow{H^+}$	$HCOCH_2CHO$ +	$4ROH$
1, 1, 3, 3-Tetraethoxypropane $(R=C_2H_5)$		Malonaldehyde	Ethanol
1, 1, 3, 3-Tetramethoxypropane $(R=CH_3)$		Malonaldehyde	Methanol
$ClCH_2CH(OC_2H_5) + H_2O$	$\xrightarrow{H^+}$	$ClCH_2CHO$ +	$2C_2H_5OH$
1, 1-Diethoxy-2-chloroethane		Chloroacetaldehyde	Ethanol

b. Ketals

$(CH_3)_2C(OR)_2 + H_2O$	$\xrightarrow{H^+}$	CH_3COCH_3 +	$2ROH$
2, 2-Dimethoxypropane $(R=CH_3)$		Acetone	Methanol
2, 2-Diethoxypropane $(R=C_2H_5)$			Ethanol
2, 2-Diisopropoxypropane $(R=CH(CH_3)_2)$			Isopropanol
2, 2-Dibenzyloxypropane $(R=CH_2C_6H_5)$			Benzylalcohol

c. Orthoesters

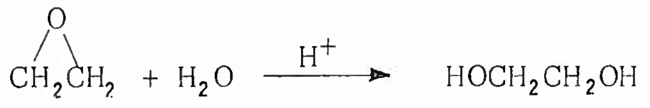
$$RC(OCH_3)_3 + H_2O \xrightarrow{H^+} RCOOCH_3 + 2CH_3OH$$

Tetramethyl orthocarbonate ($R=OCH_3$)	Dimethylcarbonate	Methanol
Trimethyl orthoformate ($R=H$)	Methyl formate	Methanol
Trimethyl orthoacetate ($R=CH_3$)	Methyl acetate	Methanol
Trimethyl orthovalerate ($R=C_4H_9$)	Methyl valerate	Methanol

$$RC(OC_2H_5)_3 + H_2O \xrightarrow{H^+} RCOOC_2H_5 + 2C_2H_5OH$$

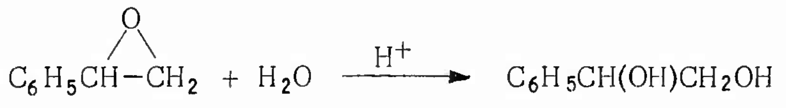
Tetraethyl orthocarbonate ($R=OC_2H_5$)	Diethyl carbonate	Ethanol
Triethyl orthoformate ($R=H$)	Ethyl formate	Ethanol
Triethyl orthoacetate ($R=CH_3$)	Ethyl acetate	Ethanol
Triethyl orthopropionate ($R=C_2H_5$)	Ethyl propionate	Ethanol

The hydrolysis of epoxides in nonpolar medium in the presence of a proton source is known to occur by nucleophilic attack on the tetrahedral carbon with concerted ring opening. The oxygen function leaves the reaction site as an oxonium ion. The mechanism is in effect an ether hydrolysis facilitated by angle strain in the three membered ring. The electronic effects that contribute in the hydrolysis of ketals and orthoesters but are absent in acetals, are also absent in the epoxides and are probably responsible for the diminished reactivity observed with ethylene and styrene oxides.



$$CH_2CH_2O + H_2O \xrightarrow{H^+} HOCH_2CH_2OH$$

Ethylene oxide — Ethylene glycol



$$C_6H_5CH{-}CH_2O + H_2O \xrightarrow{H^+} C_6H_5CH(OH)CH_2OH$$

Styrene oxide — Phenylethylene glycol

It is well known that tetrahedral silanes undergo nucleophilic substitution more readily than tetrahedral carbon atoms since silicon atoms, unlike the carbon atoms, can expand their valence shell to accommodate additional bonding electrons. Instead of forming an activated complex, nucleophilic attack on silicon results in a pentavalent intermediate which rapidly loses a leaving group. As in the case of carbon atoms, the presence of protons in the media accelerates the removal of alkoxyl groups. However, in the case of silicon, the presence of protons is not necessary.

$$2nCH_3Si(OCH_3)_3 + 3nH_2O \longrightarrow \left[(CH_3Si)_2O_3\right]_n + 6nCH_3OH$$

Methyl trimethoxy silane

Cross-linked silicone

$$3(CH_3)_2Si(OCH_3)_2 + 3H_2O \longrightarrow \left[(CH_3)_2SiO\right]_3 + 6CH_3OH$$

Dimethyl dimethoxy silane

Cyclic silicone

Nucleophilic attack on metal atoms is dependent on the particular metal. The mechanism can take a variety of forms that vary from direct displacement to the formation of an expanded shell intermediate. Since few mechanistic studies have been made in this area, we shall refrain from speculation about them and simply list those reactions investigated under this program.

$$n\text{-}CH_3(CH_2)_3Li + H_2O \longrightarrow CH_3(CH_2)_2CH_3 + LiOH$$

n-Butyl lithium

n-Butane

$$Ti\left[OCH(CH_3)_2\right]_4 + 2H_2O \longrightarrow 4(CH_3)_2CHOH + TiO_2$$

Tetraisopropyl titanate

Isopropyl alcohol

$$Al\left[OCH(CH_3)_2\right]_3 + 3H_2O \longrightarrow 3(CH_3)_2CHOH + Al(OH)_3$$

Aluminum isopropoxide

Isopropyl alcohol

$$Al(OC_2H_5)_3 + 3H_2O \longrightarrow 3C_2H_5OH + Al(OH)_3$$

Aluminum ethoxide

Ethyl alcohol

B. EVALUATION TECHNIQUES

1. Water Analysis

a. Cloud Point

The cloud point or temperature at which a cloud of moisture appears (or disappears) provides a convenient method for rapidly screening some water-reactive materials. The method is most sensitive in the temperature range 20° to -20°C. At lower temperatures vapor formation on the outside of the test tube and in the air immediately surrounding the test tube masks the cloud point. It has been found that the optical properties of some of the scavengers decrease the sensitivity of this method. Our procedure is outlined below.

Test tubes (25 x 200 mm) are dried at 125 - 135°C in an oven for one hour and allowed to cool in a desiccator over anhydrous calcium chloride. To the test tube is added 50 ml of saturated JP-4 fuel and 0.05 ml of liquid scavenger (or 50 mg of solid scavenger). The tube is sealed with a stopper containing a -50° to 50°C thermometer and agitated intermittently for five minutes. After checking the tube for colloid or precipitate formation caused by reaction products, the tube is cooled in a 2-propanol dry-ice bath until a cloud is formed. With constant agitation the tube is allowed to warm until the cloud disappears. The point of disappearance, which can be obtained with an accuracy of ± 3.0°C, is recorded as the cloud point. At least two readings are taken on each sample.

The drying of the test tubes is necessary in order to insure reproducibility. If glass surfaces in varying degrees of dryness are used, an interchange of water between the glass and the fuel is likely to occur, causing erroneous results. Even the pre-drying technique can cause difficulty if proper precautions are not taken. We have observed that the cloud point of saturated JP-4 as determined in pre-dried test tubes is about 12°C. This figure is fairly constant for two to four hours after introduction of the sample. If prolonged storage of the sample is necessary, however, the cloud point will be appreciably lowered due to adsorption and penetration of water molecules into the glass structure.

b. Karl Fischer Titration

The most commonly used method for determining water content of hydrocarbons involves titration with Karl Fischer reagent. While the exact nature of the chemical reactions involved in this technique is not well understood, the titration itself is rather straightforward and may be carried out by semiautomatic equipment. The method requires extreme care, however, in the determination of small quantities of water, since large errors may be introduced as a result of atmospheric contamination or adsorption effects. Moreover, since the Karl Fischer reagent is a complex mixture of iodine, sulfur dioxide, and pyridine in methanol, the problem of side reactions with either additives or hydrolysis products makes interpretation of results difficult in many cases.

In our work we have used a Beckman KF-3 Aquameter modified so as to reduce water contamination from external sources. The Aquameter is capable of automatically determining the end point of the titration. Our equipment arrangement, shown diagrammatically in Figure 1, is such that the reaction vessel may be emptied without exposure to the atmosphere by means of the siphon pump shown. The methanol solvent is pre-dried by the Karl Fischer reagent and is introduced through the automatic pipette. Thus, new solvent requires only a minor addition of reagent to reach an end point. The sample to be titrated is normally introduced through the sample port by means of a 30-ml hypodermic syringe. While this does involve slight exposure to the atmosphere, we have found that any errors occasioned by this procedure are negligible. In general, end points have been found very stable, and little difficulty has been encountered with the apparatus or handling techniques. Considerable trouble has been encountered with side reactions, however, so that in some cases erroneous conclusions were tentatively drawn. Because of this difficulty, we have had to rely on alternate methods for final evaluation.

c. Water Analysis by Near Infrared Absorption

We also considered, under this program, an alternate method of water analysis involving extraction of water from the hydrocarbon phase with ethylene glycol and subsequent analysis of the extract by means of near infrared absorption. The absorption spectra over the range 2.1 - 1.8μ is determined on a Beckman DK recording spectrophotometer with ethylene glycol in the reference beam. A tungsten filament light source and a lead sulfide detecting cell are used. Over the range 0 - 100 mg/l of water the difference in absorption at 1.94μ and 1.80μ is a linear function of the water concentration. Thus, the water concentration of the ethylene glycol extract can be obtained by comparing its absorption difference with a calibration curve. The water concentration of the fuel can be calculated from the known ratio of ethylene glycol to hydrocarbon in the extraction and the determined concentration of water in the glycol extract.

Our investigation indicates that this technique affords a satisfactory method for the determination of water in hydrocarbons in concentrations above 10 mg/l. Of five determinations in the range of 0 - 50 mg/l, there was a maximum deviation of 7% from results obtained by Karl Fischer titration.

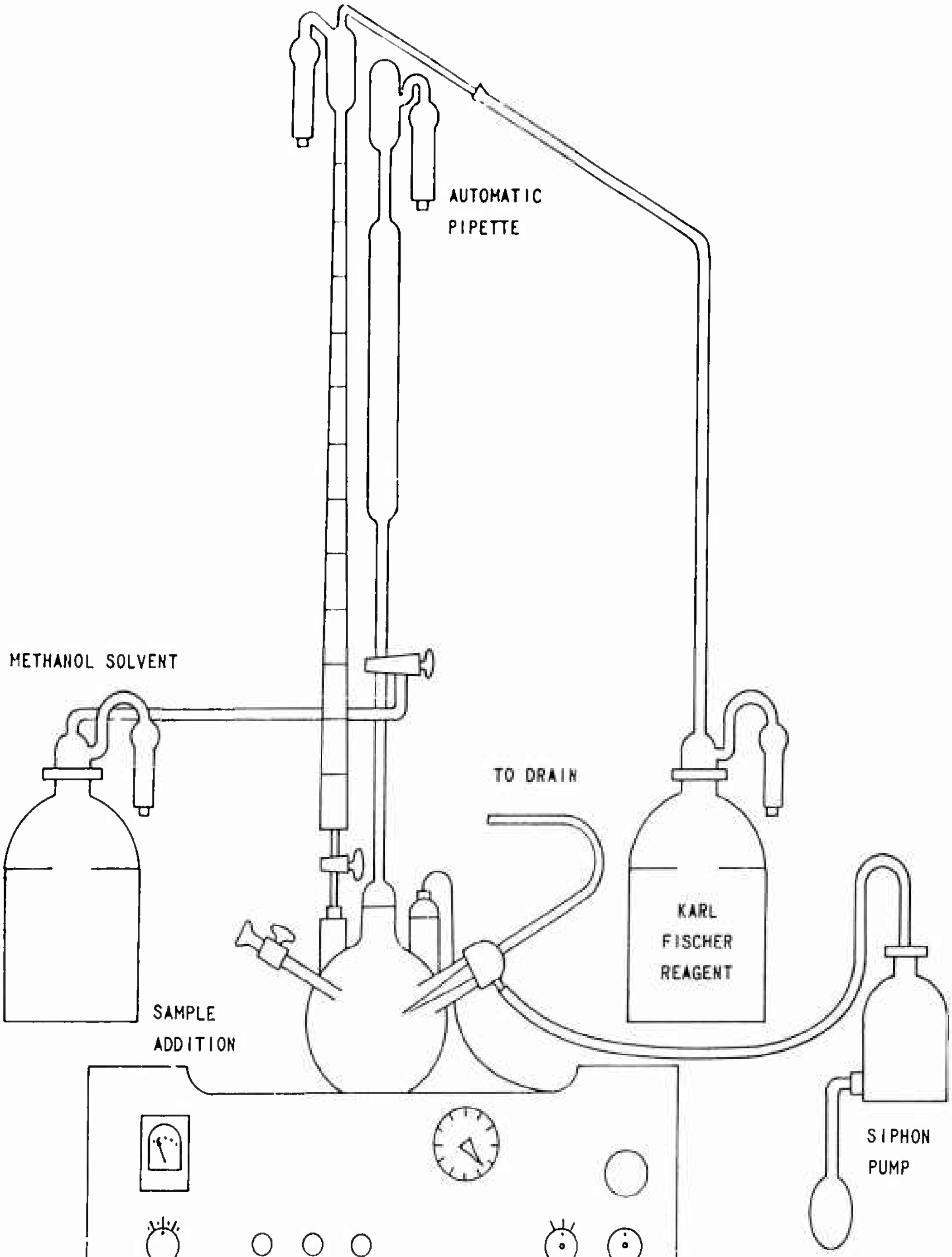


Figure I

MODIFIED BECKMAN KF-3 AQUAMETER FOR KARL FISCHER TITRATION

Although this absorption peak is theoretically specific for water, a case has been reported in the literature of methanol in concentrations exceeding 1% interfering with a water determination. We also observed interference when wet JP-4 containing acetyl chloride, 2, 2-dimethoxypropane or 2, 2-dibenzyloxypropane was analyzed. It thus appears that compounds other than those which react to form methanol may affect the absorption in the near infrared. Since no clear advantage over the Karl Fischer titration was thus observed, no additional effort was devoted to a study of this method.

d. Electrolytic Hygrometer

A method of water analysis based upon electrolytic decomposition of water has recently become available commercially. The system involves removing water from the hydrocarbon by stripping with a dry gas. The moisture thus acquired by the gas is then absorbed by P_2O_5 and electrolytically decomposed in a special cell. The electrolysis current is directly proportional to the original water content of the fuel.

We have evaluated this type of equipment as a means of following the course of a chemical reaction for removal of water. The equipment was made by Manufacturers Engineering & Equipment Corp. (MEECO).

Our experimental arrangement is such that a sample of JP-4 saturated with water is introduced into a plastic bag which feeds directly into the moisture analyzer. An equilibrium reading of the water content of the saturated fuel is first obtained. The desired amount of additive is then injected directly into the bag and mixed without interrupting flow to the analyzer. A measure of reaction rate and degree of completion is thus readily obtained.

Unfortunately, this apparatus is extremely limited in a scavenger evaluation program due to interfering reactions between either the water scavenger or its reaction products and the P_2O_5 cell. The large variety of compounds that cause the interference and the extreme tediousness required to regenerate the P_2O_5 cell after contamination caused us to abandon this method of analysis early in the program.

e. Other

We have considered several additional possible techniques for water analysis, including gas chromatography, the use of isotopic tracers, and a method involving acetyl chloride, but we did not evaluate them under this contract.

2. Low-Temperature Filter Icing Apparatus

Since difficulties were encountered in the various methods for analyzing water in our fuel scavenger systems, we have had to resort to a filter icing test to insure reliable results. Our test procedure involves circulation of fuel containing a total of 500 mg/l of water through a 200-mesh screen. The fuel temperature is continuously reduced until either the screen clogs from ice formation, or a temperature of -65°F is obtained.

A schematic diagram of the test apparatus is presented in Figure 2. The arrangement is such that fuel is pumped from a two-gallon polyethylene reservoir through a 200-mesh stainless steel screen in a Plexiglas filter housing and back to the reservoir. A separate fluid system, employing a variable speed gear pump, takes a portion of the fuel and passes it through coils immersed in a Dewar flask containing dry ice and isopropyl alcohol and returns it to the main fuel sump. Pressure drop across the screen is measured by a mercury manometer equipped with a thermocap relay to terminate fuel flow when the pressure exceeds a preset level. An additional heat exchanger is incorporated in the system to aid in maintaining constant reaction temperature and to speed the warming process after a run. Water content of the fuel can be monitored by means of an electrolytic moisture analyzer. Fuel temperatures throughout the system are determined by thermocouples located as shown.

The procedure for making a run involves the following steps:

a. Clean system thoroughly by flushing with several portions of fresh fuel.

b. Install clean screen in filter holder.

c. Add 2 gallons of fresh fuel to reservoir and circulate at 1 gpm.

d. Establish and maintain desired reaction temperature by means of main cooling system or auxiliary heat exchanger.

e. Inject required amount of free water directly into suction line in main circulating pump. Use a hypodermic syringe and add slowly to insure proper dispersion.

f. Inject additive in same manner.

g. Maintain temperature control while fuel circulates during desired reaction time.

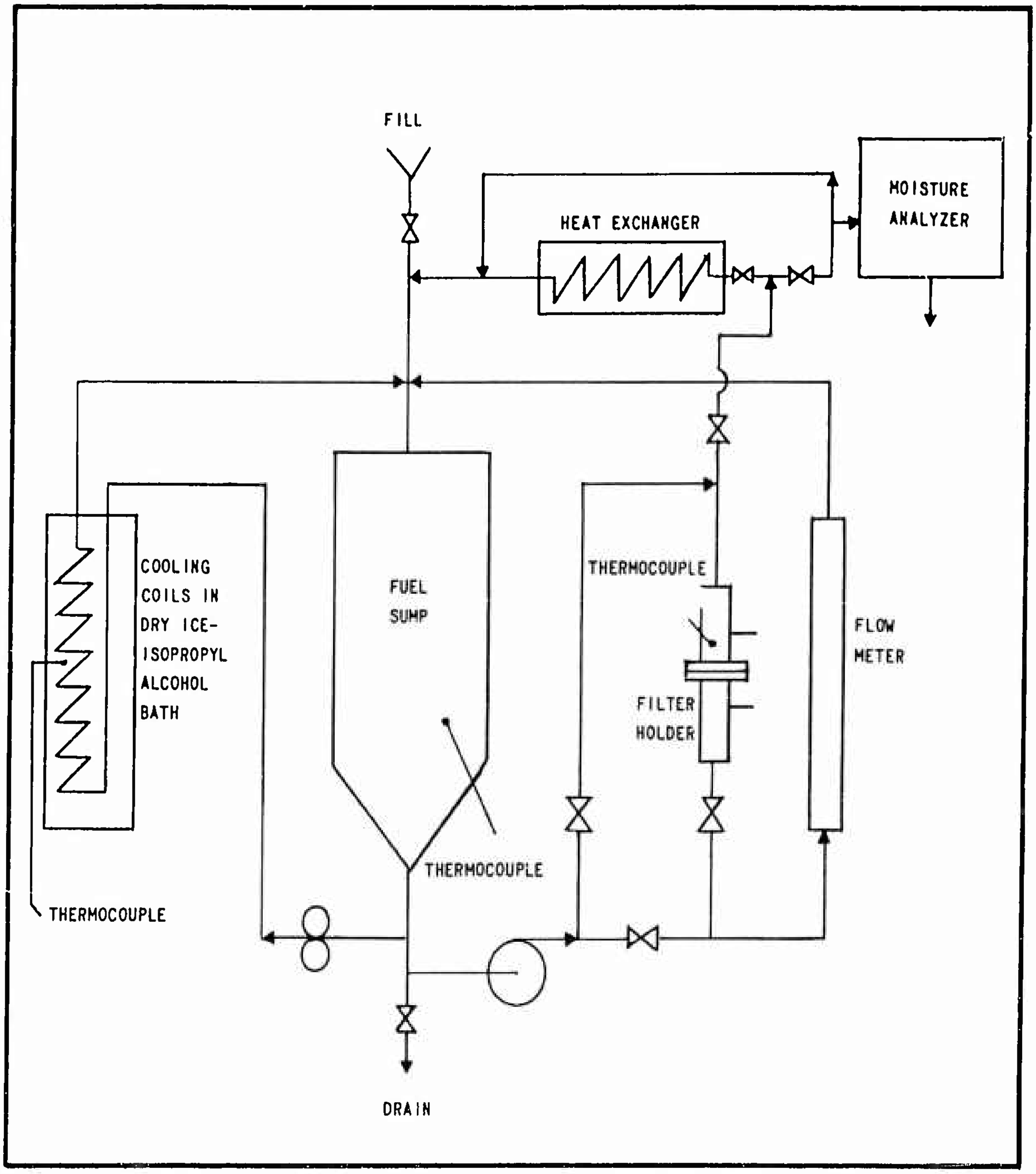


Figure 2

LOW-TEMPERATURE FILTER ICING APPARATUS

h. Start cooling pump after the proper interval. Gradually lower fuel temperature until plugging occurs or until a temperature of -65°F is attained.

i. In the event plugging does occur, raise fuel temperature until the filter clears. This melting point may provide additional information about the extent of reaction.

3. Corrosion

Our procedures for evaluating corrosion of metals generally follow methods used by WADD and Boeing Airplane Company. Since many different combinations of materials have been investigated, the number of test solutions was reduced to two to provide for more rapid screening. In general, we compare the corrosion produced by twice the normal use concentration of additive in fuel with that produced by fuel alone. In one test we use saturated fuel; and in the other, saturated fuel with 10% free water present in the vessel.

The general procedure for corrosion testing is presented below.

a. Three component couple specimens are made up of 1" x 4" strips of electrolytic copper, cadmium-plated steel (QQ-P-416, Type 1, Class 2), and 7075 aluminum bolted together at one end.

b. The copper and aluminum strips are degreased in Stoddard solvent, then polished with 240-grit aluminum oxide cloth. After polishing, the strips are immersed in hot naphtha for ten seconds, dried, then placed in boiling methanol for ten seconds.

c. The cadmium-plated steel strips are degreased and similarly cleaned in naphtha and methanol. No polishing step is required.

d. Couple specimens are assembled by bolting the three different metal strips together at one end using cadmium-plated nuts and bolts. The specimens are bent so that the only area of mutual contact is near the fasteners.

e. The coupled specimens are placed in the test solutions described above and maintained at 140°F for a period of two weeks.

f. During the two-week storage, periodic observations of corrosion of each strip are made. After the exposure period, the specimens are removed from the solutions, dried, and critically observed.

g. A numerical rating system is used to determine relative corrosivity. The following rating scale is used:

0. No change from original condition.
1. Very slight change from original condition.
2. Slight change from original condition.
3. Slight to moderate change from original condition.
4. Moderate change from original condition.
5. Moderate to severe change from original condition.
6. Severe change from original condition.

In order to accentuate differences in corrosivity, a rating is assigned to each strip after each observation. An over-all Corrosion Index is then obtained by summing all of the ratings for each couple. Corrosivity is then assessed by comparing this index to that obtained for the controls for that series.

4. Compatibility

Although an aircraft fuel system contains many elastomeric materials, previous Air Force experience with fuel additives has indicated that the Buna-N-phenolic topcoating used in integral fuel tanks probably has the most critical compatibility of all materials tested. Degradation of the topcoating may occur slowly over a long period of time; however, accelerated testing at elevated temperatures can give only an indication of long-term results.

In our evaluations we attempt to screen candidate water scavengers by observation of effects produced by immersion of topcoated aluminum specimens in fuel at 140°F for a period of two weeks. A coating of EC-776SR (Minnesota Mining and Manufacturing Co.) is applied to aluminum panels either by dipping or by a doctor blade method. After air-drying for 24 hours, the specimens are immersed in the test solutions and placed in the oven. Two test solutions containing two to five times the normal concentration of additive are used for each scavenger system. One contains saturated fuel and the other saturated fuel plus 10% free water. The test panels are arranged so that a portion of the coated area is also exposed to the vapor over the test solution.

During the two-week storage period the test solutions are changed periodically in order to simulate actual fuel servicing conditions. Visual observations of the coatings are made during this time to detect any changes in appearance.

At the conclusion of the exposure period, the panels are removed from the fuel and dried. A measure of hardness of the film is then obtained by determining its pencil hardness.

For this test a series of drafting pencils ranging from very soft (6B) to very hard (8H) is used. The pencils are sharpened and then the point is blunted with sandpaper. Each pencil is held at a 45 angle to the panel and pushed forward with pressure sufficient to either rupture the film or crumble the lead. The number of the pencil which barely ruptures the film, then crushes and glides over the film after the initial rupture is designated as the hardness rating.

While the procedure outlined above does not constitute a conclusive evaluation, it is sufficiently sensitive for initial screening. More extensive evaluation of any candidate materials is necessary before actual flight testing is attempted.

C. EXPERIMENTAL RESULTS

1. Summary of Materials Screened

In this section of the report we itemize all of the water-reactive chemicals which have been investigated for prevention of icing in JP-4 fuel at -65°F, and we summarize the pertinent data which either eliminated the compound or recommended it for further study. The data were obtained by three of the evaluation techniques described in Part B above: Cloud Point Determination, Karl Fischer Titration, and Low-Temperature Filter Icing Apparatus (LTFIA).

The Cloud Point Determination is the least critical of these evaluation techniques, but its use in the early stages of the program eliminated many of those candidates which were essentially unreactive, were too insoluble, formed insoluble reaction products in fuel, or were obviously too corrosive for further consideration.

The Karl Fischer Titration was used to determine the effectiveness of many candidate scavengers by measuring the quantity of water in JP-4 samples before and after reaction. In general, there is fairly good agreement between the Karl Fischer results and those obtained in LTFIA. Since there are some exceptions, however, the Karl Fischer results were usually checked by a run in the LTFIA. Eventually the Karl Fischer method was eliminated in favor of the LTFIA method.

The data in Table I show that the following compounds are effective in preventing filter icing in JP-4 at -65°F: 2,2-dimethoxypropane (acetone dimethyl acetal), anhydrous hydrazine, trimethyl orthoacetate, trimethyl orthoformate, trimethyl orthovalerate, and two silanes. Anhydrous hydrazine was found to be too corrosive for further consideration, and most silanes form insoluble reaction products. The other effective materials were further investigated to determine minimum effective concentration, catalyst requirements, and temperature dependence as described below in Section II-C-2.

The effective reactive chemicals, then, are a methyl ketal and the trimethyl orthoesters. The methyl ketal (2,2-dimethoxypropane) hydrolyzes to form methyl alcohol and acetone. As the methoxyl groups are replaced by higher molecular weight alkoxyl groups, the filter-icing temperature in JP-4 increases as shown in Table II.

The acetals, which yield alcohols and aldehydes, are not as effective as the ketals because they hydrolyze more slowly. In addition, the aldehydes easily polymerize to form high molecular weight products which have high freezing points and are less effective freezing point depressants for water. The filter-icing temperatures for various acetals are summarized in Table III.

It will be seen that none of these acetals lowers the filter-icing temperature in JP-4 to -65°F. However, the filter-icing temperature reached -57°F when 1,3,3-trimethoxypropene was present in 0.3% concentration and with 1.0% of acetyl chloride (0.14 milliequivalents per ml of 1,3,3-trimethoxypropene). At a lower catalyst concentration (0.2%), the filter-icing point is -52°F. It appears that the double bond in this acetal makes it appreciably more reactive than any of the other acetals tested. While this compound may be of interest in future work, it is neither as efficient nor as economical as the ketal (2,2-dimethoxypropane) or the trimethyl orthoesters.

The trimethyl orthoesters were found to be generally as effective as the 2,2-dimethoxypropane. As in the case of the ketal, substitution of higher alcohols for methyl resulted in slower reactions and higher icing temperatures. Because the trimethyl orthoesters are so effective, our investigation of orthoesters was extended to include the orthocarbonates. Although tetraethyl orthocarbonate is available in research quantities from Kay-Fries Chemicals, Inc., no source of tetramethyl orthocarbonate could be found. A quantity of the latter chemical was, therefore, synthesized for test. The orthocarbonates proved to be less effective than other orthoesters. This may be because the dialkyl carbonates which are formed on hydrolysis are too insoluble and high melting (dimethyl carbonate melts at 0.5°C). The anti-icing effectiveness of various orthoesters is summarized in Table IV.

TABLE I

SUMMARY OF WATER-REACTIVE CHEMICALS INVESTIGATED TO PREVENT ICE FORMATION IN JP-4 AT -65° F

Chemical	Source[a]	Cloud Point[b] (° F)	Percent Effective[c] (Karl Fischer)	Filter[d] Icing Temperature (° F)	Observations
Acetic Anhydride	DPI	40	--	--	Slow reaction, even with HCl catalyst.
Acetyl Chloride	DPI	-30	89	--	Excessively corrosive.
Aluminum Ethoxide	DPI	-36	--	--	Forms aluminum hydroxide.
Aluminum Isopropoxide	DPI	-22	--	+75	Forms aluminum hydroxide.
Benzoyl Chloride	MCB	57	--	--	Very slow reaction.
n-Butyl Isocyanate	Carwin	46	--	--	Insoluble n-butyl urea product.
n-Butyl Vinyl Ether	DPI	35	--	--	Slow reaction, even with HCl catalyst.
n-Butyl Lithium	Foote	35	--	--	Insoluble lithium hydroxide produced.
Cyclohexyl Carbodiimide	MCB	55	--	--	Forms insoluble hydrochloride with HCl.
2, 2-Dibenzyloxypropane	DOW	--	95	+8	
1, 1Diethoxy-2-Chloroethane	DPI	--	--	+28	
1, 1-Diethoxyethane	DPI	--	60	-4	
2, 2-Diethoxypropane	DPI	--	--	-56	
2, 2-Diisopropoxypropane	(e)	--	93	-32	
1, 1-Dimethoxyethane	MCB	--	66	-17	
Dimethoxymethane	DPI	--	23	+8	
2, 2-Dimethoxypropane	DOW	-60	96	below -65	Effective in 0.1% conc., acid catalyst.
Dimethyl Dimethoxy Silane	A	--	--	-62	Gradually forms gel, plugs screen.
Dimethyl Sulfoxide	Baker	68	--	--	Forms hydrate slowly.
Ethylene Oxide	MGC	--	65	+8	Slow hydrolysis.
Hydrazine (Anhydrous)	MCB	--	--	below -65	Excessively corrosive.
Ketene	(f)	--	--	+31	Gas, only slightly soluble in dry JP-4.
Methyl Dimethoxy Acetate	K-F	--	--	+7	
Methyl Trimethoxy Silane	A	--	--	below -65	Forms gel, plugs screen.
1-Naphthoyl Chloride	DPI	0	--	--	Excessively corrosive.
1-Naphthyl Isocyanate	MCB	55	--	--	Insoluble naphthyl urea produced.

TABLE I (Continued)

Chemical	Source[a]	Cloud Point[b] (°F)	Percent Effective[c] (Karl Fischer)	Filter[d] Icing Temperature (°F)	Observations
p-Nitrophenyl Isocyanate	DPI	75	--	--	Insoluble p-nitrophenyl urea produced.
Phenyl Isocyanate	MCB	60	--	--	Insoluble phenyl urea produced.
Phosphorus Oxychloride	MCB	60	--	--	Reacts with fuel, corrosive.
2-propiolactone	DPI	-60	--	--	Reactive product incompatible with topcoating.
Propylene Carbonate	UCC	--	--	+18	Hydrolyzes too slowly.
Styrene Oxide	DOW	40	--	--	Slow reaction, even with HCl catalyst.
1, 1, 3, 3-Tetraethoxypropane	K-F	--	50	+20	
Tetraethyl Orthocarbonate	K-F	--	20	-12	
Tetraisopropyl Titanate	Du Pont	75	--	--	Reacts with fuel, insoluble TiO .
1, 1, 3, 3-Tetramethoxypropane	K-F	--	--	+28	
Tetramethyl Orthocarbonate	(g)	--	--	-14	
Thionyl Chloride	MCB	-60	--	--	Excessively corrosive.
Titanium Tetrachloride	MCB	75	--	--	Insoluble TiO produced.
Triethyl Orthoacetate	DPI	--	90	+19	
Triethyl Orthoformate	DPI	--	96	-10	Goes to -55°F with 0.7 meq HCl/ml.
Triethyl Orthopropionate	K-F	--	52	-46	
1, 3, 3-Trimethoxypropane	DPI	--	--	-57	
Trimethyl Orthoacetate	K-F	--	--	below -65	Effective in 0.15% concentration, acid catalyst.
Trimethyl Orthoformate	K-F	--	96	below -65	Effective in 0.15% concentration, acid catalyst.
Trimethyl Orthovalerate	DPI	--	--	below -65	Effective in 0.4% concentration, acid catalyst.

a. DPI (Distillation Products Industries); MCB (Matheson, Coleman, and Bell); A (Anderson); MGC (Matheson Gas); K-F (Kay-Fries); UCC (Union Carbide Chemical).

b. Used 1% of the chemical reactant with anhydrous HCl catalysis where indicated, with JP-4 containing 60 mg water/liter. Reacted 5 minutes.

c. Used 0.3% of additive with 0.42 meq HCl/ml of additive with JP-4 containing between 70 and 115 mg water/liter of fuel.

d. LTFIA method using 0.2 to 0.4% of additive, 0.03 to 0.14 meq HCl/ml of additive, and 500 ml water/liter of JP-4, reacted 30 minutes at 75°F.

e. Synthesized in Arthur D. Little laboratories according to Howard & Lorette, J. Org. Chem., 25, 525 (1960).

f. Synthesized in Arthur D. Little laboratories according to Williams & Hurd, J. Org. Chem., 5, 122 (1940). Only 14% of stoichiometric quantity was present.

g. Synthesized in Arthur D. Little laboratories according to Smith & Delin, Svensk. Kem. Tidskr., 65, 10-16 (1953).

TABLE II

EFFECT OF SUBSTITUENT GROUPS ON KETALS AS ANTI-ICING ADDITIVES IN JP-4

Ketal	MW of Substituent	Percent Concentration	Icing Temperature (°F)
2, 2-Dimethoxypropane	15	0.2	Below -65
2, 2-Diethoxypropane	29	0.2	-22[a]
2, 2-Diisopropoxypropane	43	0.3[b]	-32
2, 2-Dibenzyloxypropane	77	0.2	+ 8

a. The value of -56°F in Table I was for 0.4% concentration.

b. This concentration is equivalent to 0.2% of 2, 2-dimethoxypropane on a stoichiometric basis.

TABLE III

EVALUATION OF ACETALS AS ANTI-ICING ADDITIVES IN JP-4

Acetal	Percent Concentration	Icing Temperature (°F)
Dimethoxymethane	0.3	+ 8
1, 1-Dimethoxyethane	0.3	-17
1, 1-Diethoxyethane	0.3	- 4
1, 1-Diethoxy-2-Chloroethane	0.2	+28
Methyl Dimethoxy Acetate	0.3	+ 7
1, 1, 3, 3-Tetramethoxypropane	0.2	+28
1, 1, 3, 3-Tetraethoxypropane	0.3	+20
1, 3, 3-Trimethoxypropene	0.3	-57

TABLE IV

EVALUATION OF ORTHOESTERS AS ANTI-ICING ADDITIVES IN JP-4

Orthoesters	Percent Concentration	Icing Temperature (°F)
Trimethyl Orthoformate	0.2	Below -65
Trimethyl Orthoacetate	0.2	Below -65
Trimethyl Orthovalerate	0.4	Below -65
Triethyl Orthoformate	0.3	-55[a]
Triethyl Orthoacetate	0.3	+19
Triethyl Orthopropionate	0.3	-46
Tetramethyl Orthocarbonate	0.2	-14
Tetraethyl Orthocarbonate	0.3	-12

a. Higher acid catalyst concentration used.

Other chemical classes which were investigated include: acid anhydrides and chlorides, metallo-organic compounds, isocyanates, vinyl ethers, lactones, carbodiimides, cyclic oxides, sulfoxides, hydrazine, ketene, and propylene carbonate.

The acid anhydride (acetic) hydrolyzed much too slowly to be of interest, even with the addition of an acid catalyst. Anhydrides of the higher molecular weight acids were, therefore, not further considered as possible reactants.

The acid chlorides (acetyl, benzoyl, naphthoyl, and thionyl) were eliminated as additives because of the corrosive action of the hydrogen chloride formed on hydrolysis. The inorganic acid chlorides (titanium tetrachloride and phosphorus oxychloride) also form hydrogen chloride. Further, titanium tetrachloride forms titanium dioxide which is insoluble in JP-4 and would plug the filters and strainers.

Other metallo-organic compounds (aluminum ethoxide, aluminum isopropoxide, n-butyl lithium, dimethyl dimethoxy silane, methyl trimethoxy silane, and tetraisopropyl titanate) also form insoluble oxides and hydroxides on hydrolysis in JP-4. The two silicon compounds are analogs of 2, 2-dimethoxypropane and trimethyl orthoacetate respectively. These materials hydrolyze even more easily than the carbon compounds. The methyl trimethoxy silane will react without any acid catalyst. However, the silicon compounds slowly form gels which would plug filters and fuel strainers.

The isocyanates (n-butyl, 1-naphthyl, p-nitrophenyl, and phenyl) react with water to form amines. The amines, however, further react with isocyanates to form substituted ureas which can also react with isocyanates to form biurets. These high molecular weight products are insoluble solids in cold JP-4, and the isocyanates are, therefore, not suitable water scavengers for JP-4.

n-Butyl vinyl ether was chosen as representative of the vinyl ethers, but it does not react fast enough for further consideration even with acid catalyst.

2-Propiolactone hydrolyzes rapidly to 2-hydroxy propionic acid and it depresses the cloud point of JP-4 saturated with water to -60°F. However, this acid is corrosive and is incompatible with fuel-system components.

Cyclohexyl carbodiimide is a condensation agent for water-eliminating reactions. However, this compound is not effective in low concentrations and is insoluble in higher concentrations. The hydrochloride formed by the reaction with water and HCl catalyst is probably responsible for the high cloud point.

The cyclic oxides (ethylene and styrene) hydrolyze slowly even with acid catalyst. Ethylene oxide is the more effective, but only 65% of the water in JP-4 is used up in the Karl Fischer Determination, and the filter-icing temperature is +8°F in the LTFIA test.

Dimethyl sulfoxide forms a hydrate with water but the reaction is too slow to be effective. Hydrazine rapidly forms a low freezing hydrate without the need of a catalyst. This compound was eliminated due to corrosion.

Ketene reacts rapidly with water to form acetic acid. Ketene gas was generated in the laboratory and passed through 380 ml of JP-4 until it was saturated. The 380 ml of ketene solution was then added to 8 liters of JP-4 containing 500 mg of water per liter. The amount of ketene used was found to be 14% of the stoichiometric quantity necessary, but the icing temperature was not depressed. Further experiments were not conducted because of this ineffectiveness.

Propylene carbonate was found to hydrolyze too slowly, even with an acid catalyst, for further consideration. Other carboxylic esters were not tried because they hydrolyze more slowly than the orthoesters.

2. Further Study of Promising Materials

a. Minimum Effective Concentration of Additives

The minimum effective concentrations of 2, 2-dimethoxypropane, trimethyl orthoformate, trimethyl orthoacetate, and trimethyl orthovalerate were determined in LTFIA runs with 500 mg of water per liter of JP-4. A 30-minute reaction time at 75° was allowed with acid catalyst as shown in Table V.

The stoichiometry of the reaction of 2, 2-dimethoxypropane with water indicates that 0.34% by volume is required for complete reaction in JP-4 containing 500 mg of water per liter. Since the filter-icing temperature drops below -65°F with only 0.10% by volume, there is considerable antifreeze action of the reaction products, methanol and acetone, on the residual unreacted water. This value of 0.10% is, therefore, only 29% of the stoichiometric volume required for complete reaction of water when 500 mg/l are present.

In a similar calculation, we find that 49% of the stoichiometric amount of trimethyl orthoformate is required, assuming that the hydrolysis products are methanol and methyl formate. With trimethyl orthoacetate, 90% of stoichiometric is required for a filter-icing temperature below -65°F, while 60% of stoichiometric is required to reach -52°F, assuming the reaction products are methanol and methyl acetate. We find that 76% of the stoichiometric amount of trimethyl orthovalerate is required for a filter-icing temperature below -65°F.

b. Alternate Catalysts and Concentrations

All of the promising water-reactive additives require acid catalysis for rapid reaction. For our evaluation, we have defined a rapid reaction as that which is essentially complete after 30 minutes at 75°F. Degree of completion is measured by observing the filter-icing temperature in JP-4.

The function of the acid is protonation of the scavenger compound to an active intermediate which forms hydration derivatives of the scavenger and a hydrogen ion on reaction with water. Since the hydrogen ion is regenerated in the process, only a catalytic amount of acid is necessary to cause complete reaction. A summary of the acid catalysts investigated with 2, 2-dimethoxypropane is presented in Table VI.

TABLE V

MINIMUM EFFECTIVE CONCENTRATIONS OF WATER SCAVENGERS

Additive	Percent Concentration	Meq HCl per ml Additive	Icing Temperature (°F)
2, 2-Dimethoxypropane	0.30	0.040	Below -65
	0.20	0.142	Below -65
	0.20	0.026	Below -65
	0.15	0.026	Below -65
	0.10	0.142	Below -65
	0.075	0.142	-48
	0.050	0.142	-32
Trimethyl Orthoformate	0.30	0.085	Below -65
	0.20	0.140	Below -65
	0.20	0.014	Below -65
	0.15	0.028	Below -65
	0.10	0.028	-53
Trimethyl Orthoacetate	0.30	0.140	Below -65
	0.20	0.028	Below -65
	0.15	0.014	Below -65
	0.10	0.028	-52
Trimethyl Orthovalerate	0.40	0.028	Below -65
	0.2	0.028	+1

It will be seen that the minimum volume of each additive necessary to reach a freezing point below -65° F is:

2, 2-Dimethoxypropane	0.10%
Trimethyl Orthoformate	0.15%
Trimethyl Orthoacetate	0.15%
Trimethyl Orthovalerate	0.40%

TABLE VI

SUMMARY OF ACID CATALYSTS USED WITH 0.2% 2, 2-DIMETHOXYPROPANE

Acid	Concentration[a]	Filter-Icing Temperature[b] (°F)	Observations
Acetyl Chloride	0.014	Below -65	Effective
Acetyl Chloride	0.007	-43	
Methanolic HCl	0.017	Below -65	Effective
Methanolic HCl	0.009	-37	
Methanolic H_3PO_4	0.042	Below -65	Effective
Methanolic H_3PO_4	0.034	-50	
Methanolic BF_3	0.026	Below -65	Effective
Methanolic BF_3	0.017	-53	
Methanolic HF	0.034	0	
Nitric Acid	0.10	Below -65	Added with water
p-Toluene Sulfonic Acid	0.10	Below -65	Added with water
Trichloroacetic Acid	0.10	Below -65	Added with water
Trifluoroacetic Acid	0.10	Below -65	Effective
Acetic Acid	0.10	-7	
Formic Acid	0.10	-1	
Benzenesulfonyl Chloride	0.10	-20	
Phenol	--	--	No cloud point depression
Picric Acid	--	--	Decomposes additive
Acetyl Bromide	0.005	--	96% effective[c]

a. Milliequivalents of acid per ml of 2, 2-dimethoxypropane.

b. In LTFIA with 500 mg of water per liter of JP-4 after reacting for 30 minutes at 75°F.

c. Karl Fischer Titration with 0.3% concentration.

Very small amounts of the stronger acids catalyze the hydrolysis of 2,2-dimethoxypropane. The minimum quantity of HCl is 0.014 meq per ml of additive. As a quantitative convenience, a measured amount of HCl may be added as a saturated solution in methanol, or it may be generated in situ by the reaction of a measured amount of acetyl chloride with the water in the fuel. This generation of HCl is the reason why acetyl chloride is too corrosive for use as a water scavenger. However, the relatively small amount of HCl required for catalysis of other scavengers has not presented a serious corrosion problem (see II-B-3). Wherever acetyl chloride is mentioned as an acid catalyst, HCl is the acid implied.

Between 0.034 and 0.042 meq/ml of phosphoric acid and between 0.017 and 0.026 meq/ml of boron trifluoride is required for catalytic action. Other strong acids such as nitric, p-toluene sulfonic, trichloroacetic, and trifluoroacetic were also found to be effective at higher concentrations. Although lower concentrations of these latter acids were not evaluated, we would expect a similar performance. Acetyl bromide was shown to be effective in low concentration by the Karl Fischer Determination and we, therefore, expect that the hydrobromic acid generated is as effective as hydrochloric acid from acetyl chloride.

Acids which were found to be poor catalysts were hydrofluoric, formic, and acetic. Benzene sulfonyl chloride hydrolyzes too slowly. Phenol was tried on cloud point depression but was found ineffective. It was thought that phenol might exhibit stronger acidic properties in the high hydrocarbon-to-water ratio than it does in aqueous solutions.

Although this study of acid catalysts and required concentration of catalyst has been confined to 2,2-dimethoxypropane, the results are applicable to the trimethyl orthoesters which also require acid catalysis for rapid hydrolysis.

c. Temperature Dependence of Hydrolysis Reactions

Since the rate of a chemical reaction is generally a function of temperature, and since a successful scavenger must be capable of reaction over a wide range of temperatures, we have attempted to determine the effectiveness of 2,2-dimethoxypropane at reaction temperatures below 75°F. Karl Fischer Titrations cannot be used for such determinations since the low temperature would also inhibit the Karl Fischer reaction with water. Accordingly, rate of reaction at low temperatures has been studied using the filter-icing apparatus.

A series of LTFIA runs was made after reaction of 2,2-dimethoxypropane and water at various temperatures below 75°F. The concentration of additive was 0.2% by volume with 0.2% of acetyl chloride catalyst in JP-4 fuel containing 500 mg of water per liter. The data are presented in Table VII.

TABLE VII

TEMPERATURE DEPENDENCE OF HYDROLYSIS OF 2, 2-DIMETHOXYPROPANE IN JP-4

Reaction Temperature (°F)	Reaction Time (Hr)	Freezing Point (°F)
75	1/2	Below -65
55	1/2	Below -65
35	2	Below -65
35	1	-35
0	5	Above 0

Essentially complete reaction occurs at temperatures as low as 35°F during a two-hour period. At temperatures below the freezing point of water, the system includes dispersed ice-crystals, and the rate of reaction is very slow at 0°F. Reaction is incomplete after five hours.

However, some reaction does take place at 0°F, since the ice which plugged the screen melted well below 32°F. This result is most encouraging because it indicates that reaction takes place even when water is present in the solid phase. In addition, under actual flight conditions, longer reaction times would be possible, since rate of decrease of fuel temperature on an aircraft would be quite slow. Moreover, if filter/separation equipment were working satisfactorily, water contents as high as 500 mg/l, or even 100 mg/l, would be unlikely.

Therefore, one run was made in which 83 mg of water/l of JP-4 was reacted with 0.2% of 2, 2-dimethoxypropane containing 0.2% of acetyl chloride catalyst for one hour at 0°F. The filter-icing temperature in JP-4 was below -65°F.

This reaction of 2, 2-dimethoxypropane with ice at 0°F has led to an investigation of the possibility of removing bulk ice from fuel systems by additive treated fuels. This subject is covered in Section II-D-2.

3. Corrosion

Because all of the effective water-reactive materials require acid catalysis, the study and control of possible corrosive conditions has been of major concern in this program. Much of our initial work which involved relatively high concentrations of strong mineral acids as catalysts indicated that corrosion of copper, cadmium-plated steel, and aluminum was a serious problem. As the work progressed, however, lower catalyst concentrations were found to be effective so that corrosion could be more easily controlled In addition, alternate catalysts were also evaluated and found to cause much less difficulty.

As one possible method of controlling additive system corrosivity, we have investigated the use of corrosion inhibitors currently approved for use in military aviation fuels. It is quite possible that such corrosion inhibitors may already be present in the fuel at the time of delivery to the aircraft. In many cases, however, such inhibitors, which are used primarily to protect refinery transfer and storage systems, are nearly exhausted by the time the fuel reaches the use point. Moreover, there is no control over the amount or type of inhibitor which may be present at this time.

We proposed then to incorporate enough inhibitor in the additive-catalyst mixture to prevent corrosion in the treated fuel. We realized that most inhibitors function by means of surface active phenomena. Accordingly the interfacial tension between fuel and water is generally lowered by their use. This often has a detrimental effect upon water separation equipment and can, in severe cases, result in essentially complete breakdown of filter/separator performance. In the present case this is not a problem, however, in that final filtration of the fuel and removal of all free water should take place before the injection of additive.

A summary of our corrosion testing results is presented in Table VIII. Since the corrosion produced by different fuels under slightly different conditions may vary over a wide range it is necessary to evaluate each result by comparison with the control samples run at the same time. Accordingly proper interpretation of Table VIII involves comparison with the control samples presented at the top of each subdivision.

It may be seen from these results that in the minimum range of effective amounts of catalysts even the strong mineral acids such as hydrogen chloride are not excessively corrosive. Moreover, boron trifluoride has no apparent corrosive effect and phosphoric acid only a slight one By choosing the proper corrosion inhibitor from those that are already qualified for use in military aviation fuels, it is also possible to reduce the corrosivity of HCl catalyst systems to a level equal to or lower than the controls. In addition, it should be noted that some of the inhibitors which appear to offer no great advantage from these results should not be completely eliminated. Many inhibitors function by means of a thin surface coating which may in itself produce a color change or tarnish, but which may effectively prevent further corrosion.

4. Compatibility

Table IX presents a summary of results obtained in evaluating potential water scavenger systems for compatibility with integral fuel-tank topcoating material. In the concentrations investigated, which contained up to five times the expected use concentration, no serious softening of the film was observed for any of the effective additives. Additional laboratory tests have shown that if either additives or reaction products are present in high concentrations, a serious effect can be produced. It would appear, however, that such concentrations would never be encountered in practice.

Compatibility with other nonmetallic fuel-system components was not evaluated under this program since the topcoating has been found to be the most troublesome material. Before actual use of a water-reactive additive is undertaken, it will be necessary to run screening tests to establish compatibility with all other fuel-system components.

D. PRACTICAL CONSIDERATIONS

1. Additive Utilization

a. Methods of Injection

Ideally, a reactive chemical additive would be injected into the fuel stream just prior to loading on board an aircraft. In this manner the turbulence in the line downstream of the injection point would provide for uniform mixing. Reaction would start in the fuel line and would continue in the aircraft fuel storage system.

The necessary catalyst (and corrosion inhibitor) would be combined with the reactive scavenger prior to injection. Thus a metering system and storage vessel would be the only equipment required for additive utilization.

It is likely that the present arrangement of most U. S. Air Force bases would not be conducive to the ideal injection system described above. If the arrangement were such that several fueling stations were serviced by individual fuel lines, a requirement for many injection systems at each base might arise. In such a case, it would be possible to inject the additive further back in the fuel transfer system, provided certain conditions were maintained.

1

TABLE VIII

SUMMARY OF CORROSION TEST RESULTS FOR WATER SCAVE

Additive	Additive Concentration Percent	Catalyst	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/l)	Water Present	1st Ratin	
							Cu	Cd
None	-	None	-	-	-	No	0	0
None	-	None	-	-	-	Yes	1	0
Aluminum Isopropoxide	0.2	None	-	-	-	No	0	0
Aluminum Isopropoxide	0.2	None	-	-	-	Yes	1	1
Naphthoyl Chloride	2.0	None	-	-	-	No	0	0
Naphthoyl Chloride	2.0	None	-	-	-	Yes	1	1
Acetyl Chloride	0.2	None	-	-	-	No	1	0
Acetyl Chloride	0.2	None	-	-	-	Yes	2	2
Thionyl Chloride	0.2	None	-	-	-	No	6	0
Thionyl Chloride	0.2	None	-	-	-	Yes	6	6
None	-	None	-	-	-	No	1	0
None	-	None	-	-	-	Yes	4	4
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	-	-	No	3	0
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	-	-	Yes	4	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.034	-	-	No	3	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.034	-	-	Yes	4	5
2, 2-dimethoxypropane	0.4	Methanolic BF_3	0.052	-	-	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic BF_3	0.052	-	-	Yes	4	4
2, 2-dimethoxypropane	0.4	Methanolic H_3PO_4	0.076	-	-	No	3	0
2, 2-dimethoxypropane	0.4	Methanolic H_3PO_4	0.076	-	-	Yes	4	4
Phillips 55MB	0.4	None	-	-	-	No	1	0
Phillips 55MB	0.4	None	-	-	-	Yes	3	5

TABLE VIII

OF CORROSION TEST RESULTS FOR WATER SCAVENGER SYSTEMS

	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/l)	Water Present	1st Rating Cu	1st Rating Cd	1st Rating Al	2nd Rating Cu	2nd Rating Cd	2nd Rating Al	Final Rating Cu	Final Rating Cd	Final Rating Al	Over-all Corrosion Index	Remarks
	-	-	-	No	0	0	0	1	0	0	2	0	0	3	Control I[b]
	-	-	-	Yes	1	0	0	2	1	1	4	2	2	13	Control I[b]
	-		-	No	0	0	0	0	0	0	0	0	0	0	
	-	-		Yes	1	1	1	1	2	2	2	2	2	14	
	-	-		No	0	0	0	0	0	0	0	0	0	0	
	-	-	-	Yes	1	1	2	4	2	4	6	6	6	32	
	-	-	-	No	1	0	0	4	2	0	6	4	0	17	
	-	-	-	Yes	2	2	2	6	6	6	6	6	6	42	
	-	-	-	No	6	0	0	-	-	-	-	-	-	18	
	-	-	-	Yes	6	6	6	-	-	-	-	-	-	54	
	-	-	-	No	1	0	0	1	0	0	1	0	0	3	Control II[b]
	-	-		Yes	4	4	2	4	5	3	4	5	3	34	Control II[b]
e	0.028	-	-	No	3	0	0	3	0	0	3	0	0	9	
e	0.028	-	-	Yes	4	3	3	4	4	4	5	5	5	37	
l	0.034	-	-	No	3	0	0	3	0	0	3	1	0	10	
l	0.034	-	-	Yes	4	5	5	4	5	5	5	5	5	43	
3	0.052	-	-	No	1	0	0	1	0	0	1	0	0	3	
3	0.052	-	-	Yes	4	4	3	4	4	3	4	4	4	34	
PO_4	0.076	-	-	No	3	0	0	3	0	0	3	0	0	9	
PO_4	0.076	-	-	Yes	4	4	3	4	4	3	4	4	5	35	
	-	-	-	No	1	0	0	1	0	0	1	1	0	4	
	-	-	-	Yes	3	5	4	3	5	4	3	5	5	37	

TABLE VIII (Continued)

Additive	Additive Concentration Percent	Catalyst	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/ml)	Water Present	1st Ratin	
							Cu	Cd
None	-	None	-	None		No	0	0
None	-	None	-	None	-	Yes	2	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	None	-	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	None	-	Yes	4	4
2, 2-dimethoxypropane	0.2	Methanolic HCl	0.017	None		No	0	0
2, 2-dimethoxypropane	0.2	Methanolic HCl	0.017	None		Yes	2	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	A	60	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	A	60	Yes	2	2
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	B	75	No	2	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	B	75	Yes	2	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	C	60	No	3	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	C	60	Yes	3	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	D	75	No	0	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	D	75	Yes	3	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	E	75	No	0	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	E	75	Yes	2	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	F	75	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	F	75	Yes	3	4
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	G	75	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	G	75	Yes	3	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	H	75	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	H	75	Yes	4	3
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	I	60	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	I	60	Yes	3	2
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	J	75	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	J	75	Yes	2	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	K	75	No	1	0
2, 2-dimethoxypropane	0.4	Methanolic HCl	0.017	K	75	Yes	2	1

TABLE VIII (Continued)

	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/ml)	Water Present	1st Rating			2nd Rating			Final Rating			Over all Corrosion Index	Remarks
					Cu	Cd	Al	Cu	Cd	Al	Cu	Cd	Al		
	-	None	-	No	0	0	0	0	0	0	1	0	0	1	Control III[b]
	-	None	-	Yes	2	3	3	5	5	4	6	6	6	40	Control III[b]
Cl	0.017	None	-	No	1	0	0	3	1	0	3	1	0	9	
Cl	0.017	None	-	Yes	4	4	3	5	5	4	6	6	5	42	
Cl	0.017	None		No	0	0	0	0	0	0	0	0	0	0	
Cl	0.017	None	-	Yes	2	3	3	3	5	3	5	6	4	34	
HCl	0.017	A	60	No	1	0	0	3	0	0	3	0	0	7	
HCl	0.017	A	60	Yes	2	2	2	3	3	4	3	3	4	26	
HCl	0.017	B	75	No	2	0	0	3	1	0	3	2	0	11	
HCl	0.017	B	75	Yes	2	0	1	4	5	3	4	6	3	28	
HCl	0.017	C	60	No	3	0	0	3	0	0	3	3	0	12	
HCl	0.017	C	60	Yes	3	3	4	4	6	5	4	6	6	41	
HCl	0.017	D	75	No	0	0	0	0	0	2	0	0	2	4	
HCl	0.017	D	75	Yes	3	3	3	4	5	4	5	5	5	37	
HCl	0.017	E	75	No	0	0	0	1	0	0	2	1	0	4	
HCl	0.017	E	75	Yes	2	0	0	3	2	1	4	3	1	16	
HCl	0.017	F	75	No	1	0	0	3	0	0	3	0	0	7	
HCl	0.017	F	75	Yes	3	4	4	4	5	4	5	5	5	39	
HCl	0.017	G	75	No	1	0	0	2	0	0	3	0	0	6	
HCl	0.017	G	75	Yes	3	0	0	4	5	0	5	5	1	23	
HCl	0.017	H	75	No	1	0	0	2	0	0	3	0	0	6	
HCl	0.017	H	75	Yes	4	3	3	5	4	5	5	4	5	38	
HCl	0.017	I	60	No	1	0	0	2	0	0	2	0	0	5	
HCl	0.017	I	60	Yes	3	2	3	5	5	6	6	5	6	41	
HCl	0.017	J	75	No	1	0	0	1	0	0	1	0	0	3	
HCl	0.017	J	75	Yes	2	0	0	4	3	4	4	3	4	24	
HCl	0.017	K	75	No	1	0	0	2	0	0	2	0	0	5	
HCl	0.017	K	75	Yes	2	1	2	4	3	4	4	3	4	27	

TABLE VIII (Continued)

Additive	Additive Concentration Percent	Catalyst	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/l)	Water Present	1s Rat Cu
None	-	None	-	None	-	No	2
None	-	None	-	None	-	Yes	4
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	None	-	No	3
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	None	-	Yes	5
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	25	No	2
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	25	Yes	4
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	50	No	1
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	50	Yes	2
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	75	No	1
2, 2-dimethoxypropane	0.2	Acetyl Chloride	0.14	E	75	Yes	2

a. Catalyst concentration given in milliequivalents per ml additive.

b. For proper interpretation of results, compare ratings with controls in same subsection.

Rating Code:

0 = No change from original condition
1 = Very slight change from original condition
2 = Slight change from original condition
3 = Slight to moderate change from original condition
4 = Moderate change from original condition
5 = Moderate to severe change from original condition
6 = Severe change from original condition

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TABLE VIII (Continued)

	Catalyst Concentration[a]	Corrosion Inhibitor	Inhibitor Concentration (mg/l)	Water Present	1st Rating Cu	1st Rating Cd	1st Rating Al	2nd Rating Cu	2nd Rating Cd	2nd Rating Al	Final Rating Cu	Final Rating Cd	Final Rating Al	Over-all Corrosion Index	Remarks
	-	None	-	No	2	0	0	3	0	0	3	2	1	11	Control IV[b]
	-	None	-	Yes	4	5	6	4	5	6	6	5	6	47	Control IV[b]
ride	0.14	None		No	3	0	0	3	0	0	3	2	3	14	
ride	0.14	None	-	Yes	5	6	4	5	6	4	5	6	6	47	
ride	0.14	E	25	No	2	0	0	2	0	0	2	0	0	6	
ride	0.14	E	25	Yes	4	1	4	4	1	4	5	3	5	31	
ride	0.14	E	50	No	1	0	0	2	0	0	2	0	0	5	
ride	0.14	E	50	Yes	2	3	4	3	3	4	4	4	6	33	
ride	0.14	E	75	No	1	0	0	2	0	0	2	1	0	6	
ride	0.14	E	75	Yes	2	1	0	3	2	0	3	4	3	18	

ents per ml additive.
re ratings with controls in same subsection.

l condition
n original condition
ginal condition
ge from original condition
original condition
nge from original condition
ginal condition

TABLE IX

SUMMARY OF TOPCOATING COMPATIBILITY RESULTS

Additive	Additive Concentration Percent	Catalyst	Catalyst Concentration[a]	Water Present	P Vapor
None	-	None	-	No	H
None	-	None	-	Yes	2
Styrene Oxide	1.0	HCl Gas	-	No	2
Styrene Oxide	1.0	HCl Gas	-	Yes	2
2-Propiolactone	0.1	HCl Gas	-	No	4
2-Propiolactone	0.1	HCl Gas	-	Yes	H
None	-	None	-	No	H
None	-	None	-	Yes	F
Triethyl orthoformate	0.5	Methanolic HCl	0.017	No	H
Triethyl orthoformate	0.5	Methanolic HCl	0.017	Yes	H
Trimethyl orthoformate	0.5	Methanolic HCl	0.017	No	H
Trimethyl orthoformate	0.5	Methanolic HCl	0.017	Yes	B
Trimethyl orthoacetate	0.5	Methanolic HCl	0.017	No	B
Trimethyl orthoacetate	0.5	Methanolic HCl	0.017	Yes	2
2, 2-dimethoxypropane	0.5	Acetyl Chloride	0.028	No	B
2, 2-dimethoxypropane	0.5	Acetyl Chloride	0.028	Yes	H
2, 2-dimethoxypropane	0.5	Acetyl Chloride	0.028	No	B
2, 2-dimethoxypropane	0.5	Acetyl Chloride	0.028	Yes	B
2, 2-dimethoxypropane	0.5	Methanolic BF_3	0.025	No	B
2, 2-dimethoxypropane	0.5	Methanolic BF_3	0.025	Yes	B
2, 2-dimethoxypropane	0.5	Methanolic H_3PO_4	0.035	No	B
2, 2-dimethoxypropane	0.5	Methanolic H_3PO_4	0.035	Yes	B

TABLE IX

SUMMARY OF TOPCOATING COMPATIBILITY RESULTS

Catalyst	Catalyst Concentration[a]	Water Present	Pencil Hardness		Remarks
			Vapor Phase	Fuel Phase	
None	-	No	HB	HB	Control Ia[b]
None	-	Yes	2H	2H	Control Ib
HCl Gas	-	No	2H	2H	
HCl Gas	-	Yes	2H	2H	
HCl Gas	-	No	4B	>6B	
HCl Gas	-	Yes	HB	HB	
None	-	No	H	H	Control IIa[b]
None	-	Yes	F	B	Control IIb[b]
Methanolic HCl	0.017	No	H	B	
Methanolic HCl	0.017	Yes	H	H	
Methanolic HCl	0.017	No	H	2H	
Methanolic HCl	0.017	Yes	B	H	
Methanolic HCl	0.017	No	B	B	
Methanolic HCl	0.017	Yes	2H	H	
Acetyl Chloride	0.028	No	B	B	
Acetyl Chloride	0.028	Yes	H	H	
Acetyl Chloride	0.028	No	B	B	75 mg 1 of Additive [illegible]
Acetyl Chloride	0.028	Yes	B	B	75 mg 1 of Additive [illegible]
Methanolic BF_3	0.025	No	B	B	
Methanolic BF_3	0.025	Yes	B	B	
Methanolic H_3PO_4	0.035	No	B	B	
Methanolic H_3PO_4	0.035	Yes	B	B	

TABLE IX (Continued)

Additive	Additive Concentration Percent	Catalyst	Catalyst Concentration[a]	Wate Prese
None	-	None	-	No
None	-	None	-	Yes
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	No
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	Yes
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	No
2, 2-dimethoxypropane	0.4	Acetyl Chloride	0.028	Yes
Phillips 55MB	0.4	None	-	No
Phillips 55MB	0.4	None	-	Yes

a. Catalyst concentration given in milliequivalents per ml of additive.

b. For proper interpretation of results, compare pencil hardness with controls in same subsect

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TABLE IX (Continued)

Catalyst	Catalyst Concentration[a]	Water Present	Pencil Hardness Vapor Phase	Pencil Hardness Fuel Phase	Remarks
None	-	No	B	2B	Control IIIa[b]
None	-	Yes	HB	B	Control IIIb[b]
Acetyl Chloride	0.028	No	B	2B	75 mg/l Additive J used
Acetyl Chloride	0.028	Yes	HB	B	75 mg/l Additive J used
Acetyl Chloride	0.028	No	B	4B	75 mg/l Additive G used
Acetyl Chloride	0.028	Yes	B	2B	75 mg/l Additive G used
None	-	No	H	2B	
None	-	Yes	HB	B	

ents per ml of additive.
re pencil hardness with controls in same subsection.

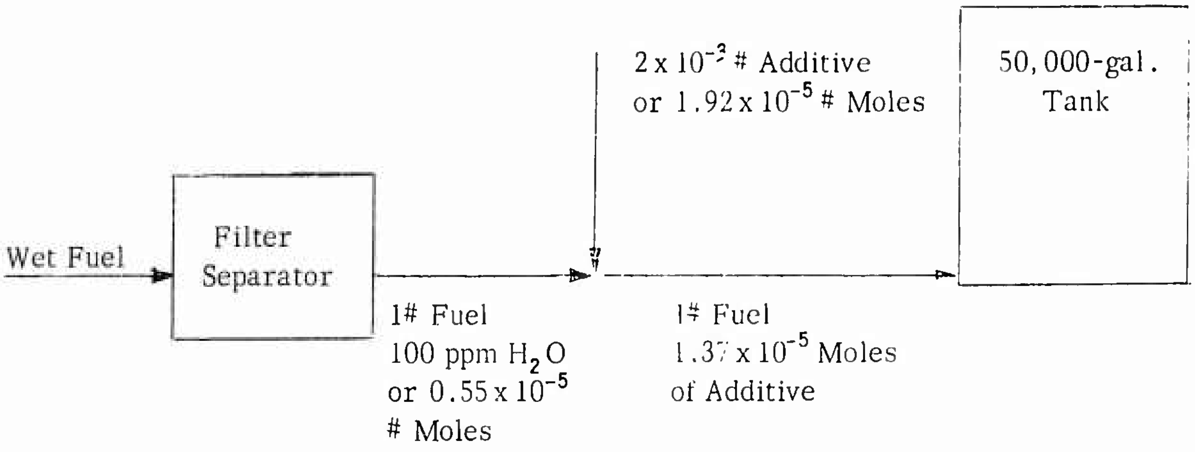
The present utilization of Phillips 55MB at WPAFB is accomplished by injecting the additive into a high flow-rate (600 gpm) transfer line between bulk storage and the SAC flight line "ready" tanks. So long as free water is removed from the fuel prior to injection, the same technique could be used with a reactive additive. If filter/separation were not accomplished prior to injection, additive might be needlessly consumed.

Once the additive-treated fuel reaches the ready tanks, the problem of contamination from atmospheric moisture must be considered. Certain aspects of this situation are discussed and analyzed in the section which follows.

b. Storage of Additive-Treated Fuel

The following calculations were carried out to estimate: 1) the loss of reactive additive which may occur when dry fuel with 0.2% additive (2, 2-dimethoxypropane) is fed to a 50, 000 gallon ready tank containing humid air; 2) the loss of additive when the same fuel is drained from a ready tank with humid air being drawn in; and 3) the loss of additive in a tank breathing cycle caused by an extreme swing in ambient temperature.

(1) Composition of Feed to Ready Tank. Taking a material balance with a basis of 1 lb of fuel, we can summarize the feed composition to the service tank as follows:



The concentration of additive in the feed, hereafter called X_a, is therefore

$$6\ 24 \times 0.8 \times 1.37^{-5} = 6.84 \times 10^{-4} \frac{\#\,\text{Moles}}{\text{ft}^3}$$

(2) Contamination on Filling. If we assume equilibrium between the water vapor in the residual air and water content of the fuel, the result of the calculation is the most extreme removal of additive that can occur during filling. In reality, equilibrium will not be attained, particularly if the tank is fed from the bottom. Assuming equilibrium, as the first small increment of fuel enters, additive in the fuel reacts to completion, water dissolves in the fuel, and some water vapor is vented. This could undoubtedly be solved analytically, but it does not seem worthwhile in view of the results of the approximate calculation which follows.

The simplest approach is to neglect the water vapor vented. Water vapor present in the tank at 70°F, and saturation is:

$$\frac{50,000}{7.5} \times \frac{1}{359} \times \frac{22}{760} \times \frac{492}{530} = 0.5 \text{ \# Moles}$$

Tank capacity is 6,670 ft^3

The volume of fuel needed to completely react with all water vapor originally present in the tank is:

$$\frac{0.5}{6.84 \times 10^{-4}} = 730 \text{ ft}^3$$

or 11% of the tank volume. Thus, by the time the tank is 11% filled, further reaction between additive and water vapor will not occur since, under the equilibrium assumption, the air above the fuel will be dry. When the tank is completely filled, at least 89% of the total additive fed will be present, and

$$X_a = 6.1 \times 10^{-4} \frac{\text{\# Moles}}{\text{ft}^3}$$

(3) Contamination on Withdrawal. A situation may be visualized where humid air is vented in as fuel is being withdrawn from the ready tank. Again assuming that water vapor in the air can readily react with additive, we can estimate this additive loss as shown below.

A material balance on additive present in the fuel can be written as

$$d(X_a V_L) = - X_a dV_a - Y_h dV_a$$

with V_L = the liquid volume present

V_a = the gas volume present

$$Y_h = \frac{\text{\# moles water vapor}}{\text{ft}^3 \text{ of air}}$$

The first term on the right represents additive withdrawal with the fuel, and the second term the mole for mole reaction with entering vapor. As air is drawn in, X_a in the fuel phase gradually falls If is the fraction of the tank volume occupied by air, then solution to the equation is

$$X_{a2} = X_{a1} - Y_h \ln \frac{1 - 1}{1 - 2}$$

Solving this expression for $X_{a1} = 6.1 \times 10^{-4}$, $\epsilon_1 = 0$ and $\epsilon_2 = 0.9$,

$$X_{a2} = 4.33 \times 10^{-4} ∷ \text{moles/ft}^3, \text{ or } 70\% \text{ of the original}$$

additive concentration when the tank contains 10% of the fuel originally present.

We can take an opposite approach to the problem by assuming that rates of mass transfer for water vapor into the fuel during the withdrawal period are very slow. Thus, we can imagine that 90% of the total fuel is withdrawn from the tank with a constant additive concentration equal to the original value of 6.1×10^{-4}. The residual fuel (10%) is then allowed to come to equilibrium over a period of days with the water vapor which has been drawn in.

At saturation and 70°F, $Y_h = 7.5 \times 10^{-5}$, and the water vapor which has been drawn in is

$$0.9 \times 6,670 \times 7.5 \times 10^{-5} = 0.45 \text{ moles}$$

Additive in the residual fuel is

$$0.1 \times 6,670 \times 6.1 \times 10^{-4} = 0.41 \text{ moles}$$

Under these extreme conditions then, the final 5,000 gallons of fuel would contain small amounts of dissolved water and be stripped of additive. In actual practice X_a for the final 5,000 gallons will lie between the extremes cited for the two calculations.

Alternatively, if the ready tank is not allowed to fall below 50% of full capacity at any time, a repeat of the second calculation shows that X_a could not drop below 88% of the initial value by a process such as that described.

(4) Contamination Due to Tank Breathing. To evaluate the magnitude of this effect, we postulate a rather extreme hypothetical breathing cycle where a ready tank, 20% full of fuel, reaches a temperature of 100°F and is then cooled to 32°F. At 100°F the vapor pressure of the JP-4 fuel is taken as 3 psi. The amount of air present in the tank is

$$\frac{6,670 \times 0.8}{359} \times \frac{11.7}{14.7} \times \frac{492}{560} = 10.2 \text{ moles}$$

At 32°F, the total moles of gas present must be

$$\frac{6,670 \times 0.8}{359} = 14.8$$

Neglecting the vapor pressure of the fuel at 32°F and taking the average value of the water vapor pressure for inflowing gas as that at 70°F, we determine the amount of water vapor which will enter at approximately

$$(14.8 - 10.2) \times \frac{22}{760} = 0.133 \text{ moles } H_2O$$

Additive originally present in the fuel phase is

$$0.2 \times 6,670 \times 6.1 \times 10^{-4} = 0.81 \text{ moles additive.}$$

The additive removed is thus approximately 16% of that present in one cycle. For a single breathing cycle with the tank 50% full of fuel, the additive loss is found to be only 4% per breathing cycle.

These calculations indicate that under the worst conditions appreciable quantities of reactive chemical additive may be lost before the fuel ever reaches the aircraft. Moreover, if less than a 0.2% concentration of additive is used, the proportion of additive protection lost would be greater. Thus it appears that consideration should be given to the use of an air dehydrating device on the tank breather. A simple silica gel dryer, for example, could entirely eliminate the problem of additive losses in storage so that full protection to the aircraft would always be provided.

It should be realized, however, that the necessity for such a device is also dependent upon the mode of usage of the ready tank. If the tank is used daily, and if it is kept at least half full at all times, protection would probably not be necessary. Moreover, the above calculations represent rather severe assumptions of interchange rates of water between air and fuel. As such, they represent the extreme cases of contamination which might never be realized or even approached in actual practice.

2. Removal of Bulk Water and Ice from Aircraft Fuel Systems

One of the major sources of water in airborne fuel arises from there being a number of undrainable pockets within current aircraft fuel systems. Since these cannot be periodically drained, water accumulates in them. In winter such pockets may freeze and increase in size so that as much as 100 gallons of free water may be continuously present. There is currently no satisfactory method of eliminating such water from an aircraft.

In view of the fact that 2, 2-dimethoxypropane reacted with water in fuel even when the temperature was well below 32°F, we have investigated the possibility of using a chemical additive to dehydrate an aircraft fuel system. Ideally such dehydration might be accomplished by introducing a quantity of pure additive into the drained fuel tanks, allowing a period of time for reaction to occur, then draining and flushing the system with fuel. Our initial experimentation indicated that reaction of pure additive with water or ice could be readily accomplished, and the reaction products formed by the hydrolysis aided ice removal due to the antifreeze action. This direct approach had to be eliminated from present consideration, however, due to compatibility problems. The additive itself in high concentration has an adverse effect upon the Buna N - phenolic topcoating. In addition the acetone and methanol formed in the reaction would dissolve the topcoating in such high concentrations.

Since a potential compatibility problem was found to exist, our efforts were concentrated upon low-concentration methods of control. A number of experiments were carried out using 2, 2-dimethoxypropane at concentrations of 0.1 - 0.4% in fuel. The general experimental procedure involved the introduction of a measured volume of water in a quart jar filled with fuel. Since only a limited amount of interfacial area would be present in an actual aircraft fuel system, our samples were not vigorously agitated. Instead, the jar was allowed to stand for 24 hours, sufficient time for diffusion of reactants and products. At the end of the 24-hour period, the fuel layer was decanted and fresh additive-treated fuel was added to the jar. A total of four or five such changes were made before the volume of the aqueous layer was redetermined.

On the basis of a limited number of experiments with this type of system we have drawn the following conclusions:

a. Additive-treated fuel is capable of reacting with and removing bulk water and ice from storage vessels.

b. Rate of removal is dependent upon interfacial area, additive concentration, and the geometry of the storage chamber (since diffusion will normally be the controlling mechanism).

c. Under certain conditions, the volume of the aqueous phase may be temporarily increased because the reaction products are soluble in water. Subsequent fuel changes will eventually eliminate the entire aqueous phase, however.

d. Extraction of the reaction products into the aqueous phase may lead to difficulty because the acetone is not compatible with the top coating.

e. Although more work is needed in this area, it appears that under normal conditions where a very small water or ice phase is in contact with a large quantity of additive treated fuel for a period of up to three days, the aqueous phase may be removed completely without any detrimental effects.

f. The optimum additive concentration for bulk water or ice removal is probably in the same range as the expected use concentration of the additive (0.1 - 0.2%).

3. Aging of Additive Systems

Additive systems under consideration in this section are composed of a mixture of additive and acid catalyst, or a mixture of additive, acid catalyst, and corrosion inhibitor, which may be injected directly into the fuel. It is important to know the shelf-life of such mixtures and the effect of catalyst and corrosion inhibitor on each other, as well as on the water-reactive additive. We have studied the aging stability of 2, 2-dimethoxypropane with various acid catalysts and corrosion inhibitors by examining the filter-plugging temperatures when 500 mg of water/liter of JP-4 are reacted with 0.2% of the additive system for 30 minutes at 75°F. The data are presented in Table X.

Aging of 2, 2-dimethoxypropane with various acid catalysts for at least 25 days does not reduce the rate of reaction. The presence of acetyl chloride with corrosion inhibitors E and J does not affect the rate of reaction after storage at least 29 days. However, the presence of corrosion inhibitor G results in a filter-icing point of -63°F after five days and -58°F after 18 days. In addition, the solubility of G in the additive is limited.

The lower reactivity with additive G is also shown in Table XI which summarizes data obtained by reacting aged 2, 2-dimethoxypropane systems in 0.2% concentration with 500 mg of water per liter of JP-4 at 35°F for one hour.

These data show that the hydrolysis reaction is incomplete after a reaction time of only one hour at 35°C, since the filter-icing temperature was only about -35°F with the better acid catalysts (HCl and BF_3). Nearly the same filter-icing temperature was obtained with additive systems containing corrosion inhibitors J and E which apparently have no adverse effect on the catalyst or the 2, 2-dimethoxypropane. It should be mentioned that a concentration of 0.028 milliequivalents of HCl (from acetyl chloride) per ml of 2, 2-dimethoxypropane depressed the freezing point to below -65°F after a two-hour reaction period at 35°F. Moreover, under actual use conditions up to three days of storage time may be encountered prior to flight.

TABLE X

AGING STABILITY OF 2, 2-DIMETHOXYPROPANE ADDITIVE SYSTEMS

Catalyst	Corrosion[a] Inhibitor	Days Aged	Filter-Icing Temperature (°F)
0.2% Acetyl Chloride	None	20	Below -65
(0.028 meq/ml of Additive)	J	4	Below -65
	J	17	Below -65
	E	3	Below -65
	E	18	Below -65
	E	29	Below -65
	G	5	-63
	G	16	-58
0.4% 8.5N Methanolic	None	7	Below -65
HCl (0.034 meq/ml)	None	25	Below -65
0.5% 12.2N Methanolic	None	7	Below -65
BF_3 (0.052 meq/ml)	None	25	Below -65
1.0% 7.4N Methanolic	None	7	Below -65
H_3PO_4 (0.076 meq/ml)	None	25	Below -65

a. 75 mg per liter of JP-4.

TABLE XI

HYDROLYSIS OF 2, 2-DIMETHOXYPROPANE IN JP-4 AT LOW TEMPERATURES WITH ALTERNATE CATALYST SYSTEMS

Catalyst	Conc.[a]	Corrosion Inhibitor[b]	Days Aged	Filter-Icing Temperature (°F)
Acetyl Chloride	0.028	J	8	-36
Acetyl Chloride	0.028	E	7	-38
Acetyl Chloride	0.028	G	8	+ 1
Methanolic HCl	0.034	--	12	-35
Methanolic BF_3	0.052	--	11	-37
Methanolic H_3PO_4	0.076	--	11	-19

a. Milliequivalents of acid per ml of 2, 2-dimethoxypropane.

b. 75 mg per liter of JP-4.

4. Additive Utilization in Fuels Other Than JP-4

It is apparent that military aviation fuels other than JP-4 may also encounter filter-icing problems due to dissolved and free water. Therefore, the scope of our original investigation was broadened to include the applicability of water-reactive additives to JP-5 and JP-6 containing 500 mg/l of water. The following data were obtained in our LTFIA with 0.2% of 2, 2-dimethoxypropane after a reaction time of 30 minutes at 75°F.

Fuel	Bulk Fuel Temperature (°F)	Filter-Icing Temperature (°F)
JP-5	-62	Below -43
JP-6	-59	Below -40

These temperatures were the minimum obtainable in our test system. The relatively high freezing point of the fuel prevented further circulation through the cooling coil. However, the fuel and filter temperatures are low enough to indicate that the 2, 2-dimethoxypropane will dehydrate JP-5 and JP-6 with about the same effectiveness as JP-4. We would also expect similar results with other scavengers such as the orthoesters.

Corrosion and compatibility tests were not made with these fuels since there should be nothing present to alter results obtained with JP-4 fuel.

5. Quantitative Analysis of 2, 2-Dimethoxypropane in JP-4

A simple procedure for the analysis of 2, 2-dimethoxypropane in JP-4 in concentrations within the range of "use concentrations" (less than 0.2%) has been developed. The method avoids the numerous difficulties involved in a direct analysis of 2, 2-dimethoxypropane by allowing determination of the total amount of methanol and acetone in the JP-4 before and after hydrolysis of the 2, 2-dimethoxypropane. Since the quantities of acetone and methanol are directly related to the amount of 2, 2-dimethoxypropane that has been hydrolyzed, the difference in the above determinations indicates the concentration of 2, 2-dimethoxypropane in the fuel.

One milliliter of distilled water is added to 100 ml of the JP-4-additive sample. The mixture is vigorously agitated for 15 minutes, and the two phases are allowed to settle for 30 minutes. Similarly, a 100 ml JP-4-additive sample is extracted with 1.0 ml of 0.1 N sodium hydroxide. One-microliter portions of the aqueous extracts are chromatographed on a Perkin Elmer Vaporfractometer equipped with an 8-ft column of 60-80 mesh firebrick coated with 10% triethyleneglycol. At a flow rate of 65 cc. of helium per minute and a column temperature of 75°C the retention times of acetone, methanol and water are 1.56, 4.09, and 11 minutes, respectively. The areas under the acetone and methanol peaks are measured by a planimeter. Correlations between peak areas and concentrations are obtained by adding known amounts of acetone and methanol to additive-free JP-4 samples, extracting and chromatographing. Since the partition coefficients for acetone and methanol in water and JP-4 are slightly different from acetone and methanol in 0.1 N sodium hydroxide and JP-4 it is necessary to prepare standards for both extracts. Since complete hydrolysis of the 2, 2-dimethoxypropane additive occurs in the water extract and since no hydrolysis occurs in the 0.1 N sodium hydroxide extract, the difference in the two measurements is directly related by the stoichiometry of the hydrolysis reaction to the concentration of 2, 2-dimethoxypropane.

It is quite likely that similar analytical techniques could be worked out for alternate reactive chemical scavengers, such as the orthoesters.

6. Comparison of Scavengers with Phillips 55MB

Phillips Fuel Additive 55MB was run in our Low-Temperature Filter-Icing Apparatus for comparison with water-reactive additives. Phillips, Boeing, and WADD have reported that 0.1% of additive will depress the filter-icing temperature of JP-4 containing 500 mg/l of water to less than -65°F. In our LTFIA method, a 0.1% concentration of 55MB resulted in a filter-icing temperature of -27°F, and 0.15% of 55 MB resulted in a filter-icing temperature below -65°F.

This indicates that different factors may be present in the various filter-plugging test rigs. In general, however, it appears that the results obtained under this contract may be conservative.

A summary of minimum concentrations to achieve pumpability below -65°F shows that one of the water-reactive additives is more efficient than 55MB, and two others are equally efficient:

Phillips 55MB	0.15%
2, 2-Dimethoxypropane	0.10%
Trimethyl Orthoformate	0.15%
Trimethyl Orthoacetate	0.15%
Trimethyl Orthovalerate	0.40%

A brief comparison of compatibility with EC776SR topcoating has indicated that Phillips 55MB has about the same characteristics as 2, 2-dimethoxypropane.

7. Economic Considerations

The cost of effective water-reactive chemicals must be considered in the final selection of a fuel additive. We have obtained current market prices for the most promising additives. These prices are summarized in Table XII. It should, of course, be understood that these figures are based upon current demand and capacity. In the event that large-scale use of such materials in aviation fuels occurred, appreciable reductions in cost would be obtained.

The prices in Table XII show that on a pound-for-pound basis the 2, 2-dimethoxypropane and the trimethyl orthoformate are roughly competitive since about the same weight of either additive would be required. The trimethyl orthoesters of the higher acids are much too expensive for consideration at the present time.

TABLE XII

COMPARATIVE PRICES OF ADDITIVES FOR JET FUEL

Additive	Manufacturer	Price per Pound
2, 2-Dimethoxypropane	Dow Chemical	$0.525
Trimethyl Orthoformate	Kay-Fries	0.76
Trimethyl Orthoacetate	Kay-Fries	7.50
Trimethyl Orthovalerate	Distillation Products Ind.	Above 7.50/lb
Phillips 55MB	Phillips Petroleum Co.	0.25

The price of Phillips 55MB is included because this nonreactive additive is effective in depressing the freezing point of water and is currently being flight-tested by the Air Force. In general it appears that the reactive scavengers are as effective in preventing filter icing as a nonreactive additive such as Phillips 55MB. That is, 0.1% by volume of either type of additive is sufficient to insure fuel pumpability at temperatures as low as -65°F. Thus, outwardly the nonreactive system would appear to cost approximately one half as much as a reactive water scavenger.

Under actual use conditions, however, it is possible that much smaller quantities of the reactive additive could be used. Since water would be destroyed and removed from the aircraft, there should be a gradual dehydration of the aircraft fuel system. Pockets of trapped water would be consumed so that the only concern would be the moisture which enters with the fuel and that which enters the system from the atmosphere. On the basis of current knowledge it appears that such moisture could be effectively controlled by lower concentrations of reactive additive. Thus additional study would be required to predict accurately the economics involved in reactive additive utilization.

8. Patent Situation

The use of 2, 2-dimethoxypropane in liquid hydrocarbon fuels is described in U. S. Patent No. 2, 878, 109, which was issued on March 17, 1959, to the Skelly Oil Co. This patent, entitled Liquid Fuel Composition, concerns liquid hydrocarbon fuels containing about 0.1 to 2.0 volume per cent of 2, 2-dimethoxypropane. The use of this additive in fuel oils such as gasoline is described and its use in jet fuels is mentioned. The acid catalysts described in this patent are selected from a listing of amine hydrochlorides.

III. SUMMARY

On the basis of work accomplished under this contract, it now appears that the use of a water-reactive chemical additive to prevent icing in military aviation fuels is a completely feasible technique. Four compounds have been found effective in preventing filter icing when fuel temperatures are reduced to -65° F. Although each of the effective compounds requires acid catalysis for the desired hydrolysis reaction, several alternate catalyst systems have been evaluated to overcome potential problems associated with corrosion.

Since we do not have at this time complete information on compatibility of the effective materials with all fuel system components, it is not possible to make a single recommendation for a reactive additive system. Instead, we shall present a summary here of the effective materials and catalysts, the required concentrations, and the performance to be expected of a successful water scavenger system.

A. EFFECTIVE SCAVENGERS

1. 2,2-Dimethoxypropane

This material is effective at a concentration of 0.1% in preventing filter plugging when 500 mg of water per liter of fuel is present. This is the most effective reactive material we have found. It is available commercially at $0.525 per pound and has passed all of the evaluation tests.

2. Trimethyl Orthoformate

This material is effective at a concentration of 0.15% in preventing filter plugging when 500 mg of water per liter of fuel is present. It is available commercially at $0.76 per pound. While this material has not been subjected to as many evaluation tests as the 2, 2 dimethoxypropane, it appears to be about as effective in every respect.

3. Trimethyl Orthoacetate

This material is effective at a concentration of 0.15% in preventing filter plugging when 500 mg of water per liter of fuel is present. While it appears to be as effective as the two previously mentioned materials, its cost of $7.50 per pound makes it less attractive.

4. Trimethyl Orthovalerate

Because of its higher molecular weight, this material requires 0.4% concentration to prevent filter plugging when 500 mg of water per liter of fuel is present. This material is the most expensive of the four candidates. Because of its higher cost and the higher concentration required, it should be considered only as a last resort.

B. EFFECTIVE CATALYSTS

1. Hydrogen Chloride

HCl may be used either in methanolic solution or it may be generated *in situ* by the hydrolysis of acetyl chloride. A concentration in the range of 0.015 milliequivalents of acid per ml of additive is required. In these low concentrations corrosivity is greatly reduced. Corrosion inhibitors E and J have been found effective in reducing corrosion.

2. Phosphoric Acid

H_3PO_4 has been used in methanolic solution. A concentration in the range of 0.040 milliequivalents per ml of additive is required. This material is less corrosive than HCl.

3. Boron Trifluoride

BF_3 has been used in methanolic solution. A concentration in the range of 0.025 milliequivalents per ml of additive is required. Essentially no corrosive action has been observed with this material.

4. Other

Other effective catalysts which have not been thoroughly screened include: nitric acid, p-toluene sulfonic acid, trichloroacetic acid, trifluoroacetic acid.

C. CONCLUSIONS

We can expect that a reactive chemical additive system, including a proper catalyst and a corrosion inhibitor, could be injected directly into military aviation fuels during transfer operations. The additive should immediately react with any water present in the fuel and should provide continued protection as the fuel is stored or transferred to the aircraft. Once the additive-treated fuel is in the aircraft storage system it should start to react with and remove any free water or ice trapped in the system. Total removal of such water or ice should be accomplished after a period of continual use of additive-treated fuel. The additive system and the reaction products are soluble in the fuel and are combustible so that no detrimental effects upon the fuel system or the engine should be expected.

D. RECOMMENDATIONS

We recommend that the Air Force give serious consideration to utilization of a chemically reactive anti-icing additive for aviation fuels. While additional testing will be required before actual flight tests can be made, we feel that the potential advantages of such a reactive system are more than sufficient to warrant the necessary expenditure of time and money.