

NATIONAL BUREAU OF STANDARDS REPORT

9499

SNOWMELTING SYSTEMS FOR HANGAR DOORS

By

J. C. Davis and P. R. Achenbach

Environmental Engineering Section

Building Research Division

Institute ~~of~~ Applied Research *Technology*
for

Final Report

to

Naval Facilities Engineering Command

Office of Chief of Engineers

United States Air Force



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Snow-melting Systems for Hangar Doors

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I. Introduction

The agencies of the Department of Defense employ snow-melting systems in cold climates for the area under and adjacent to the large sliding doors of aircraft hangars to expedite snow removal and thus facilitate rapid movement of aircraft into and out of these structures. These systems usually are installed in areas where the winter design temperature is 10 °F or lower, and in any climate where the average annual snowfall is 20 inches or more.

A typical snow-melting system, as used by the U.S. Air Force for this purpose, consists of a heat exchanger with steam at 40 to 100 psig, or high-temperature water circulating through the primary circuit of the exchanger; with an antifreeze heat-transfer fluid circulating through the secondary circuit; pipe coils embedded in the concrete under and adjacent to the doors; one or more circulating pumps; and automatic controls for regulating the flow rate and temperature of the antifreeze liquid in response to the need for heat in the embedded pipes. The antifreeze heat-transfer fluid is usually a glycol solution, although special oils have been used in some cases. A few installations have used two stages of heat exchange between the primary heating fluid and the antifreeze heat-transfer medium. The Bureau of Yards and Docks makes considerable use of electric heating elements embedded in concrete for snow melting at hangar doors. The U.S. Air Force also uses similar systems to provide floor panel heating in some of their aircraft hangars.

At the request of the Tri-Service Defense Agencies, the National Bureau of Standards made an investigation of corrosion and sludge formation, which have created serious operating and maintenance problems in glycol systems. A concurrent study also was made of the properties of a number of other heat-transfer liquids to determine their suitability for snow-melting and panel-heating systems.

1.1 Scope and Purpose

The U.S. Air Force has experienced operating problems related principally to the formation of sludge and to corrosion in the antifreeze pipe circuit in snow-melting systems using glycol solutions. These problems were particularly serious at Minot Air Force Base. In the Minot system, where sludge formation was excessive, the high-temperature water at an inlet to the heat exchanger was 380 °F, and the temperature of the ethylene glycol solution at the supply to the pipe grid in the concrete was as high as 160 °F. Furthermore, the spigot water used for making the ethylene-glycol-water solution had an abnormally high percentage of dissolved solids. Purchase specifications for the glycol solutions have not provided for any specific grade of glycol for this application, and the operating practices have not prevented mixing of different proprietary products, nor provided for periodic analysis and control of the corrosion inhibitors in the system at any of the Air Bases employing snow-melting systems. Apparently, spigot water has typically been used at these Air Bases, rather than making any attempt to use water with a smaller amount of dissolved solids.

The first objective of this study, was (a) to evaluate the present state of knowledge on the chemical, physical, and engineering properties of glycol solutions, special oils that have been used in snow-melting systems, certain halogenated hydrocarbons, silicate esters and related derivatives, organo silanes and disiloxanes, and other fluids that possess many of the desired characteristics for this application. Snow-melting systems that do not employ liquid antifreezes were also investigated. Further objectives were (b) to prepare a specification for the purchase of heat-transfer media, and (c) to describe the operating conditions under which glycol solutions and oils could be used in snow-melting systems. Included in the third objective was the description of procedures for monitoring the depletion and for replacement of the corrosion inhibitor in glycol solutions, or for replacement of the solution itself; finding methods for monitoring oil; determining what modifications in the heat-exchange apparatus and controls might improve the application of various heat-transfer media to snow-melting; and determining whether laboratory work in this field was needed or appeared desirable. These objectives, in the main, have been reached.

Information on the design and construction of snow-melting systems was not requested originally, but a number of important factors, which might lead to improved operation, were investigated. These are discussed as an aid to engineers, designers, and maintenance personnel. Many of the findings would be applicable to floor radiant-heating systems employing ethylene glycol. Some of the reported data were taken from these radiant systems.

Only a limited amount of experimental work, which was on the study of the use of ion-exchange resins for producing de-ionized water in a snow-melting system, was done by the National Bureau of Standards. Information was obtained largely through literature search, visits to the chemistry or engineering departments of the manufacturers of heat-transfer media, to Government agencies such as Aberdeen Proving Ground, to snow-melting systems in office buildings or plants, and through discussions with staff members of the National Bureau of Standards.

2. THE ETHYLENE GLYCOL SYSTEM

2.1 Description of Air Force Base Snow-Melting Systems Visited by the National Bureau of Standards Personnel

Personnel of the National Bureau of Standards visited Westover Air Force Base, Mass., the Plattsburg Air Force Base at Plattsburg, N.Y., and the Minot Air Force Base at Minot, N. Dak.

At these three Bases, the source of heat at the primary circuit of the snow-melting or floor radiant-heating systems was either steam or high-temperature water (HTW). Plattsburg AFB and Minot AFB used only HTW, while Westover AFB used both heating media. The temperature of the water at the supply to the heat exchanger (converter) in the HTW systems was about 380 °F at all three Bases. At Westover AFB and Plattsburg AFB, the temperature of the glycol solution at the supply to the pipe grids within the concrete was about 110 °F; but at Minot AFB, the antifreeze temperature at the supply to this grid was in the range from 125 to 160 °F.

Typical temperatures of the HTW or steam in the primary circuit of the heat exchanger, and the ethylene glycol solution in the secondary circuit, for snow-melting or radiant-heating systems at all three Bases are shown in table 1.

During the 1962-63 winter season at Minot Air Force Base, it was reported by the office of the Civil Engineer at that Base that the use of automotive types of inhibited ethylene glycols produced sludge at the strainers in a number of snowmelting systems. All of the glycols were purchased on the open market without specification. It was also reported that conversion to a product designed especially for snow-melting systems and known as Dowtherm SR-1 was tried on an experimental basis in one building with good results. In the following thirty-day period no plugged strainers were evident in that building. It was reported finally in April 1954 that conversion to the new material was made in almost all of the snow-melting systems and radiant heating systems with the same good results.

The Dowtherm SR-1 was mixed with water in the ratio of 40 parts of Dowtherm to 60 parts of water. Untreated spigot water was used with the 40/60 solution. The Dow Company has assisted in the monitoring of the Dowtherm solution, but no significant addition of the inhibitors or replacement of the antifreeze had been made by 1965.

Investigations revealed that two factors contributed to the formation of the sludge when the commercial types of automotive antifreezes were used: (1) the large proportion of dissolved solids in the spigot water and (2) the high temperatures encountered in the systems.

TABLE 1

FLUID TEMPERATURES OF PRIMARY AND SECONDARY SYSTEMS IN THE HEAT EXCHANGER
FOR SNOW-MELTING OR RADIANT-HEAT SYSTEMS AT WESTOVER,
PLATTSBURG, AND MINOT AIR FORCE BASES, °F

Westover Air Force Base

Multipurpose Hangar Nose Dock, 23 (HTW)

	<u>Primary</u>	<u>Secondary</u>
Supply	377	119
Return	181	108

Multipurpose Hangar Nose Dock, 32 (Steam)

Supply	240	98
Return	Not available	87

Multipurpose Hangar Nose Dock, 34 (Steam)

Supply	233	118
Return	Not available	103

D.C. Hangar System (Snow-Melting System) (HTW)

Supply	383	123
Return	245	104

Plattsburg Air Force Base

Building 2763 (M.A.B. Hangar) (HTW)

Supply	370	113
Return	150	97

Building 2763 (Radiant Heating, Floor)(with HTW control valve closed)

Supply	385	102
Return	150	98

Building 2763 (with HTW control valve open)

Supply	382	111
Return	135	98

Nose Dock 2808 (with HTW control valve open)

Supply	352	88
Return	330	Not available

Minot Air Force Base

Nose Docks (HTW)

Supply	380	135 - 140
Return	Not available	Not available

The ethylene glycol used at Westover AFB and Plattsburg AFB, where less corrosion occurred in the system, was also purchased without specifications, and was of the type commercially available for automotive antifreeze solutions. No attempt was made to consistently use one brand in the same system from season to season, and there was evidence that brands were mixed in several of the systems. In some cases there had been no clean-out and recharging of the systems for 6 or 7 years. Despite these deviations from good practice, deterioration of the antifreeze solutions was not excessive, although replacements have been recommended in some cases. Samples were obtained from three systems from each base and analyses made later at NBS. Tables 2 and 3 give identification and results of the analyses of the samples from the three systems at Westover AFB, and tables 4 and 5 provide similar information for the samples from the three systems at Plattsburg AFB.

Plattsburg AFB and Westover AFB are in a northern area of the United States, but do not experience the extreme cold temperatures and high winds that occur at Minot AFB in North Dakota.

The snow-melting system at Westover AFB was an open type, and those at Plattsburg AFB and Minot AFB were closed types. There was an expansion tank in the system in each case; at Westover AFB it was about 50 feet above ground level and 15 or 20 feet above ground level at the other two Bases. The high level of 50 feet at Westover AFB prevented overflow of the tank if air became trapped in the system or if boiling of the solution occurred.

Each of the snow-melting systems at the three bases used a branched pipe grid in the concrete near the rails for the sliding doors. In each system there were balancing cocks to equalize the rate of flow in the different branches.

Table 2

Identification of Antifreeze Samples

from Westover Air Force Base		
Sample No.	Systems from which sample was taken	Color or other identification
1	Floor radiant-heating system, D.C. Hangar	Pink, light, clear.
2	Snow-melting system, Nose Dock No 32	Brownish pink, no sediment. In system about 6 years.
3	Snow-melting system, D.C. Hangar	Almost colorless. Small amount of sediment in bottom of bottle and some in suspension. Sediment dark brown. In system 6 to 8 years.

TABLE 3

Analysis of Antifreeze Samples from Westover Air Force Base

Sample No.	pH of sample as received	Reserve alkalinity of a 20 ml sample titrated with 0.1N HCl a/ ml	Boron Mg/20 ml	Sediment Mg/100 ml	Iron calculated as Fe_2O_3 Mg/100 ml	Freezing point °F
1	7.8	6.6	13	1	1	+4
2	7.5	6.3	11	2	1	-50
3	7.7	7.8	17	28	22	-6

a/ 20 ml sample used on the assumption that the material was 50 percent aqueous solution. For the Standard ASTM method of test D1121-54 in which the ethylene glycol is not diluted, 10 ml is used. A discussion of this test is given in Section 3.

When the reports of the analyses were supplied to Headquarters USAF, it was recommended that some attention be given to solutions 1 and 3, due to their high freezing points. Reserve alkalinity was low for all three samples, but such low values without knowledge of previous history are not always indicative of the need for renewal.

Table 4

Identification of Antifreeze Samples

from Plattsburg Air Force Base

Sample No.	Systems from which sample was taken	Color or other identification
1	Building 2763, snow-melting system	Cider colored, murky. In system since 1956.
2	Nose Dock 2809, snow-melting system	Brown-orange color, clear with very small trace of black and brown sediment.
3	Building 2763, radiant-heating system	Light brown, murky. Brown sediment in bottom of bottle.

Table 5

Analysis of Antifreeze Samples

from Plattsburg Air Force Base

Sample No.	pH of sample as received	Reserve alkalinity of a 20 ml sample titrated with 0.1N HCl a/	Boron Mg/20 ml	Sediment Mg/100 ml	Iron calculated as Fe ₂ O ₃ Mg/100 ml	Freezing point °F
1	7.1	21.0	42	55	38	-50
2	7.0	25.0	49	7	6	-50
3	7.3	9.5	16	200	143	-26

a/ 20 ml sample used on the assumption that the material was 50 percent aqueous solution. (See note a in table 2).

New solutions for systems 1 and 3 were recommended by NBS, due to the large amount of sediment.

Heat exchange between the steam and glycol solution, or the HTW and the glycol solution, was accomplished with the use of heat exchangers, the high-temperature media flowing through the tubes of the heat exchanger and the glycol between the tubes and the shell. All systems used modulating valves to control the flow of the steam or water into the heat exchanger, and ultimately the delivered temperature of the glycol solution. Pneumatic or electronic controls were used for the valves, which responded to the outdoor temperature or the temperature of the glycol solution in the heat exchanger. In nearly all cases, the modulating valve was "normally closed", so that when a power outage occurred, or the circulating pump was otherwise automatically shut off, the primary medium would not overheat the glycol solution lying stagnant in the heat exchanger. At Westover AFB, however, one floor radiant-heating system employed an electronically-controlled valve which was "normally open". However, according to the engineers, power failure or manual shut-down did not occur frequently at this Base.

At Plattsburg AFB, a by-pass around the heat exchanger was part of the control system for one floor radiant-heating system. When the outdoor temperature was high, a large proportion of the HTW by-passed the heat exchanger, keeping the temperature of the glycol solution in the heat exchanger at a relatively low temperature. Modulation of the flow of HTW through the heat exchanger was regulated pneumatically by a 3-way valve. There was an orifice in this valve so there could be no positive shut-off to allow the temperature in the heat exchanger to become excessive. In a snow-melting system in one nose dock at this Base, the modulating valve was by-passed with a manual valve, to be used if the modulating valve failed.

Steam and HTW were used as a heat source in different systems at Westover AFB. Where steam was used, the heat exchangers were about 2-1/2 feet long. Pressure of the steam at the input to these heat exchangers was about 10 pounds, with a saturation temperature of about 240 °F. The heat exchangers used with the HTW at the other two Bases were about 5 feet long. Most were manufactured by the Old Dominion Iron and Steel Corporation.

There were no strainers in the systems at Westover AFB and Plattsburg AFB. The spigot water used for the ethylene glycol solutions at these two bases was relatively low in dissolved solids. Analyses of water samples from Westover, Plattsburg, and Minot Air Force Bases were obtained from the Geological Survey and the Hall Co., of Pittsburgh, with the following results. The low concentration of ions at Westover AFB will be noted.

Table 6

Analysis of Water

	(Concentration of ions in ppm)		
	<u>Westover AFB*</u> Feb 1, 1965)	<u>Plattsburg AFB</u>	<u>Minot AFB</u>
Chlorides	2.8	6	105
Sulfates	6.9	10	180
Bicarbonates	6.0	55	230
Carbonates	0	--	10
Iron	0.2	--	0.1
Copper	---	--	0.3
Calcium plus magnesium	4 5	21	150
pH	6.4	7.0	9.0

* Conductivity at 70 °F, 35 μ mhos.

Although most of the systems at Minot AFB eventually used Dowtherm SR-1 as the heat-transfer medium, one system was filled with a clear solution, slightly green in color, which contained globules of black material having diameters of 1/4 to 1/2 inch. These were analyzed at NBS with following results:

Table 7

Analysis of Black Deposit in Sample
From Minot AFB

Weight of the deposit in sample, 16.7 g.
Volume of liquid in sample, 400 ml.
Percentage by weight of materials in sample:

Organic Material	16%
Fe ₂ O ₃ ,	80%
Material not soluble in HCl,	1%
Not determined,	<u>3%</u>
	100%

It is generally recognized in the literature [1,2,3] and by investigators, that the temperature of the older types of inhibited ethylene glycol for automotive use should be maintained at 300 °F or less. When these types of glycol were used at Minot AFB and the temperature of the medium in the primary system was about 330 °F, it is probable that the ethylene glycol in areas of the heat-exchanger where the glycol was stagnant or in other areas where sludge had collected, was subjected to temperatures in excess of 300 °F. The analysis of the spigot water used for the solutions showed a high concentration of chloride, bicarbonate, sulfate, and carbonate ions, all of which will accelerate corrosion, according to the principal manufacturers' literature.

At the Westover and Plattsburg AFB's, where the water had a low percentage of dissolved solids, and where the temperatures in the system were well below 300 °F, sludge was generated at a much slower rate. The NBS representatives were advised that the solution had not been changed, except for make-up, for from 5 to 7 years. Make-up was reported to be about 10 percent a year.

Further information on installation and maintenance practices at Grand Forks Air Force Base was supplied by letter from Mr. John J. Kotalik, Deputy Civil Engineer, Grand Forks AFB, North Dakota. Information from this Base was significant because of its northern climate, and because this Base had experienced some sludge at the strainers in one system. Table 8 shows an analysis of the water at the Grand Forks AFB.

Table 8

Concentration of ions in ppm	
Chlorides	3
Sulfates	16
Bicarbonates	128
Carbonates	0
Iron	0.2
Copper	--
Calcium plus magnesium	38
pH	7.6
Conductivity at 70 °F, 293 μmhos	

It is interesting to note the marked difference in amounts of dissolved solids between the water at Grand Forks AFB and at Minot AFB, which is less than 200 miles away.

3. GLYCOLS AND THEIR INHIBITORS

3.1 Aqueous Glycol Solutions

Glycols can be defined as those compounds which have two hydroxyl (OH) groups attached to separate carbon atoms in an aliphatic carbon chain. They are known as polyhydric alcohols, and sometimes as diols. The simple glycols are stable, odorless, water-white liquids when pure. They have higher boiling points than water, and those used most often in antifreeze solutions freeze at temperatures below 32 °F. Aqueous glycol solutions of selected proportions have been used extensively throughout the world as heat-transfer liquids, because of their low freezing point, low viscosity, and good heat-transfer properties. Ethylene glycol is used most often in antifreeze systems. Propylene glycol is used where it is believed that food might be exposed to the solutions.

Until a few years ago snow-melting systems employing ethylene glycol as the heat transfer media used automotive ethylene glycol solutions entirely. Solutions for snow-melting systems are typically 40 percent by weight of ethylene glycol, with a freezing point of -11 °F, or 50 percent by weight of ethylene glycol, with a freezing point of -32 °F. Federal Specification No. 0-A-548a is available for use in purchasing ethylene glycol for automotive purposes. Two types are covered: type I, based on a fixed formulation with borax as the chief inhibitor, and type II which allows the use of any type inhibitor, and which must pass certain qualification tests. The automotive ethylene glycols, however, are designed principally for use in automobile systems where the glycol is subjected to different conditions and sometimes different materials than those encountered in snow-melting systems. Specifications for their purchase allow marginal products

according to present-day standards. Further, the inhibitors in these glycols vary from one manufacturer to another, and mixtures of different types of inhibitors can lead to difficulty.

Two proprietary products were found by the NBS investigations to be satisfactory and designed specifically for snow-melting systems: Dowtherm SR-1, manufactured by the Dow Chemical Co., of Midland, Mich., and UCAR 17 Thermofluid, manufactured by the Union Carbide Chemicals Co., a division of the Union Carbide Co., of New York, N Y. The UCAR 17 Thermofluid material is similar to its predecessor, PM 1717, made by the same company. Both products consist largely of ethylene glycol with inhibitors. All additives in these products are not known; however, analyses performed at NBS revealed that both products contain mercaptobenzothiazole and either sodium hydrogen phosphate or potassium hydrogen phosphate. The investigation also showed that an ethylene glycol solution developed by the Coatings and Chemical Laboratory of the U.S. Army at Aberdeen Proving Ground was satisfactory for snow-melting systems.

Dowtherm SR-1 does not contain borax. The buffering agent in Dowtherm SR-1 is not known. The UCAR-17 Thermofluid contains borax, which belongs to a class of anodic inhibitors and acts as an agent to neutralize the action of contamination products [4], as well as a buffering agent to maintain a high pH [5]. The use of a buffering agent is a technique employed in many commercial products in which, for a considerable range, relatively large additions of acidic products have very little effect on pH. A good exposition of the chemical theory of the buffering action is given by Koltoff and Sandell [6].

The purpose of the mercaptobenzothiazole (MBT) is to inhibit corrosion of copper, and certain of its alloys, in water and aqueous solutions [7]. A water solution of sodium MBT is sometimes known by the proprietary name of "Nacap". The purpose of the potassium hydrogen phosphate or sodium hydrogen phosphate is to provide anodic protection, and protection for ferrous and certain non-ferrous metals [5,7]. This inhibitor also serves as a buffer. Both of these inhibitors are relatively new to the industry and their use has contributed to the greatly increased life of ethylene glycol solutions.

The NBS was informed by a technical representative of the Union Carbide Chemicals Co. that UCAR 17 has approximately the same formulation as the ethylene glycol product developed by the Chemical Coatings Laboratory of the U.S. Army Aberdeen Proving Ground. Analysis of the UCAR 17 material at NBS showed this to be essentially true, except that potassium hydrogen phosphate is used instead of sodium hydrogen phosphate, and the amount of MBT is considerably less.

The inhibited ethylene glycol developed by the Chemical Coatings Laboratory has shown long life, both in simulated service tests in the laboratory, and in actual automotive service tests at the Proving Ground. The simulated service test consists of a mechanical unit arranged to permit the test solution to be circulated in a closed system at a controlled circulation rate and temperature. In these simulated service tests, using a 50/50 mixture of ethylene glycol and water, good performance was obtained for 7000 hours. (The old type I glycol with borax of Federal Specification O-A-548a had an average life of about 2000 hours). Good performance also

was obtained for about 20,000 miles of service for staff cars, and about 50,000 miles of service for private cars. Information on the development and testing of the Chemical Coatings Laboratory formulas can be found in Aberdeen Proving Ground CCL Report No. 156 [8]. In bench-corrosion tests described in this report, a set of six metal test specimens known as coupons were immersed in a glass flask containing the test solution. The solution is aerated and refluxed at 180 °F for 192 hours, after which the metal specimens are examined for extent of corrosion. The report states that in almost every instance use of the Coatings and Chemical Formula (Formula B by their designation) lessened the weight-loss of metal coupons, including aluminum, over other formulas tested. The formula also performed satisfactorily with water containing 100 ppm of Cl^- , $\text{SO}_4^{=}$, and HCO_3^- . Results relating to protection against solder corrosion were not conclusive, however. The laboratory stated that a harmless white flocculent precipitate consisting of undissolved MBT is suspended in the solution for reserve purposes. This precipitate will pass through the strainers and will not deposit anywhere in a snow-melting system.

To purchase Dowtherm SR-1, or equivalent material manufactured by a company other than the Dow Chemical Co., it is suggested the specification given in Table 9 for Type A inhibited ethylene glycol be used. To purchase UCAR 17 or equivalent, it is suggested the specification in Table 10 for Type B material be used.

TABLE 9

SPECIFICATIONS

FOR

TYPE A INHIBITED ETHYLENE GLYCOL FOR SNOW-MELTING SYSTEMS

(For use in the purchase of Dowtherm SR-1 or equivalent material)

Property	Limits	Test Method
pH (50% solution by volume)	8.0 - 9.5	ASTM Designation D1287
Reserve alkalinity (ml 0.1 N HC/10 ml), minimum	10	ASTM Designation D1121
Phosphate ion content, % by weight, minimum	1.0	Paragraph A ^a
Mercaptobenzothiazole ion content, % by weight, minimum	0.04	Para. 4.4.3.1. of Federal Specification 0-1-490a, Inhibitor Corrosion, Liquid- Cooled System
Total glycols having hydroxyls on adjacent carbons, % by weight, minimum	92	Para. 4.6.4. of Federal Specification 0-A-548a, Anti- freeze, Ethylene Glycol, Inhibited
Water, % by weight, maximum	3.0	ASTM Designation D1123
Glycols [*] other than ethylene glycol, % by weight, maximum	3.0	Obtained by calculating the difference between the total of percentages for all other items and 100 percent.
Chlorides	To pass test	Paragraph B ^b
Ash, % by weight, maximum	3.0	ASTM Designation D1119
Arsenic, % by weight, maximum	100 ppm	Gutzeit method. Described in Reagent Chemicals, Am. Chem. Soc. Specifications, 1955

* Glycols can be defined as those compounds which have two hydroxyl (OH) groups attached to separate carbon atoms in an aliphatic carbon chain.

(a) Shown on page 20

(b) Shown on page 21

TABLE 10
SPECIFICATIONS
FOR

TYPE B INHIBITED ETHYLENE GLYCOL FOR SNOW-MELTING SYSTEMS

(For use in the purchase of UCAR-17 Thermofluid or equivalent material)

Property	Limits	Test Method
pH (50% solution by volume)	8.3 - 9.8	ASTM Designation D1287
Reserve alkalinity	20	ASTM Designation D1121
Phosphate ion content, % by weight, minimum	0.45	Paragraph A ^a
Mercaptobenzothiazole ion content, % by weight, minimum	0.07	Para. 4.4.3.1 of Federal Specification 0-1-490a, Inhibitor Corrosion, Liquid Cooled System
Borax, % by weight, minimum	1.3	Para. 4.4.3.2 of Federal Specification 0-1-490a, Inhibitor Corrosion, Liquid Cooled System
Total glycols, having hydroxyls on adjacent carbons, % by weight, minimum	93	Para. 4.6.4 of Federal Specification 0-A-548a, Anti- freeze, Ethylene Glycol Inhibited
Water, other than water of hydration in borax % by weight, maximum	3.0	ASTM Designation D1123
Glycols* other than ethylene glycol, % by weight, maximum	3.0	Obtained by calculating the difference between the total of percentages for all other items and 100 percent
Chlorides	To pass test	Paragraph B ^b
Ash, % by weight, maximum	3.0	ASTM Designation D1119
Arsenic, % by weight, maximum	100 ppm	Gutzeit method. Described in Reagent Chemicals, Am. Chem. Soc. Specifications, 1955

* Glycols can be defined as those compounds which have two hydroxyl (OH) groups attached to separate carbon atoms in an aliphatic carbon chain.

(a) Shown on page 20

(b) Shown on page 21

Paragraph A. Phosphate (PO_4^{3-})

A weighed 5-ml sample is diluted to 1 liter in a 1-liter volumetric flask and a 2-ml aliquot of this is used. Twenty-five ml of 0.5 N hydrochloric acid is added, followed by 1 ml of ammonium molybdate reagent and 1 ml of p-methylaminophenol sulfate reagent. The color is allowed to develop for 2 hours and then the volume is made up to 50 ml with 0.5 N hydrochloric acid. The transmittance of the solution is read at 650 m μ . Standards containing 0, 10, 25, 50, and 100 μg are colored in a similar manner for a standard curve. The amount of phosphate present in the aliquot is determined from the curve.

Ammonium molybdate reagent solution. 50 grams of ammonium molybdate reagent $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ are dissolved in one liter of 1 N sulfuric acid.

p-Methylaminophenol sulfate solution. 2 grams of p-methylaminophenol sulfate are dissolved in 100 ml of water. To 10 ml of this solution, add 90 ml water and 20 grams of sodium bisulfite.

Standard phosphate solution (1 ml = 1 μg PO_4^{3-}). 0.143 grams of KH_2PO_4 are dissolved in water and diluted to 1 liter. 10 ml of this solution are diluted to 1 liter.

Alternate Method for Determination of Phosphate (PO_4^{3-}). Para. 4.4.3.3 of Federal Specification 0-1-490a, Inhibitor Corrosion, Liquid-Cooled System, except that for the calculation of the weight of the phosphate ions use the milli-equivalent of PO_4 which is equal to $0.004129 = \left(\frac{94.97}{23 \times 1000}\right)$.

Paragraph B. Chlorides

To 10 ml of concentrated inhibited ethylene glycol add 10 drops of concentrated nitric acid and agitate. Add 1 ml of a 3 percent aqueous solution of silver nitrate and filter. Discard the filtrate. Wash the residue with concentrated ammonium hydroxide, recovering the filtrate. Acidify the filtrate with concentrated nitric acid. No precipitate shall form within 30 minutes. A slight turbidity is allowed.

Paragraph C.

The undiluted glycol shall be shipped to the user in containers made of steel and which do not contain tin.

To obtain the glycol solution recommended by the Coatings and Chemical Laboratory at Aberdeen Proving Ground, the purchaser buys the relatively inexpensive Type I borax inhibited ethylene glycol under Federal Specification O-A-548a, then adds packaged inhibitors in accordance with the weight requirements shown below. The inhibitors are added at the optimum rate of 1 oz. of the inhibitor to each two quarts of the water used. The Type I borax inhibited ethylene glycol can be procured through the military supply system. The packaged inhibitors are covered by Federal Specification O-I-490a and can be procured from the General Services Administration stock No. 6850-5842707.

Table 11

Weight Requirements for 6 and 8-1/2 oz Packages of Formula B

Composition	6 oz (170 gm) package weight, <u>in grams</u>		8½ oz (242 gm) package weight, <u>in grams</u>	
	Units			
	<u>Min.</u>	<u>Max.</u>	<u>Min.</u>	<u>Max.</u>
Mercaptobenzothiazole	24.8	26.6	35.3	37.7
Na ₂ B ₄ O ₇ , anhydrous	67.0	68.8	95.5	97.9
Na ₂ HPO ₄ , anhydrous	14.7	16.5	21.1	23.5

Specification O-I-490a also lists methods for testing for the three chemicals in the package.

A further advantage of the new inhibitors is their ability to recondition the solution with the addition of small amounts of inhibiting material.

Type A, Type B or the Coatings and Chemical Laboratory Solution can be stored satisfactorily in large steel drums, but precaution must be taken not to expose them to a temperature of less than 10 °F, since the freezing point of undiluted ethylene glycol is +9 °F. In all cases, the glycol should be thoroughly stirred and mixed before use in the system. None of the three types should be stored in tin-lined containers. Mercapto-benzothiazole, an organic compound, will react with the tin.

As a result of the findings at Minot Air Force Base and of discussions with the Coatings and Chemical Laboratory, the Dow Company and Union Carbide Company, there is some evidence to show that Dowtherm SR-1, UCAR 17, and type I borax - inhibited glycol with formula B material added, can be used for somewhat higher temperatures than the borax-inhibited glycols purchased under specification 0-A-548a.

3.2. MONITORING AND MAINTENENCE OF ETHYLENE GLYCOL SYSTEMS

3.2.1 Importance of Water Quality

It is well known that water high in dissolved solids, when used in aqueous glycol solutions, will speed corrosion of the metals in an automotive or snow-melting system. Chlorides and sulfates have been long established as water contaminants that aggravate corrosion [9], and also bicarbonates and carbonates. Some indication of the effect of water quality on auto-cooling-system corrosion is presented in a paper by Boehmer and Compton [10]. These effects should apply, in some measure, to snow-melting systems.

Several ways to obtain de-ionized water were investigated. Distilled water is satisfactory, but expensive. The use of steam condensate offers another satisfactory method, and the use of de-ionization systems with exchange resins, another. The latter method is too expensive generally for the production of water for new systems containing 500 to 2000 gallons, but shows some promise for the production of make-up water. To quantitatively determine the feasibility of their use for make-up water in a system, the National Bureau of Standards performed special laboratory tests on a number of de-ionizing cartridges purchased from the Illinois Water Treatment Co., of Rockford, Ill. They were all of the same type, known as the Universal Model, commonly used in laboratories to convert spigot water into de-ionized water at a rate of about 5 gal/hr. The cost per cartridge was about \$10 in 1963.

Each cartridge was essentially a transparent plastic cylinder with two end pieces, the cylinder containing resin crystals through which the water ran from top to bottom and out through a spigot. The crystals were initially lavender in color. With time, as water passed through them and was de-ionized, they turned yellow, the change in color slowly moving from top to bottom. According to the manufacturer, when the yellow color reached a point about 2 inches from the bottom, the cylinder was expended.

The cartridge is a mixed-bed de-ionizing type. This designation signifies the mixing of a quantity of a strongly basic anion exchanger with an equivalent quantity of a strong cation exchanger, such that complete de-ionization of a solution may be accomplished and a neutral pH maintained throughout the entire exchange process [11]. This technique surpasses older techniques in existence only a few years ago.

For the first two laboratory tests, the water to be neutralized was placed in a 55-gallon drum, supported near the ceiling of the laboratory by a wooden structure, and allowed to run through a cartridge. During the first test, distilled water with a known amount of dissolved solids, approximating that in the spigot water at Minot AFB, was used. The amounts used are shown in Table 12. This charge of dissolved solids was known as charge No. 1. The synthetically ionized water passed through the filter and collected in 5-gallon jars, then the conductivity of the water in each jar was determined. The flow of water was continued until its conductivity reached a value in the range from 100 to 200 μ mhos. By totaling the volumes of collected water in the jars, a determination of the useful life of a cartridge was obtained. The test was repeated four times, four cartridges being tested sequentially. Performance of the four cartridges was essentially the same.

Table 12

<u>Dissolved solids, ions</u>	<u>Parts/million</u>
Chlorides	105
Sulfates	180
Bicarbonates	230
Carbonates	10
Calcium+magnesium	600*

*By NBS analysis, the water at Minot AFB showed 150 ppm for the combination of calcium and magnesium ions. It was impossible to obtain a smaller concentration of calcium and magnesium ions than the above, when easily available and reasonably priced calcium carbonate and magnesium sulfate were used. The Water Resources Board of the Geological Survey advised that finished spigot water at Minot, N. Dak., often showed a concentration of 600 ppm for these two types of ions to obtain the level of bicarbonate and sulfate ions shown in Table 6.

For the second test, the dissolved solids were in the same proportion, but the amount of each was one-half that in charge No. 1. The charge for this solution was designated as charge No. 2, and roughly represented the dissolved solids found in a number of localities in the United States. Two cartridges were used sequentially in the test and the performance of both cartridges was essentially the same.

A third test was performed with Washington, D.C. city water. This de-ionized water ran from the cartridge into a metal drum, and samples were collected periodically for determination of conductivity. Two cartridges were used sequentially in this test, and their performance was essentially the same. An analysis of Washington city water is shown in Table 13.

Table 13

Concentration of Ions
Washington City Water (May 1964)

<u>Dissolved solids,</u> <u>ions</u>	<u>Parts/ million</u>
Chlorides	9.8
Sulfates	35.0
Bicarbonates	45.0
Carbonates	0.0
Iron	0.05
Copper	0.01
Calcium+magnesium	30.6
pH	7.5

Before each test, determinations were made of the conductivity of the synthetically ionized water in the 55-gallon drum, and of the city water. The rate of flow of water for all tests was 5 gal/hr. Results of the three tests are shown in Table 14.

TABLE 14

Conductivities of Samples of De-Ionized Water

Test No. 1

(Charge No. 1)

	1st Cartridge		2nd Cartridge		3rd Cartridge		4th Cartridge	
	Conduc'y (μ mos)	Gal/ sample	Conduc'y (μ mos)	Gal/ sample	Conduc'y (μ mos)	Gal/ sample	Conduc'y (μ mos)	Gal/ sample
Initial Conduc'y	883		883		831		831	
Sample No.								
1	2.0	5	3.4	5	2.6	5	1.2	5
2	6.0	5	7.5	5	9.7	5	5.6	5
3	15.0	5	15.8	5	16.7	5	13.3	5
4	18.9	5	25.5	2	22.7	5	17.1	5
5	177.0	5			580	5	15.7	5
6	1035	5			1075	5	237	5
7	1500	3			1500	2	1500	5
Total		33		17		32		33

Test No. 2

(Charge No. 2)

Test No. 3

(Washington, D.C.
City Water)

	1st Cartridge		2nd Cartridge		1st Cartridge		2nd Cartridge	
	Conduc'y (μ mos)	Gal/ sample	Conduc'y (μ mos)	Gal/ sample	Conduc'y (μ mos)	Cum. (gal.)	Conduc'y (μ mos)	Cum. (gal.)
Initial Conduc'y	430		398		319		370	
Sample No.								
1	1.3	5	1.4	5	1.5	15	8.8	25
2	1.6	5	1.3	5	10.7	50	136	60
3	1.0	5	1.3	5	10.9	65	970	104
4	2.5	5	2.1	5	35.3	75		
5	5.0	5	5.4	5	240	85		
6	7.1	5	6.7	5	682	95		
7	7.5	5	9.7	5	812	103		
8	7.7	5	10.0	5				
9	8.1	5	10.0	5				
10	12.2	5	9.7	5				
11	13.6	5	11.5	5				
12	30	5	33	5				
13	316	5	108	5				
14	880	5	670	5				
15	1200	5	1070	5				
16	1300	5	1200	5				
17	1360	2	910	2				
Total		82		82		103		104

One cartridge of the 12 purchased for the tests failed to allow a sufficient flow rate of 5 gal/hr and was discarded. For some cartridges, water was allowed to wet the crystals from top to bottom, the entire cartridge turned upside down momentarily to remove the air, returned to its normal vertical position, and then the spigot opened. Tests showed there was no significant difference in performance between this operation and when the cartridge remained upright.

Figure 1 shows curves of conductivity with respect to amount of water de-ionized as determined from the tests. The curve marked (a) was drawn from the data of Table 14 for Test No. 1, first cartridge; (b) from data of the same table Test No. 2, first cartridge; and (c) from that of the same table for Test No. 3, first cartridge. It will be noted that the cartridges exhibited a quick deterioration at a certain point. Once a conductivity of about 20 μ mhos had been reached, a rapid increase occurred for subsequent samples.

Analyses of two samples of water taken during the second test with charge No. 2 at about the 30 μ mho point are given in table 15. These two samples are identified in Curve (b) of Figure 1.

TABLE 15

PARTS PER MILLION OF DE-IONIZED WATER HAVING A CONDUCTIVITY OF
ABOUT 30 μ mhos, SECOND TEST, CHARGE NO.2
(Beginning of test - conductivity 430 μ mhos)

<u>Sample</u>	<u>Cl⁻</u>	<u>SO₄⁼</u>	<u>CO₃</u>	<u>H₂CO₃</u>	<u>HCO₃</u>	<u>CO₃⁼</u>	<u>pH</u>	<u>Conduc'ty (μmhos)</u>
1st Cartridge	2	<2	4	4	-	-	5to6	30
2nd Cartridge	2	<2	5	5	-	-	5to6	33

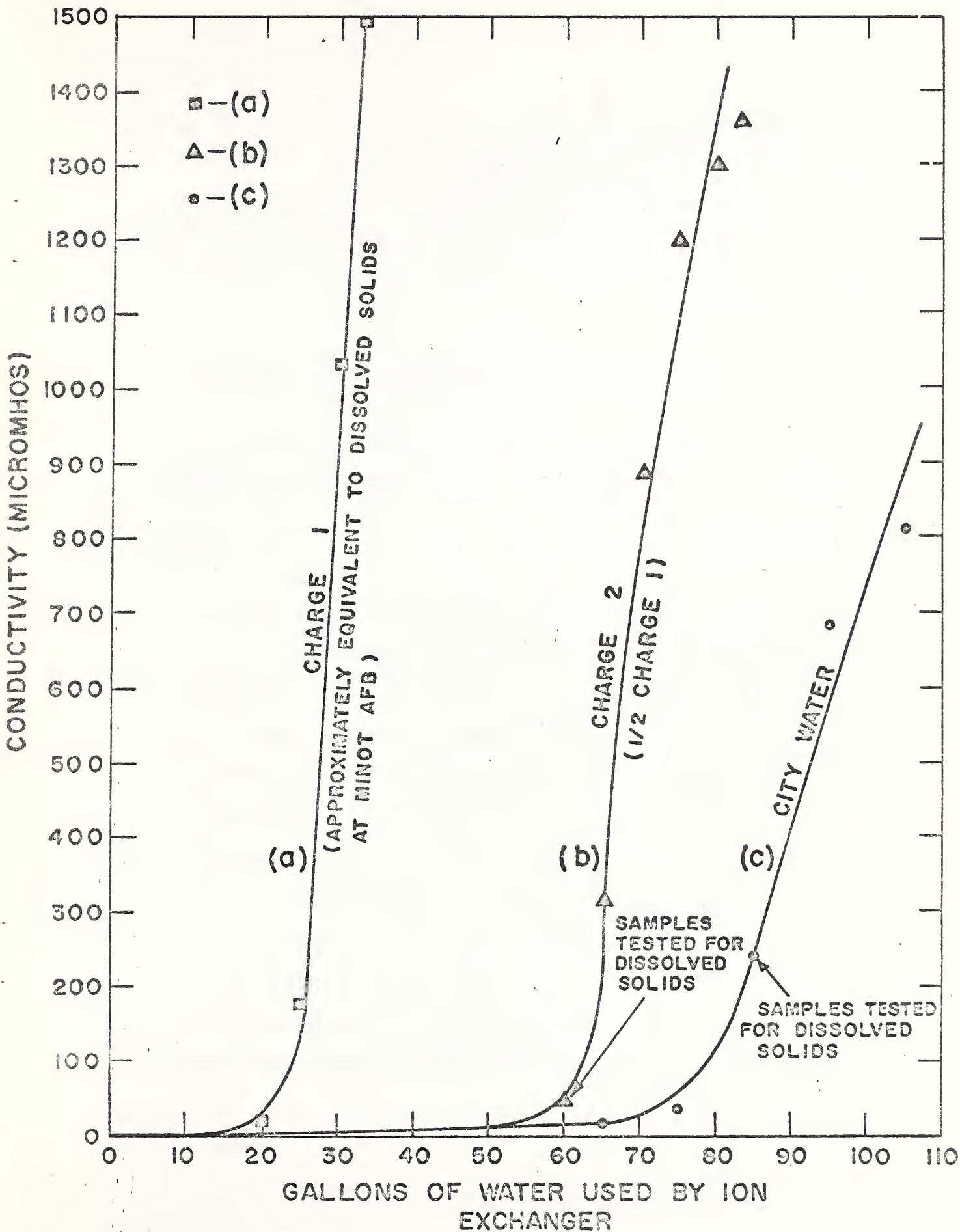


FIG. 1.

Table 15 shows a very light ion concentration. About 60 gal of water had been de-ionized when the samples were taken.

An analysis of each of the two samples of Washington city water taken during test 3 is shown in table 16. These two samples are identified in Curve (c) of Figure 1.

TABLE 16

PARTS PER MILLION OF DE-IONIZED WATER, THIRD TEST,
WASHINGTON CITY WATER

(Beginning of test - conductivity 319 μ mhos)

Sample	Cl^-	$SO_4^{=}$	CO_2	$H_2CO_3^-$	HCO_3^-	$CO_3^{=}$	pH	Conduc'y (μ mhos)
1st Cartridge	27	25-30	20	-	19	1	8.1	Approx. 240
2nd Cartridge	23	<2	6	6	-	-	3.3	Approx. 240

Table 16 shows a moderate ion concentration. About 85 gal of water had been de-ionized when the samples were taken .

The results of these two analyses show that at 30 μ mhos (charge No. 2), the parts per million of chloride, sulfate, bicarbonate, and carbonate ions were very small, but at 250 μ mhos (when city water was demineralized), the concentration of chloride ions had increased; chloride ions, for example, were about 25 ppm. This performance is consistent with the expected behavior of the mixed-bed type of de-ionizer, where the ion content is insignificant for the first few gallons of operation and remains small until the de-ionizer is nearly spent. At this point, the negative ions are produced from the mixed bed in increasing numbers and the conductivity rises sharply, as shown for all curves of Figure 1.

As shown in Table 15 the pH at the 30- μ mho point is 5 to 6. It was found during the study that it was very difficult to make a positive determination of pH for samples of de-ionized water, which had conductivities of less than 30 μ mhos. Unless extreme care is taken the results will be low. For the determination made during this study, a pH meter was employed by which two electrodes were placed in the sample under test and the pH reading was observed by a dial reading on the face of the meter. To calibrate the pH meter, a given buffer solution was used, and an adjustment was made in the electrical circuit of the meter so that the dial reading was exactly 40. After calibration, the electrodes were rinsed thoroughly with distilled water and the sample tested, but it was virtually impossible to remove all traces of contaminants left on the electrodes from previous tests and traces of the buffer used during calibration. For water which had a low conductivity, the traces of contaminants and the buffer had a relatively large effect, thus removing some accuracy from the determination. Reference is made to Section 3.1, where some explanation is made of the buffering action by ethylene glycol inhibitors.

After extremely careful measurement techniques had been followed and comparisons were made of pH readings where different buffers were used, the meter indicated that the pH for samples having conductivities in the range 1 to 20 μ mhos was between 5.5 and 6, which is satisfactory for make-up water in a snow-melting system. Distilled water will show a pH of about 7 and will drop in a very short time to about 5.7, due to the formation of carbonic acid from the CO_2 in the air. Cases have been reported where de-ionized water is highly corrosive. This is true because of the complete lack of a buffer. However, for inhibited ethylene glycol solutions where a buffering material is always present, appreciable corrosion will not occur.

The pH values of 5 to 6 for water having a conductivity of from 1 to 30 μ mhos appears to be in agreement with chemical theory. Assuming that

all the anions are chloride ions, and all the cations are hydrogen ions, a conductivity of 30 μ mhos will be equivalent to a pH somewhere between 5 and 6.

Based on considerations of conductivity and pH, it is reasonable to establish 20 μ mhos as a limit for conductivity of water de-ionized by a cartridge of the type used during the test. Referring to Fig. 1, it is feasible to use only about 20 gallons of water with dissolved solids similar to those in charge No. 1, about 55 gallons with dissolved solids similar to those in charge No. 2, and about 65 gallons for city water similar to that in Washington, D. C. for each deionizer cartridge of the type employed in this study.

The manufacturer's advice that the cartridges may be used until the yellow coloring in the crystals reaches a point 2 inches from the bottom of the cartridge was found to be inappropriate for the present application. During the study of pH it was found that after 62.5 gallons of water had been de-ionized, the crystals were yellow to a point 10 inches from the bottom of the cartridge; after 103 gallons, when the conductivity was 32 μ mhos and the pH 4.2, a point 6-1/2 inches from the bottom; and after 120 gallons, when the conductivity was 441 μ mhos and the pH 3, a point 4 inches from the bottom. It is probable that not only would the de-ionized water be highly acidic when the yellow coloring reached a point 2 inches from the bottom, but there would be a high concentration of mineral ions, many of which have been shown to be detrimental to inhibited ethylene glycol solutions.

There is no absolute assurance that the performance of cartridges from other manufacturers will be similar to those tested. However, staff members of the National Bureau of Standards have been advised that the resins used in the mixed-bed type of filters are manufactured by only one or two chemical companies. Therefore similar performance would be expected.

Large de-ionizers of other types might profitably be used at certain installations, especially de-ionizers in which the crystals can be re-activated and re-used. Water de-mineralization costs for four types of systems, including the mixed-bed type, are compared in a paper by Kahler and Reents [12].

3.2.2 Determination of Water Quality

The following methods are suggested for determining if local water requires de-ionizing because of chloride and sulphate ion concentration. If the concentration of these ions is less than 20 ppm and 30 ppm, respectively, it probably will not be necessary to use condensate or de-ionized water.

3.2.2.1 Chloride Ion Concentration

Reagents: The following test can be used for determining the chloride ion concentration of the water:

Standard Methods for the Examination of Water and Wastewater [13], 11th Edition, 1960, American Public Health Association, Inc., Test for Chloride, pp. 78 and 79.

3.2.2.2. Sulfate Ion Concentration

For determination of the sulfate ion concentration of the water, use the test specified on pages 237-243 of Standard Methods for the Examination of Water and Wastewater [13].

3.2.3. Determination of Amount of Depletion of the Inhibitors of an Ethylene Glycol Solution During Service

Without special apparatus, there is no easy and certain method for monitoring inhibitor effectiveness of the aqueous ethylene glycol solution in a snow-melting system. For Dowtherm SR-1, the Dow Company offers a monitoring service whereby the customer sends representative samples of the solution from its snow-melting system for analysis. After analysis and without charge, the Dow Company recommends whether the additives should be increased or whether the solution has reached a point where a complete change is necessary.

The Union Carbide Company does not offer this service for UCAR 17, but an advertising brochure suggests a set of criteria for maintaining the quality of the solution, which includes tests and limits for appearance, pH, phosphate ion content, sodium MBT content, chloride content, and freezing point. This brochure can be obtained by writing to Union Carbide Corp., Chemicals Division, 270 Park Ave., New York, N. Y., 10017. A test for reserve alkalinity also should be added. Reserve alkalinity as a partial means for monitoring will be discussed later in further detail.

If one of the three newer types of inhibited ethylene glycol described in this report is used in the system, usually only tests for reserve alkalinity, freezing point, and pH are necessary. Reserve alkalinity is defined as "the number of milliliters of 0.1 N hydrochloric acid required to titrate 10 milliliters of concentrated glycol to a pH of 5.5." The tests should be performed at least once a year for the first two years, and every six months thereafter, either by the manufacturer, if a testing service is supplied, or by the engineering staff at the site of the snow-melting system. If the test values for reserve alkalinity, freezing point, and pH approach the following minimum limits, further tests, as enumerated below, should be performed to determine the need either for reconditioning or placing a new charge in the system. Some of the limits shown were supplied by the manufacturer.

Dowtherm SR-1

Reserve alkalinity, minimum, ASTM Designation D1121	8.0
pH, minimum, ASTM Designation D1287	7.0
Phosphate ion content, %by <u>weight of concentrated ethylene glycol</u>	.54

No limits are given for the mercaptobenzothiazole ion content.

However, the Dow Company states [14], that "if the phosphate ion level drops below 0.54 percent, based upon 100 percent Dowtherm SR-1, the solution should be re-inhibited. Addition of the Dowtherm SR-1 inhibitor will replenish both sodium mercaptobenzothiazole and dipotassium phosphate in proper ratio and to the required levels". This inhibitor can be obtained from the Dow Company.

UCAR 17 Thermofluid

Reserve alkalinity, minimum, ASTM Designation D1121	7.0
pH, minimum, ASTM Designation D1287	7.8
Mercaptobenzothiazole ion content, % by weight, minimum	0.01
Phosphate ion content, % by weight, minimum	0.1

If the values fall below the minimum limits, it is suggested that the Union Carbide Chemicals Company be contacted for methods of reconditioning the solution.

Type I Inhibited Ethylene Glycol with Formula B Inhibitors

Reserve alkalinity, minimum, ASTM Designation D1121	7.0
pH, minimum, ASTM Designation D1287	7.8
Mercaptobenzothiazole ion content, % by weight, minimum	0.01
Phosphate ion content, % by weight, minimum	0.1

It is highly improbable that the value for the mercaptobenzothiazole ion will fall below 0.01 percent, because of the heavy reserve amount in the material (approx. 0.25% when the solution is new); however, should either the value for the MBT ion content, or the phosphate ion content fall to the specified minimum values, new formula B inhibiting material should be used to recondition the solution, or the solution should be discarded if there is evidence of heavy amounts of rust, foreign deposits, crystalline material, or amorphous material other than the white flocculant precipitate of mercaptobenzothiazole normal for the solution. Federal Specification O-I-490a gives information on the size package of the formula B inhibiting material to use.

3.2.3.1 Discussion of Applicable Tests

a. Reserve Alkalinity. The test for reserve alkalinity is one of the most positive methods to determine the amount of inhibitor depletion. This determination gives an indication of the buffering agent remaining in the solution. A value greater than 20 is common for the new and unused automotive antifreeze solutions. Of 91 samples of new ethylene glycol automotive antifreeze products tested by the State Laboratories Department of North Dakota, only 7 had values for reserve alkalinity that were lower than 20 [15], of which 5 had values greater than 15. Most of these contained borax. For solutions which have been in the snow-melting system for some time, the amount of change from year to year is a better criterion for renewal than a lower limit.

ASTM D1121 specifies that the test be performed on a sample of undiluted material. In making a test for reserve alkalinity in accordance with ASTM D1121, the analyst must consider the amount of water in the solution. For example, if a sample of 50/50 ethylene glycol and water is tested he must use a 20 ml sample instead of the 10 ml sample specified by D1121. To obtain an approximate indication of the ratio of glycol to water in a used solution, determine the freezing point of the solution.

b. Determination of the Freezing Point of the Solution. The desired freezing point at a given site depends upon the weather conditions at the Base where the snow-melting system is under use. The hydrometer method can be used. Cleanliness is important. The hydrometers can be washed with soap and water, dried, and wiped with a cloth moistened with alcohol to remove any residual soap film [16]. However, even with a clean hydrometer, certain precautions should be taken to insure correct readings. In order that a hydrometer may indicate correctly the density or strength of a specified liquid, it is essential that the liquid be uniform throughout, and at the temperature specified on the instrument [16]. The influence of surface tension of the liquid is another important factor [16]. This liquid adhering to the stem above the general level of the liquid in which the instrument is floating has the same effect as adding to the mass of the hydrometer, thus increasing the depth of immersion.

A much simpler and more accurate device for measuring the freezing point is the type which measures this point directly. A small amount of the aqueous glycol solution is placed in a small cup, then carbon dioxide is released from a capsule and directed on the exterior of the cup. Because of the expansion of the gas, the solution freezes. The cup and solution are then allowed to warm up. The point at which the solution melts can be readily observed on an alcohol-in-glass thermometer, whose bulb is fixed in the solution in the cup.

The NBS laboratory has used this kind of device and found it to be very satisfactory. The only commercially available tester of this type known to the National Bureau of Standards is the Cold Cup Antifreeze Tester,

made by Rolf Darbo, Box 2158, University Station, Madison, Wisconsin, USA. One of the Cadillac agencies in Washington, D. C., has used this device for a number of years and recommended it highly in preference to the hydrometer.

c. Determination of pH of a Solution. In an article describing research of the British Cast Iron Research Association, it was stated that the pH value of an antifreeze solution is probably not an adequate criterion of its corrosivity in a snow melting system, since a solution of pH value as high as 7.5 had been found to be associated with very rapid corrosion; whereas, it previously had been assumed that all solutions of pH value greater than 6.4 were safe [17]. The article also states that a better criterion of renewal is reserve alkalinity. The test specified by ASTM Designation D1287 requires the use of a pH meter. If circumstances make use of a pH meter impracticable, the Union Carbide Company advises the use of a Taylor Model T-O pH slide comparator, with a slide covering the range 7.8 to 9.2, Catalog No. 1000L. If necessary, suitable pH test papers that change color over a narrow pH range are also recommended by the Union Carbide Company.

d. Determination of Amount of MBT in Solution:

Weigh 25 to 30 g of the antifreeze into a 250 ml beaker and dilute to 100 ml with water.

Add 15 ml of copper sulfate solution (10 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 ml of water) and let the mixture stand for one hour.

Add 5 ml of N hydrochloric acid and stir. Digest the mixture at approximately 50 °C for 30 minutes and then allow to cool to room temperature.

Filter the precipitate of copper mercaptobenzothiazole through a tared Gooch or sintered glass crucible, wash once with 0.5 N hydrochloric acid solution and then with water until the washings are free from chloride. Dry in oven at 100 °C. Cool and weigh.

Mercaptobenzothiazole ion, percent by weight =

$$\frac{84 \times \text{weight of copper mercaptobenzothiazole}}{\text{weight of sample}}$$

This specification is from British Standard Specification 3150:1959 [18].

The Union Carbide Company specified the following qualitative test for MBT, which is easy to perform:

Fill a 4- to 6-inch test tube 1/3 to 1/2 full with the sample test solution. Add 10 to 15 drops of a 50-percent ammonium hydroxide solution, NH_4OH ; stopper the tube and shake. Add a few drops of a 1.5- to 2.0-percent silver nitrate, AgNO_3 , solution to the test tube, and examine visually. The immediate formation of a white precipitate indicates the presence of MBT.

e. Determination of Phosphate Content. The Union Carbide Company recommends that the phosphate ion concentration in UCAR 17 should be not less than 1000 ppm. The following method of analysis for phosphate ion content in UCAR 17 is recommended by that company*. The same limit should apply for the ethylene glycol developed by the Coating and Chemical Laboratory purchased under Federal Specification 0-I-490a.

Equipment and Reagents

- (1) Taylor Slide Comparator for phosphate ion content;
Catalog No. 1100.
- (2) pH base, Catalog No. 531
- (3) Low phosphate comparator slide, 0- to 25-ppm, Catalog
No. 1105.
- (4) Reagent vial with 0.1-ml pipette (3 ea.); Catalog No. 502A.
- (5) Low phosphate mixing tubes (6); Catalog No. 516.

* Brochure on UCAR-17 Thermofluid published by the Union Carbide Company.

- (6) Test tubes, 5-ml capacity (12 ea.); Catalog No. 500.
- (7) Molybdate reagent for phosphate determination, 32 oz;
Catalog No. 601.
- (8) Stannous chloride reagent for phosphate determination,
4 oz; Catalog No. 602.

Sample Dilution

UCAR Thermofluid 17 contains 4800 ppm phosphate ion and antifreeze solutions made by mixture with water normally would be expected to fall in the 1000- to 3000-ppm range. Using the specified equipment, an appropriate dilution of the sample solution from the system can be made to facilitate evaluation on the low phosphate comparator slide (0- to 25-ppm). For example, if the sample solution is diluted 1:100, and the phosphate ion content upon examination is found to be 10 ppm for this dilution, then simply multiplying 10 by 100 will give 1000 ppm as the phosphate ion content of the original sample system solution.

Procedure

Add the diluted sample solution from the system to the first line on the low phosphate mixing tube; addition is equal to 10 ml. Then add molybdate reagent to the second line on the tube; addition is equal to 4 ml. Stopper the tube and shake. Now add 1 ml of the stannous chloride solution prepared by following the directions on the reagent vial, using the marked pipette. Transfer this blue-colored solution to a 5-ml test tube and place it in the base of the Taylor Slide Comparator. Place two 5-ml test tubes, filled with water, on either side. Using the 0- to 25-ppm, low phosphate, comparator slide,

compare the various color intensities, and select the one best matching the color intensity of the blue-colored solution.

Adjusting of System Solution

When an adjustment in the phosphate ion content of an antifreeze solution is necessary, the addition should be based on the fact that adding 1.5 lb of potassium hydrogen phosphate K_2HPO_4 , to each 100 gallons of system solution is equivalent to adding approximately 1000 ppm of phosphate ion to the system solution. A good grade phosphate, low in chloride and sulfate ion content, should be employed and be pre-dissolved in water, or a portion of the glycol coolant apart from the system.

3.2.4. Importance of Cleanliness

Cleanliness of a system is very important. A letter received from the Chief Engineer of the Torrington Company, Torrington, Connecticut, who has had success for a number of years with an ethylene glycol snow melting system, says: "One point that cannot be emphasized too strongly is the desirability of using new pipe when installing such a system, and being sure that it is thoroughly clean and free of scale and rust before introducing the solution in the system" [19].

If a system has been used for some time and contains water-formed deposits, and the solution requires changing, it is necessary that it be washed thoroughly before recharging. The following suggested instructions were sent to the NBS by the Union Carbide Company:

- a. Flush the system thoroughly with water to remove previously used coolant.

- b. Purge the flush water from the system, using air or nitrogen.
 - c. The system should be filled with a solvent formulated to efficiently remove corrosion products and scale. A 15- to 25-percent solution of inhibited hydrochloric acid is suggested. The system should be filled with the solvent and the solvent allowed to remain in the system for a period of 6 hours at ground temperature.
 - d. Following the contact time of 6 hours, the cleaning solvent should be displaced from the system, using water containing 0.05-percent citric acid (4 lb/1000 gal). This flushing procedure should be continued until the chloride content of the effluent flush water is less than 50 ppm. To test for chloride content of the water, follow the procedure outlined in section 3.2.1., Importance of Water Quality.
 - e. Purge the remaining flush water from the system, using nitrogen. This will prevent after-rusting of the metal surfaces. The system is then ready for installation of the heat transfer media.
- NOTE: If the system is to remain empty for any period of time, it might be advisable to maintain a positive nitrogen pressure.

The Dow Company recommends the use of Vertan 690, one of their own products, especially if sweated joints are used; or Vertan 675 Compounded Chelant, if there is copper in the system.

The Oakite Products Corp., 46A Rector St., New York, N. Y., 10006, offers a service for cleaning snow-melting systems.

3.2.5. Importance of Using Only One Type of Antifreeze Solution in the Snow-Melting System

It is important that only one type of inhibited ethylene glycol solution be used in a snow melting system. Manufacturers of antifreeze fluids advise that mixtures of certain types of inhibitors can cause the formation of precipitates. There is no certainty that one mixture of any two types of the three ethylene glycol products recommended in this report will cause difficulty and if the UCAR-17 Thermofluid Type product and the Type I Borax inhibited product which have essentially the same chemicals but in different proportions are mixed, it is probable that no difficulty will occur. Nevertheless, it is strongly recommended that advice be obtained from the Union Carbide Company (or manufacturer of equivalent material), the Coatings and Chemical Laboratory of Aberdeen Proving Ground, or another qualified laboratory, before such a mixture is made.

3.3. Toxicity of the Inhibited Glycols

Toxicological information on the various glycols is summarized in Patty's Industrial Hygiene and Toxicology [20]. Di-ethylene glycol, small amounts of which usually appear in a drum of new ethylene glycol, is regarded as toxic for applications where there is a possibility of ingestion. Toxicity is greater at high temperatures. In some ethylene glycol products small amounts of arsenites are used as inhibitors. Because of the toxicity of these compounds and their inhibitors, it is suggested that working personnel wash their hands upon completion of their work. Reference is made to section 5.2.8, which discusses safeguards for keeping the main water supply pure when applying make-up water to the snow-melting system.

Propylene glycol is considered safe for use near foods and is used for certain applications in restaurants and food-handling installations.

According to Patty [20], tri-ethylene glycol is not as toxic as ethylene glycol on ingestion.

4.0 Other Types of Heat Transfer Media

During the investigations a search was made for satisfactory heat transfer media other than ethylene glycol. Among those investigated were fluorinated hydrocarbons, silicate esters and their related derivatives, organo silanes and disiloxanes, oil and water. Only the oil seemed to be entirely practicable for use in snow melting systems for hangar doors.

Discussions of each of these media investigated are given below.

4.1. Fluorinated Hydrocarbons

Of the fluorinated hydrocarbons used conventionally in refrigeration systems, R 11, (CCl_3F), and R 113, ($\text{CCl}_2\text{F} - \text{CClF}_2$) appeared to be the most promising for use in snow-melting systems. The more commonly used types such as R 12 and R 22 have critical temperatures of 233.6 °F and 204.8 °F respectively, indicating that a change of state would be likely to occur in the range of temperature normally encountered in a snow-melting system.

R 11 and R 113, like most of the fluorinated hydrocarbons, have an absolute viscosity of approximately 0.5 centipoise at 86 °F and densities 30 to 40 percent higher than that for aqueous solutions of the glycols. They both have specific heats of about 0.22 Btu/lb (deg), however, as compared to about 0.81 for a 50 percent solution of ethylene glycol. The freezing points of R 11 and R 113 are -168 °F and -31 °F, respectively. R 11 has a boiling point of 75 °F whereas R 113 has a boiling point of 118 °F at atmospheric pressure. All the conventional ferrous and non-ferrous metals

except zinc, magnesium, and aluminum alloys can be used with both liquids. None of the fluorinated hydrocarbon materials is flammable or explosive. The low order of toxicity of these materials is well-known.

4.2. Silicate Esters and Related Derivatives; Organo Silanes and Disiloxanes

The silicate esters, developed primarily for use as lubricating fluids in systems such as aircraft hydraulic systems, are another group of possible heat-transfer media, but are relatively expensive. Certain esters of this type exhibit good viscosity-temperature characteristics and hydraulic stability in the temperature range of -65 °F and 400 °F. They have low freezing points, low vapor pressure at elevated temperatures, a high specific heat, high thermal conductivity, high flashpoint, and a low order of toxicity. Viscosity at 32 °F is generally about 3 to 20 centipoise; at 100° , it is less than 10.

Conversations with technical personnel and sales representatives revealed that these organic materials, unless they are specially treated tend to hydrolyze slowly under prolonged contact with even small amounts of water. The hydrolytic instability of the silicate esters was once considered a severe limitation. This property has been suppressed considerably by utilizing branch chained or higher alcohols for the synthesis of these hydraulic fluids.

The organo-silanes and disiloxanes composed of both alkyl- and alkoxy-substituents have approximately the same characteristics as the silicate esters, but are more stable and are highly resistant to hydrolysis. R. L. Peeler and S. A. Kovacich [21], showed that silanes and disiloxanes of this type could be prepared having hydraulic stability markedly superior to currently available silicate esters at a temperature of 400 °F. Tert-Alkoxy

and long alkyl groups were particularly effective in providing steric protection to the molecule. These materials are more difficult to synthesize than the silicate esters or require more expensive starting materials and are consequently more expensive than the silicate esters. Peeler and Kovacich [21], report the following two materials with high hydrolytic stability:

(1) Ethyl-tert-butoxydi (2-ethylhexoxy) silane

(2) 1, 3-Diethyl-1, 3-di (tert-pentoxy) 1, 3-di (2-ethylbutoxy)

The lubrication properties of these liquids with respect to their effects on circulating pumps also need investigation before they are considered for use in snow-melting system.

4.3. Oil

Oil as the heat-transfer media in a snow-melting system is reported to have good stability when properly applied [22]. The vapor pressure of some heat-transfer oils is below atmospheric pressure at 400 °F; used with most metals other than copper. The oils are not corrosive and are not toxic. Heat-transfer characteristics of the material are not as good as those of ethylene glycol, consequently, the heat exchangers must be larger. Oil has a relatively high viscosity at low temperatures; however, at a temperature of 100 °F, the pumping head of a light oil will be only 20 percent higher than for a system using water [22]. Because many installation leave their snow-melting systems operating continuously night and day once the outdoor temperature is below a certain level, the pumping head will usually be in this range. Viscosity values for satisfactory oils at 100 °F are about 40-60SUS. Pour-point for heat-transfer oils is well below 0 °F; a pour-point of -20 °F is readily attained, while some oils have a pour-point as low as -50 °F.

A description of a toll-road plaza snow-melting system which employs oil appears in Heating, Piping and Air Conditioning, March 1957 [23]. Public Building Services Specification No. 304-15 [24], contains requirements for a complete snow-melting system using heat-transfer oil. Other literature is available on the use of oil in snow-melting systems. The technical bulletin published by the Mobiltherm Company might be helpful [25].

4.3.1. Oil Requirements

Petroleum oils are made up of carbon atoms in aromatic and naphthenic rings and paraffinic chains [26]. The oils are not pure chemical compounds, but heterogeneous mixtures of many molecular structures. Petroleum fluids deteriorate at elevated temperatures as a result of two separate processes - thermal cracking and oxidation [25]. Therefore, it is important that the new oil which is to be placed into a system shall have certain characteristics that minimize such deterioration. Oils known as aromatic oils, which have a high percentage of aromatic hydrocarbons, are relatively resistant to cracking and thermal decomposition. However, viscosity is high for some oils of this type.

The GSA Specification No. 304-15 for a complete snow-melting system using oil as the heat-transfer medium requires the tests in Table 17 and approximate limits for new oil.

Table 17

	<u>Value</u>	<u>ASTM Test Method</u>
API. gravity	12.0	D287
Maximum pour point	-20 °F	D97
Flash point, minimum	250 °F	D92
Initial boiling point	450 °F	D445

A value for viscosity at 100 °F of 40-60 SUS is also recommended if the above limits are to be used for purchasing oil for snow melting systems.

The limit- of 12.0 for API gravity apparently allows only the aromatic type oil. One aromatic type oil designed specifically for snow-melting systems that meets these requirements is Mobiltherm Light Oil, produced by the Mobil Oil Company.

There is not sufficient evidence to disallow the naphthenic type oil even if it does not meet the requirements shown above. One naphthenic oil Circosol 306 (sometimes known as CIRCO XXX Lt.), produced by the Sun Oil Company, has shown good performance in a snow-melting system at the Museum of History and Technology, Smithsonian Institution, Washington, D. C., for the two winter seasons. The API gravity number for this oil is about 24. Results of monitoring the condition of this oil will be discussed in a later section of this report.

Mobiltherm Light and CIRCO XXX are the only two heat transfer oils, with a sufficiently low pour point and suitable for snow melting systems, for which the National Bureau of Standards has any information. In discussions with manufacturers' representatives consideration was given to the use of ordinary fuel oil for snow-melting systems, but investigations showed that this oil was not stable enough, with respect to oxidation and cracking. It also contains too many impurities in the form of sulfur, water, and other residue.

4.3.2. Monitoring Procedures for an Oil System

In order to effectively maintain close control of the quality of the oil in the system, it is necessary to perform certain periodic tests on samples of the oil. Sometimes these tests are performed by the company producing the oil, other times it will be necessary to perform them at the installation.

In reply to an inquiry by the National Bureau of Standards, the Customer Service Laboratories of the Mobil Oil Company sent the following suggestions for monitoring the oil in the system, regardless of the manufacturer. At the time the letter was written, these tests were used by the company for monitoring oil for their customers. They are basic petroleum tests, easily performed by technicians (initially under the supervision of a chemist) and do not require elaborate equipment. In general, these tests are employed to monitor fluids in moderate to severe service, involving continuous operation at temperatures up to 400 °F. Under such conditions, the fluid must be evaluated for evidence of cracking, as well as oxidation. Snow-melting systems operate intermittently at lower temperatures. Consequently in such a system evidence of deterioration as indicated by the tests may not develop for a number of years.

- a. API Gravity. Significant changes in the API gravity of the oil indicate the presence of large quantities of foreign materials, or that the oil has undergone a substantial amount of molecular change, such as cracking or oxidation that tends to decrease the API gravity value. The reduction may amount to several degrees API.

- b. Viscosity. The viscosities of heat-transfer oils show increases during oxidation. In addition, experiments show that the viscosity of fluid subjected to cracking at any one temperature decreases at first. This can be attributed to the production of low molecular weight materials. However, as time progresses, a certain well-defined point of minimum viscosity is reached, then the viscosity increases. In this latter stage, polymerization of molecules is the dominating feature. As the viscosity increases due to oxidation, polymerization, or a combination of the two, a point is reached where the oil is too viscous to allow for efficient heat transfer. Experience by customers of the Mobil Oil Company has demonstrated that efficient heat transfer for most systems can be maintained at viscosities up to twice that of the original oil. Thus, it is evident that viscosity is a critical parameter, whose behavior over a regulated time period gives an indication of the chemical, as well as the physical, state of the oil.
- c. Neutralization Number. The oil's neutralization number is affected by oxidation. As the oil undergoes oxidation, the neutralization number rises quite rapidly. Experience by the Mobil Oil Company has shown that oils possessing neutralization numbers up to 1.0 mgm KOH/gm can give efficient service. The neutralization number shows virtually no change during cracking.
- d. Water Content. If substantial quantities of water are present in the system when it is operating at temperatures exceeding the boiling point of water, steam will form. During periods of heat-

up, this may result in bumping and sudden increases in volume. This, in turn, will back up the fluid into the expansion tank, a problem that can be minimized by slowly bringing up the temperature. However, water can be easily removed from the oil, completely eliminating this problem, by simple oil-water separating procedures. In addition, since substantial quantities of water can be present before its presence has any effect on the system, simplified water determination tests, such as the hot-plate test, can be utilized. (The procedure outlined in ASTM Standard 1965, part 17, Designation D1796 [27], has been found to be inexpensive and effective for tests made at NBS. Tests on six samples were performed in about 4 hours by a technician having no chemical analytical experience. A centrifuge is required for this test).

- e. Flash Point. The flash point is lowered as cracking proceeds. The formation of light products in cracking is responsible for the lowering of the flash point. Determination of this point will not be as indicative as other tests; however, it is not a complicated test and it might give some indication of deterioration.

To gain some insight into the procedures for monitoring of oil, two samples, one of new, unused Mobiltherm Light Oil, and the other of used Mobiltherm Light Oil, were tested at the National Bureau of Standards or by an approved testing laboratory in accordance with those tests enumerated above. The test results are shown in Table 18.

Table 18

	<u>Mobiltherm Light, New</u>	<u>Mobiltherm Light, Used</u>
API gravity at 60 °F	12.8	13.3
Pour point	-5 °F	-10 °F
Flash point, C.O.C.	265 °F	270 °F
Viscosity at 100 °F, SUS	40.8	44.2
Neutralization No. (acid number)	0.1mg KOH/gr of sample	Unknown

These results show no significant change. The ~~neu~~ neutralization number for the used oil was not determined, however. These samples were probably from different batches and furnished by the Socony Mobil Company, and it is not known how long the used oil had been in a system.

The same tests also were made on the oil in the snow-melting system at the Museum of History and Technology of the Smithsonian Institution, which used the CIRCO XXX Oil (Circosol 306). The values obtained for the used oil were compared with the values claimed by the Sun Oil Company for new, unused oil, with the following results in Table 19.

Table 19

	<u>CIRCO XXX, New</u>	<u>CIRCO XXX, Used</u>
API gravity at 60 °F	24.1	24.5
Pour point	-50 °F	-65 °F
Flash point	300 °F	305 °F
Viscosity at 100 °F, SUS	58.0	57.6
Neutralization No. (acid number)	Unknown	0.2mg KOH/gr of sample
Water	—	Usually < 0.01 %*

*0.4% and 0.16% of water in 2 out of 9 samples. These two samples were taken from a drain (or drains).

Again the results show no significant change.

4.4. Water

Water has most of the desirable characteristics listed earlier in this report for a heat transfer medium for snow-melting systems. The principal disadvantage of water for such applications is that it freezes at 32 °F. This would not be a serious disadvantage, if automatic temperature control devices could be relied upon to maintain a minimum water temperature of 40 °F regardless of whether or not snow-melting was required. In a two-stage heat transfer system water might well be the fluid used in the higher temperature circuit.

From heat transfer and hydraulic considerations water has some advantage as compared to ethylene-glycol-water mixtures and considerable advantage with respect to light oil as a heat transfer medium. The specific heat, specific gravity, thermal conductivity, and viscosity of these fluids are listed in Table 20 for a range of temperature.

Water has higher specific heat and thermal conductivity at any temperature than either the water-glycol mixture or the heat transfer oil. Water also has a lower viscosity than the two fluids so it would require less power to pump it through a given size pipe at a given rate. The product of the specific heat and specific gravity for water at each temperature in Table 20 is higher than that for the water-glycol mixture, and very much higher than that for oil. For example, in cooling 1 °F from 200 to 199 °F, the relative magnitude of the heat given up by one gallon of water, water-glycol, and oil would be 2.13 to 2.03 to 1, respectively. Amount of heat transfer from the pipe to the fluid inside the pipe would usually follow the laws of forced convection. For a given mass velocity (lb/hr) and tube diameter the heat transfer by forced convection would be proportional to

$(k^{0.8} C^{0.4} \mu^{-0.4})$ [28a, p 92] where k is the thermal conductivity, C the specific heat at constant pressure, and μ the viscosity (in. lb/ft.hr., i.e., the viscosity in centistokes x specific gravity x 2.42) of the medium. For a given mass velocity and pipe size, calculations indicate that the heat transfer between a fluid and the pipe surface would be, for water, 1.8 times that for a water-40-percent-glycol mixture and 6.6 times that for Mobiltherm Light Oil at a temperature of 200 °F.

Table 20

Properties of Possible Heat Transfer Fluids

<u>Fluid</u>	<u>Temperature</u> °F	<u>Specific</u> <u>Heat</u> Btu/lb °F	<u>Specific</u> <u>Gravity</u>	<u>Thermal</u> <u>Conductivity</u> Btu/(hr)(ft)(°F)	<u>Viscosity</u> Centistokes
Water	100	0.998	0.993	0.363	0.681
	200	1.005	0.963	0.395	0.306
	300	1.007	0.918	0.390	0.185
Water, 40% Glycol	100	0.86	1.05	0.240	1.90
	200	0.90	1.02	0.242	0.54
	300	0.94	0.98	0.244	0.35
Mobiltherm Light	100	0.434	0.984	0.066	3.80
	200	0.480	0.944	0.064	1.40
	300	0.524	0.905	0.060	0.80

Technical Report 58-175, AD No. 151168 [28a] of the Wright Air Development Center states that 2.6 times as much heat exchanger surface is required to transfer a given amount of heat to oil as for a water-glycol mixture with other conditions being the same.

4.5. Comparison of Properties of Heat Transfer Media for Snow-Melting Systems

A comparison of the properties of different types of heat transfer media used in snow-melting systems, and types which could possibly be used in these systems is shown in Table 21 at the end of the report.

5.0. DESIGN AND CONSTRUCTION FOR SNOW-MELTING SYSTEMS USING ETHYLENE GLYCOL OR OIL

5.1. Literature on Construction Methods

The literature has many references related to design and construction of snow-melting systems. One good discussion appeared in Heating, Piping and Air Conditioning in March 1959 [3]. Some of the points that are emphasized in this reference are protection of concrete slabs from ground water, proper support and encasement of piping, the danger of electrolytic action between dissimilar metals and materials, proper allowance for venting and balancing, and proper mixing and placement of concrete. Another excellent reference is a series of 12 articles that appeared for 12 consecutive months in Air-Conditioning, Heating and Ventilating during 1956 and 1957 [29], containing general information on snowfall, and design data for determining operating characteristics of snow-melting systems. Included are climatic data, with snowfall data, classified into 11 regional areas of the United States. For each area design information and operating data are provided for three classes of snow-melting systems, the class rating being essentially dependent upon the desired rate of snow-melting; information is given on climatic peculiarities and recommendations related to economic feasibility for idling the systems.

An article appearing in Air Conditioning, Heating and Ventilating, November 1955 [30] gives a comparison of fluid properties of two aqueous ethylene glycol solutions, two heat-transfer oils, and two organic fluids. Values for kinematic viscosity, specific heat, and specific weight (density) are given for temperatures from -20 °F to 160 °F.

Other considerations discussed are the effect of these physical properties on operation, such as pumping requirement and on coil resistance; and chemical conditions such as corrosivity and flammability. An example of calculations for selection of a pump is given. A discussion of thermal stresses in snow-melting systems appears in Heating, Piping and Air Conditioning, June and August 1955 [31].

Other sources of information on design and construction are the Guide and Data Books of the American Society of Heating, Refrigerating and Air Conditioning Engineers [32]. Much of the material in reference 29 can be found in condensed form in the Guide and Data Books.

5.2. Recommendations for Design, Construction, and Maintenance

During the study many recommendations, based on experience, for improving the operation of the snow-melting system in regard to construction, design, and maintenance, were made by engineers and other technical staff members of office installations, manufacturers of ethylene glycol, and, particularly, Air Force Bases. These are presented in the following paragraphs, together with some references to the literature relating to the recommendations.

5.2.1. Expansion Tank

A closed system is generally recommended for both ethylene glycol and oil systems. This type of system subjects the heat-transfer media to less air, and the attendant oxygen that contributes to deterioration of both types of media. The Dow Chemical Company recommends the use of a closed system with Dowtherm SR-1, and other large manufacturers of ethylene glycol made the same recommendation for their products. Most of the Air Force Base engineers showed a preference of the closed system over the open. General Services Administration Specification No. 304-15 for Snow-

Melting Systems for Heat Transfer Oil [24] specifies that the expansion tank shall be of the closed type. In this type it is important that the air space in the tank be large enough to accommodate the expansion of the heat transfer fluid without creating pressure in the system, and that a relief valve be provided to discharge the fluid if excessive pressure should occur under abnormal conditions. Both of these features are required in the GSA specification.

5.2.2 Piping and Gridwork

Welded steel or wrought iron piping and pipe grids usually are recommended for ethylene glycol systems. A study by Agnew and his associates [33] showed that the corrosion rates of cast iron, steel, copper, brass, aluminum, and solder were all fairly constant for pH values between 6 and 9 in an uninhibited 40-percent ethylene-glycol-water mixture, whereas the corrosion rate of all these materials increased at pH values below 6 and the corrosion rate of aluminum and solder increased rapidly when the pH value for the solution was above 10.

Sensitivity of an aluminum alloy to corrosion in a 30:70 glycol-water mixture was reported by Dempster [34]. Twiss and Guttenplan [35] have shown the relation of corrosion of aluminum to the velocity of the moving solution, and to the impurities of the water used to make up the glycol solution. Caplan and Cohen [36] have shown that corrosion rates of some metals may be accelerated at low temperatures in certain inhibited glycol systems. Their study showed that the phenomenon was particularly true for zinc when glycol solutions with a borax inhibitor were used. A representative of the Dow Chemical Company advised the National Bureau of Standards that galvanized metals should not be used above room temperature with ethylene glycol solutions.

In the past few years, due to the increased use of aluminum in automobile engines, and of necessity, the automotive ethylene-glycol products have improved in resistance to corrosion when used with aluminum. Conley, from the Coating and Chemical Laboratory of Aberdeen Proving Ground, for example, reports good performance of Formula B material when used with aluminum [8]. There still appears to be some difficulty with solder, but the problem is not important in snow-melting systems because of the small amounts involved.

It is imperative that no copper be used in a system using oil. The oil reacts with copper to produce sludge in the system.

Normally, piping or pipe grids made of wrought iron, steel, or copper in concrete is protected from external galvanic action and corrosion, because any small amount of moisture in the concrete that might be around the metal would carry a pH of about 12, which is alkaline. If water gets to the metal via the expansion joints of the sidewalk above the metal pipe grids, rapid corrosion can occur. One office building installation in the New York area using an oil heat transfer medium has experienced a number of serious failures and a heavy loss of oil because water leaked through the expansion joints of a sidewalk. Finding the source of the oil leaks was difficult, and at one time 15 drums were lost before the leaks were found. In this installation, a polyethylene vapor barrier was placed under the pipe grids but not over it; a vapor barrier over the pipe grids might have protected the metal. Other instances of this type of failure were reported to a representative of NBS. In the article, "How to Prevent Failures in Snow-Melting Systems" [3], methods for eliminating this difficulty are described.

Another possible remedy for exterior corrosion of ferrous piping is the use of a plastic-coated steel tubing wrapped with coal-tar tapes. A snow-melting system using this polyethylene-coated material [37] recently was installed in a basement-level clothing store in West Hartford, Conn., but no information on the effectiveness of this treatment has been obtained.

Piping of a 3/4-inch diameter or larger on 12-inch centers is recommended for oil by the ASHRAE Guide [38]. For ethylene glycol, designers space the piping from about 8 to 18 inches, depending on conditions. In the past, some contractors have spaced piping up to 24 inches apart. However, an engineer of a large engineering firm specializing in the installation of heating, air-conditioning, and snow-melting equipment stated that under these conditions the snow partially melts and refreezes, causing a line of refrozen snow that is more difficult to cope with than the original condition. The same engineer recommended that there be balancing cocks for all loops.

In the September 1963 issue of Air Conditioning, Heating and Ventilating, an article on piping for snow-melting systems discusses the reason for choosing series coils over pipe grids for a large installation [39]. The author states that coils give continuous uniform circulation throughout the entire system, it is easier to eliminate air pockets, the heating is more uniform, and there is a minimum number of welds.

Smith, of the American Iron and Steel Institute, describes a steel-pipe system using oil that has given satisfactory performance since 1958 [40]. Extensive precautions were taken to protect the piping at hidden locations against external attack by seepage of rainwater and melted snow. All piping that passes through a sleeve or is buried in earth or gravel was protected by a coat of bitumastic enamel primer followed by one coat of high-melt enamel.

The latter was applied simultaneously with a single wrap of glass-fiber pipe covering, followed by a second coat of enamel and a wrap of 15-pound coal-tar-saturated asbestos pipe-lining felt.

The use of dissimilar metals in the piping of a system can induce galvanic action and corrosion. This is discussed in the article in Materials Protection, May 1964 [41].

5.2.3. Heat Exchangers

Most of the heat exchangers in the systems at the Air Force Bases visited were manufactured by the Old Dominion Company and were of the tube-in-shell type. The primary side of these exchangers is supplied with either high-temperature water or steam. The tubing, which is removable and fits snugly into the shell, was usually made of No. 18 BWG Admiralty metal and has the following approximate analysis.

Table 22

	<u>Percent</u>
Copper	71
Zinc	28
Tin	<u>1</u>
	100

This metal was used to retard dezincification, which in effect is selected corrosion of the alloy with redeposition of copper. The metal has been used successfully for condenser tubes and for salt-water applications for a number of years. The Old Dominion Company advised that the tubing sometimes was made of No. 20 BWG 90-10 copper-nickel. According to the company, the tube supports and baffles are of inhibited Muntz or non-ferrous metals.

The shells were made of steel. The HTW or steam of the primary flows through the tubes, and the aqueous ethylene glycol flows in the space between the tubes and the shell. If sediment deposits in the shell, low velocity or

stagnant areas in the ethylene glycol or oil could accelerate the deterioration. Large deposits of sludge had been found in the converters at Minot AFB before Dowtherm SR-1 was employed. There was little sludge in the systems of the other Bases.

The opposite arrangement, in which the antifreeze media traveled through the pipes, would cause a rapid flow of media and would not allow stagnation. A study has shown that there would be little loss of heat-transfer efficiency under this arrangement [42].

The Old Dominion Company was approached about this change. Although they agreed to the feasibility of the design, they pointed out that the shells now used will not withstand the pressures exerted by HTW or steam and that considerable expense would be involved. A further requirement would be increased insulation. Nevertheless, it is recommended that such a design be considered for the future. A pertinent discussion of the economic considerations of heat exchangers by Flaxbart and Schumer [43] might be helpful in studying the possibilities of a new design.

5.2.4. Controls

Control of the temperature of ethylene glycol in the heat exchanger was accomplished at the Air Force Bases visited and the Grand Forks AFB by regulating the flow of either HTW or steam at the primary side of the converter.

Regulation was accomplished in some systems by a controller with a fixed temperature setting and a sensing element placed within the ethylene glycol in the heat exchanger, and in other cases within the glycol line leaving the exchanger. The controller, in turn, adjusted the flow automatically by actuation of a modulating valve in the circuit of the HTW or steam. In at least one case, the modulating valve was by-passed by a hand valve that could be used in case the controller circuit became inoperative.

This system, with a fixed setting at the controller, was one of three types at the Grand Forks AFB. The controller for the system was not interlocked with the motor pumps and there were times when the ethylene glycol was not flowing in the heat exchanger when the primary side was heated. Experience at that Base, with a fan-coil heating system using ethylene glycol as the heat transfer medium, indicated that the resulting high temperature can cause difficulty and glycol deterioration. The greatest difficulty was when the 3-way valves in the ethylene glycol lines were closed by the room thermostat override. Under this condition of no-flow, and with the control set at a temperature of 230 °F, actual tests revealed that the glycol temperature rose to 275 °F in the heat exchanger and the actual tube surface could be higher, because the glycol boils violently for a short period of time. A discoloration of the glycol was noted, and a 45 PSI safety relief valve was activated and the entire quantity of antifreeze was discharged.

In more satisfactory snow-melting systems at Grand Forks, Westover, and Plattsburg AFB's the HTW was regulated pneumatically by a 3-way valve and controlled by the outdoor temperature (the lower the temperature, the greater the flow allowed through the heat exchanger), and usually there was continuous flow in the ethylene glycol lines. The only difficult feature in the system at Grand Forks AFB, according to operating personnel, is that the pumps are on a separate outdoor control and start only when the temperature drops below 65 °F. It is possible that the controller may call for heat in the heat exchanger at outdoor temperatures above 65 °F when the pumps are inoperative. We were advised that an override should be installed to close the pneumatic control valve in the primary circuit at any time the pumps are not operating. The type of control system at Minot AFB is not known.

Engineers advised at one Base that when the temperature of the ethylene glycol was sensed in a bulb in the glycol solution inside the heat exchanger there was a marked unsteadiness in this temperature causing erratic control of the flow in the primary circuit. A more satisfactory location for sensing, we were advised, is in the glycol line leaving the exchanger where the flow is more consistent.

At Westover AFB, the modulating valve controlling the supply of hot water was controlled electrically and was motor driven. Unlike a pneumatic control, this control would stop the valve at whatever position it was in if a failure of the electrical system occurred, possibly allowing the flow of hot water when the glycol flow had stopped.

A failure of this type actually occurred during the visit; the glycol supply at the heat exchanger was about 200 °F instead of the 120 °F normally encountered. Data taken for this system when the valve was malfunctioning are shown below:

Table 23

High Temperature Water

	<u>Supply</u>	<u>Return</u>
Temperature (°F)	383	233
Pressure (PSIG)	232	228

Ethylene Glycol

Temperature (°F)	200	170
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When the control was repaired, the glycol temperature lowered rapidly.

In light of the considerations enumerated, it is recommended that (a) the sensing element regulating the controller for the HTW be located in the glycol line leaving the heat exchanger, (b) in order to insure that there

will be a flow of ethylene glycol in the heat exchanger, there should be an interlock between the circulating pumps in the glycol circuits and the control valve for the high temperature water circuit or steam circuit, so that at least one pump is operating before the hot water or steam can be admitted to the converter, and (c) as a further precaution, the control valve in the hot water supply shall be normally closed on electrical or pneumatic failure.

These recommendations still apply, even if the new types of inhibited glycol are used. Conformance would not be expensive; and it is probable that temperatures greater than these new glycol types can tolerate would otherwise be encountered occasionally under certain conditions.

5.2.5. Pumps

The pumps for most of the systems in the three Bases had mechanical seals. The engineers at each base advised that this type of seal was important; pumps with packing glands had exhibited a number of leaks, and had increased the exposure of the glycol to the oxygen of the air.

The Chief Engineer at the Smithsonian Institution advised that teflon seals were considerably more satisfactory than the neoprene seals first used in the pumps in their oil system. The oil system installed at the H. J. Heintz Company, Cereal Building and Research Center in Pittsburgh, uses teflon seals in their pumps [40]. This system has given satisfactory service since 1958.

The engineers at Minot AFB suspected the ethylene glycol-water solution in the pumps was causing the neoprene to break down.

5.2.6. Hours of Operation for the Ethylene Glycol Snow-Melting System

All three Air Force Bases that were visited operated their snow-melting systems continuously throughout the winter. There are two principal advantages in this procedure: (a) the snow-melting system is certain to be in operation during a heavy snowfall, and (b) there is much less chance someone might turn it off inadvertently if it is well known that it is to be kept in operation full-time. One Air Force Base pointed out that, even then, on occasion inexperienced personnel would pull the wrong switch in the belief he was turning off lights or other machinery. Short of using padlocks, no method had been found to keep this from happening.

At installations visited in private and Government buildings, the systems were either turned on automatically when outdoor temperatures fell below a certain temperature (50 °F at one installation), or manually when there was threat of a snowfall. However, a chief engineer at one installation stated that a manually controlled system must have a large snow-melting capacity in case heavy snow fell during the night when no one was on duty. He cited one instance in which there was already 2-1/2 inches of snow when he turned on the system at 6 a.m. and by 8:30 a.m. the walks and driveways of the large building that it served were free of snow. There were 1500 gallons of oil in the system and it served about 10,000 square feet of area. The oil supply had a temperature of 160 to 180 °F, and the return was about 100 to 120 °F.

Detector-switches for automatically turning the snow-melting system on are mentioned frequently in the literature. One switch on the market today for this purpose is the Sno-Melter, Model EZ-AS-1, sold by the Climate Control Division of the Singer Co., Auburn, N.Y. This detector is equipped with a snow-melting funnel. The temperature of the surface of the collecting funnel is always kept above 32 °F by means of a small heater. When the first snowflakes start to fall they are converted into water which is used for unbalancing an electrical bridge so that the snow-melting electrical switch is closed. No other switches of the type were found during the investigations.

A simple method that has been used successfully, but has some disadvantages, is to place a mirror face up on the slab to be heated. Whenever the outdoor temperature falls below about 40 °F, a light is directed onto the mirror from a fixed source and is reflected to a photocell. When snowfall begins and flakes fall on the mirror, the light is attenuated and the photocell cuts off, activating the heating circuit below the slab. When the slab is heated, the snow on the mirror melts and the photocell cuts on. However, it is important to keep the mirror polished; otherwise the snow-melting system could cut on when not needed. This could be overcome by a pilot-light inserted into the system to show when it is on.

If a detector fails to cut on, or if for any other reason it is necessary to start a snow-melting system at temperatures as low as -40 °F, it is important to remember that the viscosity of aqueous ethylene glycol solutions is high at low temperatures: for a 50 percent solution the viscosity is about 100 centipoises at -40 °F and about 2 centipoises at 100 °F. Should the pumps and motors in the system not be designed for this

contingency, it might not be advisable to start the system. For some oils, such as Mobiltherm Light, the pour point is as high as -20 °F.

Two pumps are often installed in a system to operate in parallel during the heat-up period. When the heat-transfer media, either glycol or oil, have warmed up sufficiently, operation of one pump is sufficient.

5.2.7. Charging the New System with Ethylene Glycol or After Cleaning

One of the engineers at Westover AFB recommended that the solution of ethylene glycol and water be mixed in drums with mechanical mixers before charging the system. He said contractors sometimes put the glycol in the system, add water, and expect the pumping and circulation to mix the solution thoroughly, but that such mixing does not occur. Air pockets form and parts of the solution remain stagnant with excessively large proportions of either water or glycol. Ross [44], in an article describing a system at the Garden City Tollway Plaza, St. Catherines, Ontario, Canada, also recommends prior mixing of the antifreeze and water.

5.2.8. Application of Make-up Water to System

At one of the Bases visited, make-up was fed directly to the snow-melting system from the main water supply system by means of a fixed piping arrangement. This procedure is dangerous. A direct cross connection between potable and unpotable water supply sometimes results in a back flow of unpotable water. Ethylene glycol is regarded as toxic when ingested, and in some cases, small amounts of arsenites are included as an inhibitor. A better procedure is to feed the make-up water to a system through a hose which is disconnected when not in use; or to feed water into the air space of the expansion tank by gravity flow when the system is not under pressure.

5.2.9. Strainers

The systems at Westover AFB and Plattsburg AFB did not use strainers. They were used at Minot AFB and Grand Forks AFB, however. Strainers are used in a system principally to catch sludge and other impurities, but they are also recommended as a means for detecting unexpected deposits in the system between analyses.

5.2.10. Possible Thermal Shock In Hot Water Boiler

The following statement by Ross relating to the operation of large ethylene glycol systems was taken from Heating, Piping and Air Conditioning [44]. This information might be useful in the design of a new system.

"With large load variations and large volumes of water pumped through hot water boilers, precautions must be taken to prevent thermal shock. Serious damage can result if large quantities of water are circulated with a large difference between return and supply water temperatures of the boiler. A snow-melting system of this size, with the load variations expected, necessitated extra precautions.

"In this case, the boiler controls are wired to prevent either boiler from running unless the boiler water pump is running. A differential temperature controller with bulbs in supply and return boiler water connections to the antifreeze solution heat exchanger overrides all other controls. The controller starts to close the 3-way valve supply connection to the heat exchanger if the supply-return water temperature difference exceeds 20 °F. This control also insures that the administration building's heating system will not be starved when the snow-melting system is on full pickup load."

5.2.11. Removal of Water from a Snow-Melting System Area

For any type of snow-melting system, it is important that drains be provided for removal of the water which forms from the melted snow. Not only does the presence of water dissipate energy for heating, but it can lead to icy surfaces. The Michigan State Highway Department

reports [45] in a study of an experimental electrical highway system where drains could not be provided, that there was an added burden to the system due to a layer of water and that at low temperatures of about 5 °F, ice ridges formed on the lanes of the highway.

6.0 Electrical Systems

Electrical systems normally consist of insulated electrical cables buried in concrete or asphalt areas used for driveways, sidewalks, roadways, or parking lots. The insulation for the cables can be made of a mineral material such as magnesium oxide, of silicone or neoprene rubber, or of polyvinyl chloride. The General Electric Company makes an insulation known as Vulkene which, according to their literature, is a thermosetting material designed for emergency overload. Typically, this insulation is covered with copper tubing for protection against water and against heavy traffic. According to catalog information, the Climate Control Division of the Singer Co., manufactures a cable in which the inner conductors are completely surrounded and insulated with highly compressed magnesium oxide. The outer sheath is copper tubing. Lead cable is sometimes used, in which case the heating element is insulated with asbestos or glass fiber. The lead is covered by vinyl for protection of the lead from salts present in the concrete.

Sometime , pre-wired and assembled mats made up of a mesh of wiring are used instead of cables, to help the contractor cut labor costs on installation. He puts the units into place, encased in asphalt or concrete and connects the leads to the electrical distribution and timing equipment.

According to one manufacturer's catalog information, the cables can be designed for a 120, 208, 240, 277, 440, or 600 volt supply, and are rated in wattage per lineal ft. The designer selects cable wattage in accordance with design conditions of temperature, wind velocity, humidity, amount of snowfall expected, spacing of the cables, and other conditions, such as depth of cables, type of paving material, and the heat loss downward. A low value is 5 watts and a high value is 30 watts per lineal foot. Design information for electrical systems can be found in a General Electric publication on Heating Cable [46], and in publications by Mayer [47] and Potter [48]. Included in these publications are tables on snow-melting system effectiveness and the number of watts per square foot required for various climates, under various conditions of snowfall and amount of snow removal desired. Suggestions for installation techniques, spacing of coils, and electrical controls are also given. An article appearing in Actual Specifying Engineer magazine, July 1964, [49], is another good source of information that gives some admonitions and suggested specifications based upon experience in the field of electrical snow melting. One suggestion is the absolute need for waterproof junction boxes. On a visit to one Government installation, a junction box at driveway level was covered by a metal plate that was neither secure or well-gasketed. The box was half-full of water, the electrical junctions were buried in water, and the snow-melting system was almost ineffective, and dangerous when in operation. The system was restored in good working order by re-gasketing the box and fastening the top down more firmly; nevertheless, the placement of the box was at fault and repeated trouble is likely. Engineers have advised keeping the junction boxes at a high level. Some design, construction, and cost

information on an experimental electric system can be found in the Michigan State Highway Department Research Reports [45].

A specification for the furnishing and installation of a complete electrical snow-melting system by the Public Buildings Service, General Services Administration [50] is near completion and, as it now stands, it includes requirements for the heating cable, panelboards, branch heating circuits, conduits, junction boxes, circuit breakers, expansion fittings, and wattage limitations.

There are several other types of electrical systems under consideration or in the experimental stage. Impedance heating is a term used loosely to describe energization of regular or additional steel reinforcing members within the pavement [51]. Low voltage/high current power is required for this system. Another low voltage/high current system is one in which a heavy iron-core cable, covered directly with PVC, is buried in the pavement. The advantage claimed by the Electraradiant Corporation, one manufacturer who markets the components of this system, is ease of installation. Both the impedance heating and the Electraradiant type heating systems require transformers and some auxiliary equipment. Infra-red heating stems also have been used successfully for snow-melting. If an overhead infra-red radiating snow-melting system is used, loss of heat to the surrounding environment is a factor as well as reflection of the radiant heat from the snow.

7.0. Ethylene Glycol Systems For Aircraft Runways

As discussed in the foregoing pages, conventional snow-melting systems generally have been designed to use liquids circulated at temperatures from 100 to 130 °F, with temperature drops of from 20 to 30 °F, and pipes placed from 8 to 18 inches apart. When large areas are contemplated, such as aircraft runways, these systems become impracticable, due to the excessive volume of fluid which must be circulated, and the larger pipe sizes and great distances over which the fluid must be transported.

As a consequence, experimental systems with high temperature liquid and pipe spacing as great as 4 feet have been developed, making it possible to reduce pumping costs, and installation and operating costs [28]. During a 2-year test program at Loring Air Force Base on an experimental installation of this type, coil temperatures were greater than 300 °F without apparent ill effects [28]. Socony Heat Transfer Oil Light and an aqueous solution of triethylene glycol were the two types of media used during the tests. It has not proved feasible to continue operation of these experimental systems at Loring AFB.

8.0. Discussion and Conclusions

The following conclusions can be made as a result of the study described in this report:

(a) The sludge and precipitate experienced in the snow-melting systems at the Minot Air Force Base, before Dowtherm SR-1 was used, were due primarily to (1) excessive temperatures in the heat exchangers, and (2) a high concentration of dissolved solids in the water used in the aqueous solution of ethylene glycol.

(b) The relatively better performance of the snow-melting systems at Westover and Plattsburg Air Force Bases was due to the lower temperatures in the heat exchangers and the lower concentration of dissolved solids in the water used in the aqueous ethylene glycol solution.

(c) The control valve of the HTW or steam supply to the primary system should be normally closed so that when a failure occurs in the control system and the pumps for circulating the antifreeze are inoperative, heated water or steam cannot flow into the primary circuit and cause excessive heating of the stagnant antifreeze.

(d) It is advisable to design a control system so that the controls of the antifreeze pumps are interlocked with the rest of the system so that the pumps will always be in operation when there is a heated medium in the primary system. If in present installations the control for the pumps is separate, there should be an override to close the control valve in the primary circuit anytime the pumps are not operating.

(e) When the temperature of the ethylene glycol is sensed for control of the flow in the primary circuit, it is recommended that it be sensed in the glycol line leaving the exchanger and where the glycol flow is consistent.

(f) The water used in an aqueous ethylene glycol solution should be either steam condensate or de-ionized water. A small cartridge of the mixed-bed, exchange type, was found by laboratory tests at NBS to be satisfactory for use in obtaining de-ionized make-up water, providing certain precautions are taken.

(g) According to the literature, the older types of automotive inhibited ethylene glycols, which depended principally on borax, usually suffer breakdown when they are subjected to temperatures of 300 °F or higher. Studies performed at Grand Forks AFB in one system showed that when solutions with these older types of inhibitors were subjected to about 257 °F in the heat exchanger, deterioration and breakdown began to occur. At Westover and Plattsburg Air Force Bases when the temperature of the glycol in the supply to the grid system was about 120 °F there was little deterioration. At Minot Air Force Base, where the temperature of the glycol at the supply to the grid system sometimes reached 160 °F, there was serious breakdown. This trouble, however, may have been due in part to the high percentage of dissolved solids in the water used in the anti-freeze solution.

(h) The newer types of inhibited ethylene glycols, which make use of mercaptobenzothiazole, disodium- or dipotassium-phosphates, and sometimes borax, show promise of much longer life than the older automotive types. Experience at Minot Air Force Base indicated that Dowtherm SR-1 (one of these types) can tolerate water which has a high concentration of dissolved solids. It is not recommended that water with a high concentration of dissolved solids be used, however.

(i) It is recommended that one of the following types of ethylene glycol antifreeze materials be used for snow-melting systems:

Dowtherm SR-1 or equivalent covered by the specification given in this report for Type A inhibited ethylene glycol.

UCAR-17 Thermofluid or equivalent covered by the specification given in this report for Type B inhibited ethylene glycol.

The Coatings and Chemical Laboratory Formula B with Type I Borax Inhibited Ethylene Glycol. The CCL formula is covered by Federal Specification O-I-490a and the Type I glycol by O-A-548a.

(j) It is recommended that these antifreeze solutions not be mixed. Since the UCAR-17 Thermofluid or equivalent has very nearly the same inhibiting materials as the Coatings and Chemical Laboratory formula but in different proportions, it might be permissible, under emergency conditions, to mix these two fluids. It is further recommended that the Union Carbide Laboratory, the Coatings and Chemical Laboratory or another qualified laboratory, be consulted before the mixture is made.

(k) Monitoring of the types of ethylene glycol recommended in this report for snow-melting systems usually can be accomplished by performing tests for reserve alkalinity, freezing point, and pH. If the values for the tests for reserve alkalinity approach minimum values specified in the text of this report, tests usually should be performed for mercaptobenzothiazole ion content and phosphate ion content, and if the values for these tests fall below certain minimum values, reconditioning can be made by adding small amounts of inhibitors, or the solution should be changed if serious deterioration has occurred. Monitoring tests should be made once a year for the first two years, and every six months thereafter.

(1) Systems using oil as the heat transfer medium are also recommended. Heat-transfer oils such as Mobiltherm Light and CIRCO XXX (Circosol 306), manufactured by the Sun Oil Company, appear to be satisfactory for use. The General Services Administration recently has published GSA Specification No. 304-15 for a complete snow-melting system using oil. This specification is available for use by other Government agencies.

(m) A closed system is desirable for either an ethylene glycol or oil system. Other design procedures are recommended in Section 5.0.

(n) Electric snow-melting systems are not used by Government Agencies as often as ethylene glycol or oil systems. A GSA Specification for electric snow-melting systems is near completion and will be available for use by other Government agencies.

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TABLE 21

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED LIQUIDS FOR HEAT TRANSFER IN SNOW-MELTING SYSTEMS

<u>Name of Material</u> <u>Chemical</u> <u>Trade</u>		<u>General</u> <u>Class.</u>	<u>Sp. Heat</u> <u>at 100 °F^a</u> Btu/lb deg	<u>Dens.</u> <u>at 86 °F^a</u> lb/ft	<u>Liq.</u> <u>Viscos-</u> <u>ity at</u> <u>100 °F^a</u> centi- poises	<u>Freez-</u> <u>ing</u> <u>Point</u> °F	<u>Boil-</u> <u>ing</u> <u>Point</u> °F	<u>Vapor</u> <u>Pressure</u> <u>Selected</u> <u>Temp.</u> psia	<u>Crit.</u> <u>Temp.</u> °F	<u>Flash Point</u> °F	<u>Toxicity</u>	<u>Suitable</u> <u>with metals</u>	<u>Remarks</u>
Ethylene Glycol HOCH ₂ CH ₂ OH		Diol	0.581	69.0	10.4	+9	388	0.9 at 250 °F	c	245	Slightly toxic	See Report Text	
Diethylene Glycol		Diol	0.56	69.0	18.0	+18	473	0.14 at 250 °F	c	290	Lower than for Ethylene Glycol (See Remarks)	c	Low vapor pressure would tend to lessen danger from inhalation.
Triethylene Glycol		Diol	0.53	70.0	20.0	+19	550	0.03 at 250 °F	c	330	Lower than for Diethy- lene Glycol (See Remarks)	c	Extensive tests on animals have shown little ill effect after long expo- sure.
Ethylene Glycol 40% Solution (By weight) HOCH ₂ CH ₂ OH		Diol	0.86	65.0	1.7	-11	221	25.1 at 250 °F 114.0 at 350 °F	c	d	Slightly toxic	See Report Text	
Ethylene Glycol 50% Solution (By weight) HOCH ₂ CH ₂ OH		Diol	0.81	66.0	2.2	-32	225	23.3 at 250 °F 106.0 at 350 °F	c	d	Slightly toxic	See Report Text	
Ethylene Glycol 60% Solution (By weight) HOCH ₂ CH ₂ OH		Diol	0.77	67.0	2.89	Pro- bably below -50	230	21.0 at 250 °F 96.1 at 350 °F	c	d	Slightly toxic	See Report Text	
Proprietary Ethylene Glycol Product	Dowtherm SE-1	Diol	0.59	67.0	12.0	-56 for 60%	330	c	o	240	Low acute oral toxic- ity	Suitable for steel, copper, aluminum, wrought iron	Do not use with galva- nized metals over room temperature.
Propriety Ethylene Glycol Product	UCAR-17	Diol	h	h	h	h	h	h	h	h	h	h	
Methylene Chlo- ride CH ₂ Cl ₂	R-30	Chlorohydro- carbon	Approx. 0.30		0.37	-142	104	13.3 at 100 °F	458.6	i	500 ppm by volume MAC for succes- sive 8 hr days. Some- what less toxic than group 4 Underwriters.	Suitable for use with copper, steel and cast iron up to 140 °F Reacts with alu- minum and zinc.	Contact of the fluids with the skin should be avoided.

(Footnote on page 3 of Table 21)

(CONTINUATION) TABLE 21

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED LIQUIDS FOR HEAT TRANSFER IN SNOW-MELTING SYSTEMS

Name of Material Chemical Trade		General Class.	Sp. Heat at 100 °F ^a Btu/lb deg	Dens. at 86 °F ^a lb/ft	Liq. Viscos- ity at 100 °F ^a centi- poises	Freez- ing Point ^b °F	Boil- ing Point ^b °F	Vapor Pressure Selected Temp. psia	Crit. Temp. °F	Flash Point °F	Toxicity	Suitable with metals	Remarks
Monochlorodi- fluoromethane CHClF ₂	B-22	Fluorinated Hydrocarbon	0.335 at 86 °F	73.4	0.23 at 86 °F	-256	-41	716, critical pressure	204.8	Non-flamm- able	Group 5A Underwriters	All standard ferrous and non-ferrous metals can be used.	
Dichlorodi- fluoromethane CCl ₂ F ₂	B-12	Fluorinated Hydrocarbon	0.24 at 86 °F	80.7	0.25 at 86 °F	-252	-22	597, critical pressure	233.6	Non-flamm- able	Group 6 Underwriters	All standard ferrous and non-ferrous metals can be used.	
Trichlorotri- fluoromethane CCl ₂ F-CClF ₂	B-113	Fluorinated Hydrocarbon	0.22 at 86 °F	97.0	0.62 at 86 °F	-31	118	101.8 at 250 °F, 283.3 at 350 °F	417.4	Non-flamm- able	Much less than Group 4, but more than Group 5 Underwriters	All standard ferrous and non-ferrous metals can be used.	
Trichloromono- fluoromethane CCl ₃ F	B-11	Fluorinated Hydrocarbon	0.21 at 86 °F	91.4	0.41 at 86 °F	-168	75	182.0 at 250 °F, 468.0 at 350 °F	388.4	Non-flamm- able	Group 5A Underwriters	All standard ferrous and non-ferrous except zinc Mg & Al alloys can be used.	
Dichlorotetra- fl uoromethane C ₂ Cl ₂ F ₄	B-114	Fluorinated Hydrocarbon	0.24 at 86 °F	89.9	0.36 at 86 °F	-137	38	310.0 at 250 °F	294.3	Non-flamm- able	Group 6 Underwriters	All standard ferrous and non-ferrous except zinc Mg & Al alloys can be used.	
Tetra (2- Ethylbutyl) Silicate	PM 3189 (Union Carbide)	Silicate Ester	c	56 at 68 °F	3.6	Below -148	c	<.005	Lq. at wide range of temp.	335	Low order (See Remarks)	c	Ltr. to J.C. Davis,NBS of 4/3/62 stated that toxicity was low order.
Tetra (2- Ethylboxyl) Silicate	PM 3190 (Union Carbide)	Silicate Ester	0.48 at 104 °F	55 at 68 °F	6.0	Below -130	680	<.005	Lq. at wide range of temp.	390	Low order (See Remarks)	c	Ltr. to J.C. Davis,NBS of 4/3/62 stated that toxicity was low order
Aromatic Oil	Mobil- therm Light	Petroleum Oil	0.434	60 at 100 °F	4.5	-20 °	Above 400	.20 at 250 °F, .64 at 300 °F	c	300 - 350 ^f	Non-toxic	Can be used with steel, but not copper.	

Footnotes for Table 21

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED
LIQUIDS FOR HEAT TRANSFER IN SNOW-MELTING SYSTEMS

- a Unless otherwise shown at individual entry.
- b At atmospheric pressure.
- c Information not readily available.
- d Solutions containing less than 85% glycol by weight actively on heating and the flame was extinguished during test cited in reference [17].
- e Pour point.
- f Fire point.
- g AIHA Hygienic Guide Series, December 1956.
- h Essentially ethylene glycol.
- i Practically non-flammable at ordinary temperature. Forms a weekly combustible mixtures at high concentrations of solvent in air.

