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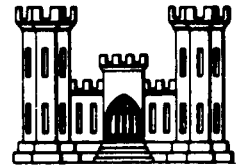
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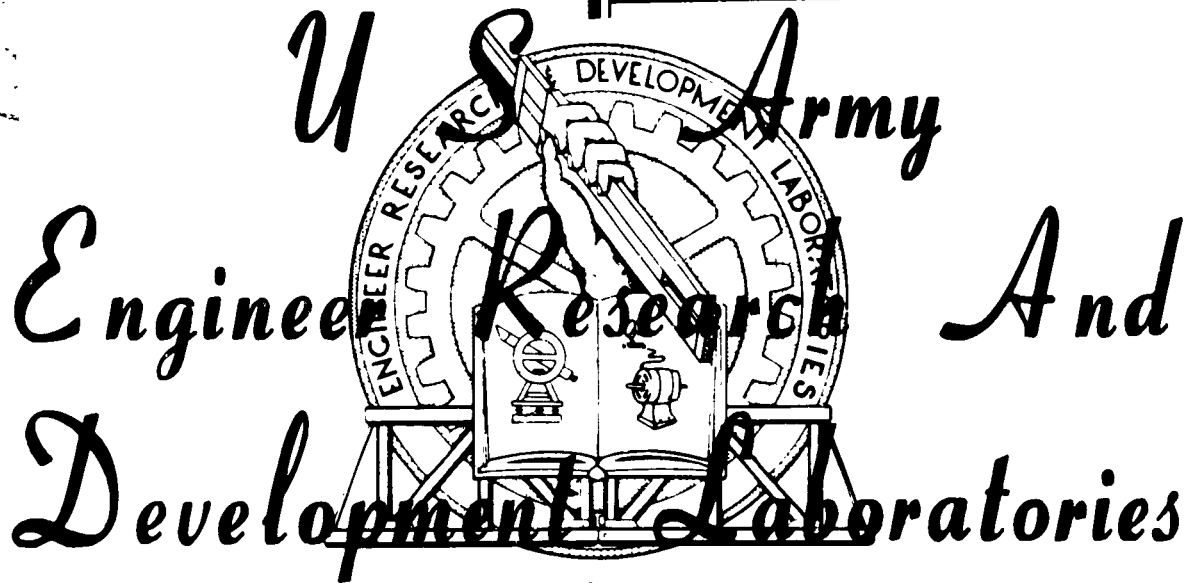
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Technical Report 1681-TR

DEVELOPMENT AND ENGINEERING TEST REPORT,
CHARGES, ANTIFREEZE, FIRE EXTINGUISHER,
LITHIUM/CALCIUM CHLORIDE BASE

Task 8M76-04-001-02
(Formerly Project 8-76-04-109)

20 July 1961



FORT BELVOIR, VIRGINIA

U. S. ARMY ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
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20 July 1961

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PREFACE

The development and investigation covered in this report were conducted under the authority of Task 8M76-04-001-02 (formerly 8-76-04-109). A copy of the project card is included in Appendix A.

Execution of the research study reported was conducted, under contract with the University of Maryland, by W. J. Huff, Senior Investigator; D. T. Bonney, Research Supervisor; and W. L. Monson, L. J. Reid, and M. Schreiner, Jr., Research Engineers of the Department of Chemical Engineering. Engineering tests and evaluation were conducted by J. E. Malcolm, Principal Project Engineer, and B. E. Camper, Senior Project Engineer, with the collaboration of A. N. Williams, Materials Engineer, at USAERDL.

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SUMMARY

This report covers development and engineering-test phases for water additive charges, antifreeze, fire extinguisher, lithium/calcium chloride base. The report summarizes literature surveys and laboratory tests made.

It is concluded that:

- a. A solution having 20.0 percent calcium chloride (CaCl_2), 8.8 percent lithium chloride (LiCl), and 71.2 percent water (H_2O) composition on a weight basis and having a density of 1.2265 at 20°C (68°F) is satisfactory as a candidate antifreeze salt for winterizing water to minus 65°F .
- b. Sodium chromate at a concentration of 1,050 mg per liter of solution effectively inhibits the corrosive effect of the above salt solution on aluminum, steel, brass, zinc, magnesium, and copper.
- c. Lithium-chloride solutions (approximately 23 percent LiCl by weight in water) are effectively nonfreezing to below minus 65°F and except for higher cost are as applicable for application in antifreeze charges as the CaCl_2 LiCl mixture in solution with water.
- d. Dry packaging of salt charges including the inhibitor is feasible.

DEVELOPMENT AND ENGINEERING TEST REPORT,
CHARGES, ANTIFREEZE, FIRE EXTINGUISHER,
LITHIUM/CALCIUM CHLORIDE BASE

I. INTRODUCTION

1. Subject. This report covers development and engineering-test phases for water additive charges, antifreeze, fire extinguisher, lithium/calcium chloride base.

2. Background. Calcium chloride charges are currently used to render water nonfreezing. Calcium chloride, however, only renders water nonfreezing down to minus 40° F ($^{\circ}$ C). The overall military operational temperature range extends from minus 65° F (minus 53.9° C) to plus 155° F (73.9° C). Water is the most effective and readily available agent for extinguishing Class A combustible fires (solid material fires including those in paper, clothing, wood, and plastics). There is, therefore, a critical requirement for rendering water suitable for fire extinguishment in Arctic climates. Subproject 8-76-04-109 (currently Task 8M76-04-001-02), Water Additives, Fire Fighting, was undertaken to investigate all phases of improving the effectiveness of water in fire fighting. The development covered by this report comprised one phase of the overall subproject objective. In this program, consideration was given to means of enhancing the inherent effectiveness of water as a fire-extinguishing agent. In the work reported here, however, the critical requirement for minus 65° F operational suitability was held paramount.

3. Development Objectives. Since the subproject concerned additives in general for improvement of water for fire fighting, specific requirements for the antifreeze charges were as follows:

a. The charges shall not detract from the extinguishing ability of water and, insofar as possible, improve the effectiveness of water for extinguishing fire.

b. When properly mixed with water, the charges shall render water nonfreezing down to minus 65° F (minus 53.9° C) and be suitable for use and storage for extended periods of time at temperatures of from minus 65° F (minus 53.9° C) to plus 155° F (73.9° C).

c. When properly mixed with water, the charges shall render water no more viscous at minus 65° F (minus 53.9° C) than SAE 30 lubricating oil at 63° F (20° C) room temperature.

d. When properly mixed with water, the charges shall render water no more corrosive than the current inhibited calcium-chloride antifreeze charges.

e. The charges shall be essentially odorless when mixed with water.

f. When properly mixed with water, the charges shall render water no more toxic or irritating than the current inhibited calcium-chloride antifreeze charge.

g. The charges shall be easily packaged and stable for extended periods of shelf storage.

h. The charges shall be readily available at a reasonable cost to the Government.

i. The charges shall be reliable and suitable for troop use while not requiring extensive apparatus or equipment for use.

4. Approach. A contract was awarded to the University of Maryland, with Dr. W. J. Huff as Senior Investigator, to study the literature pertinent to the problem and to investigate promising salt formulations. Previously, a study made at the USAERDL Materials Laboratory, with Newell Blackburn as principal investigator, showed that lithium chloride had promise as an engine-coolant antifreeze (1). Attention of the University of Maryland team was called to results of the USAERDL investigation, and lithium chloride was included as a material for study under their program. Following this program, in which a candidate formulation was chosen (2), engineering tests and investigation of packaging techniques were conducted at USAERDL.

II. TECHNICAL LITERATURE SURVEY

5. Freezing-Point Depressants. Examination of the pertinent technical literature at the University of Maryland disclosed relatively few nonflammable substances that impart the desired freezing-point lowering to water. Tables I and II include all reported inorganic substances having eutectics with water below minus 40° F. All pertinent fire-extinguisher-charge and antifreeze-solution formulations composed principally of inorganic components reported in the patent and technical literature reviewed are also included. The tables list compounds that are obviously unsuited for the purpose at hand due to their physical as well as chemical nature. The tables indicate that although a large freezing-point lowering is possible with a few compounds, the extremely acid (or alkaline), corrosive, or toxic nature of the binary mixtures obtained would in every case be contrary to fulfillment of other military requirements. Generally, it appears in these compounds that the greater the eutectic lowering, the more strongly acidic (or basic) the substance; the reverse, however, is not usually true. Of those substances giving

Table I. Freezing-Point Depressants
for Binary Aqueous Systems

System	Eutectic Freezing Point (°F)	Weight Concen- tration (%)	Data Source	Remarks
Chromic acid (CrO ₃)	-247.5	60.5	(3)	-
Ammonia (NH ₃)	-142	32.0	(3)	-
Lithium iodide (LiI)	below -132	over 51	(4)	-
Beryllium nitrate (Be(NO ₃) ₂)	below -130	over 38	(4)	-
Hydrochloric acid (HCl)	-122	24.4	(3)	-
Phosphoric acid (H ₃ PO ₄)	-122	62.4	(3)	-
Selenic acid (H ₂ SeO ₄)	-117.5	47.8	(3)	-
Pyro phosphoric acid (H ₄ P ₂ O ₇)	-104	59.1	(3)	-
Sulfuric acid (H ₂ SO ₄)	-104	37.9	(3)	-
Cyanic acid (HCNO)	-102	83.54	(4)	-
Lithium chloride (LiCl)	-88	28	(5)	-
Potassium hydroxide (KOH)	-85.5	30.7	(3)	-
Hydrobromic acid (HBr)	-85	38.2	(3)	-
Cobaltous perchlorate (Co(ClO ₄) ₂)	-81	Not given	(3)	-

Table I (cont'd)

Perchloric acid (HClO_4)	-80.5	41.6	(3)	-
Zinc chloride (ZnCl_2)	-80.0	51	(3)	29.9% CaCl_2 -51% ZnCl_2 - H_2O (6). System investigated at -50°, -70° and -100° C.
Sodium lactate ($\text{Na}(\text{C}_3\text{H}_5\text{O}_3)$)	below -77		(7)	50% solution not solid at -77° F (8). Sodium lactate/sodium carbonate system pro- posed as antifreeze solution (9).
Arsenic acid (H_3AsO_4)	-76	68.8	(3)	-
Iron chloride (FeCl_3)	-68	33	(3)	-
Aluminum chloride (AlCl_3)	-68	25.2	(4)	-
Calcium chloride (CaCl_2)	-60.3	32.3	(3)	CaCl_2 - ZnCl_2 - H_2O in- vestigated at -100° C (-148° F) (6). 3 to 4 oz. of K_2CO_3 added to 10# CaCl_2 to form 2½ gal. noncorro- sive, nonfreezing fire extinguishing charge (10). 32 oz. CaCl_2 & 7 oz. AlCl_3 in 1 gal. H_2O forms fire extinguishing charge which is liquid at -45° F. Glycerol & penetrating oil may be added (11). ½# CaCl_2 & ½# sodium thiosulfate with 1 teasp. tartaric acid form 1 gal. antifreezing fire charge (12). Glycol or Glycerol may be added to CaCl_2 solution to produce anti- freeze solution (13).

Table I (cont'd)

Calcium chloride (CaCl ₂) (cont'd)				CaCl ₂ -MgCl ₂ -H ₂ O soln. of 22.2% Be density can be cooled to -62° F without solidification (14).	
Lithium azide (LiN ₃)	-53.5	26	(4)	-	
Potassium sulfite (K ₂ SO ₃)	-50.2	51.2	(3)	-	
Lithium bromide (LiBr)	below -49	over 33	(4)	-	
Nitric acid (HNO ₃)	-46	32.5	(3)	-	
Cupric chloride (CuCl ₂)	-39.5	37.1	(3)	-	
Lithium chlorate (LiClO ₃)	-39.5	37.0	(4)	-	

Table II. Freezing-Point Depressants
for Complex Aqueous Systems

System	Freezing Point (°F)	Data Source	Remarks
Alkali metal salts of organic hydroxy acids	-	-	Salt of lactic acid is an important ingredient. Such salts surpass the action of glycerine as a freezing- point depressant. Salts of alkali metals and alkali- earth metals may be mixed with retention of the desir- able properties. Such solu- tions are noncorrosive (8).
Calcium chloride/ zinc chloride/water	Not solid at -148	(6)	Antifreeze electrolyte for dry cells.

Table II (cont'd)

10 pints ammonia acetate, 2 pints sodium bicarbonate, 30 pints water, 10 pints glycerol	-	-	Patented fire extinguisher charge with freezing-point lowering (15).
Calcium chloride/potassium carbonate/water	Not given	-	(a) 3-4 oz K_2CO_3 added to 10# $CaCl_2$ in order to reduce acidity (10). (b) Patented fire-extinguisher charge.
Potassium carbonate 34-42%, glycol 6%, chromate 3%, water	Below -40	(16)	Patented as antifreeze fire fire-extinguishing charge. Chromate added as corrosion inhibitor (16).
Potassium carbonate/concentrated potassium hydroxide solution/water	Not given	-	Patented antifreezing fire-extinguishing charge (17).
Thiocyanate/water/sodium bicarbonate	-	-	Patented fire-extinguishing charge (18).
Potassium thiocyanate/sodium bic./water	-	-	Patented fire-extinguishing charge (19).
Sodium carbonate/sodium lactate glycerol/water	-	-	Patented fire-extinguishing charge (19).
Sodium carbonate/potassium carbonate/glycol/water	Not given	-	Patented fire-extinguishing charge (20).
5.53 gm sodium carbonate, 76 gpm sodium acetate, 100 cc water	About -58	(21)	Pasty at -32° F but fluid at room temperature (21).
Alkali metal chloride/alkali metal carbonate/water			Patented fire-extinguishing charge (22).
Protein base foam lithium chloride as antifreeze agent	-50	ERDL Finding	Fire extinguisher foam.

extreme depressions, oxy-acids are in the majority; ammonia, however, gives the second greatest lowering found.

6. Antifreeze-Charge Components. Tables I and II include many complex and patented fire-extinguishing charges that are claimed to be fluid at low temperatures. In the patents covering these charges, temperatures of minus 30° F are considered low. Therefore, unless the components themselves warranted further investigation, such patented solutions were not investigated. Solutions of the alkali metal salts of the organic hydroxy acids were found to be extremely viscous at low temperatures and were, therefore, not extensively investigated. Those antifreeze systems which depended on liquid components were rejected because of the packaging requirements and flammability of organic liquids present in high concentrations. Systems which depend on hazardous oxidants such as chlorates and poor to mediocre freezing-point depressants such as the thiocyanates of sodium and potassium were also rejected. Of the complex systems listed in Table II, none of the patented fire-extinguisher charges appear to be applicable at minus 65° F and only the antifreeze solution consisting of calcium chloride and zinc chloride seems to have been investigated at extremely low temperatures. The carbonates have generally been used either with organic depressants or strong bases such as potassium hydroxide. Following is a discussion of the carbonates of potassium and ammonia as components for an antifreeze charge.

a. Potassium Carbonate. In order to produce a nonfreezing solution of potassium carbonate, the eutectic temperature in the system K_2CO_3 /water must be depressed 31° F in order to reach minus 65° F. Substances which are capable of such depression without precipitation of carbonate ion are potassium hydroxide and ammonia. The strong bases and strong acids were rejected at the beginning of this research because of their toxicity. However, there is no doubt that solutions freezing below minus 65° F can be prepared from mixtures of potassium hydroxide with other salts.

b. Ammonium Bicarbonate (NH_4HCO_3). Ammonium bicarbonate is relatively insoluble having a solubility of 12 grams per 100 grams of water at 0° C. It would not be expected to be a good depressant in such low concentrations. This salt decomposes above 88° F.

c. Ammonium Carbonate ($NH_4HCO_3 \cdot NH_4NH_2CO_2$). The eutectic of ammonium carbonate was found to be 14° F. The formula is often written $NH_4HCO_3 \cdot NH_4NH_2CO_2$ since a solution contains no carbonate ions unless NH_4OH is added. Ammonium carbonate readily decomposes, losing ammonia and forming the bicarbonate. It, therefore, must be stored in a gastight container. The ammonium carbonates were not investigated as antifreeze solutions because of the relatively low freezing-point-depressing power and instability.

7. Additive Effectiveness for Wood Fires. The literature search revealed three articles in which the results of an investigation of the efficiency of additives to water for the extinction of wood fires are described. The authors of these three articles are L. Metz (23), H. D. Tyner (24), and J. Bryan and N. D. Smith (25). In the discussion by Metz, reference is made to the results of C. D. Magirus (26). The applicability of salt solutions for extinguishment of wood fires was discussed (7, 14, and 27) in a general manner. In most instances, only calcium chloride was named as an agent. L. E. Wise and E. C. Jahn (28) in their book "Wood Chemistry" mention that the ammonium phosphates are superior fire-retarding agents. Patented fire-extinguishing mixtures which were also claimed to be freezing-point depressants are given in Tables I and II.

a. Procedure. Laboratory or small-scale apparatus was employed by the authors cited above (23-25). The testing procedure, basically the same in all three, consisted of igniting and burning a standard wood crib in a specific manner; either water or salt solution was then sprayed until all glowing had disappeared, and the volume of solution used and/or the time required for extinction was noted. The procedures and apparatus were, in each case, such that all pertinent factors remained constant (or were controllable). The effectiveness, or superiority factor, was determined by dividing the amount of water required to extinguish the fire by the amount of solution required to produce the same effect. A more complete description of the apparatus and procedures is found in paragraph 13.

The compounds listed in Table III have been reported as being capable of increasing the effectiveness of water. An examination of the complete tabulations presented in the references cited discloses some disagreement about the effectiveness of some salts (such as calcium chloride, sodium acetate, and zinc chloride). It is believed that these apparent discrepancies arise from three sources: first, the number of compounds tested; second, the nature of the compounds tested; and/or third, the concentration of the salt solution.

b. Conclusions. The following conclusions became apparent after the literature was studied:

(1) In all cases, where investigated, phosphoric acid, diammonium hydrogen phosphate, and ammonium dihydrogen phosphate proved to be most effective and were generally considerably superior to the next best substance. Superiority is very apparent in dilute solutions, 0.5 to 5.0 percent.

(2) The inorganic salts of ammonia, in general, show the most effective extinguishing properties. Otherwise, there

Table III. Compounds Reported as Water Additives
Having Effective Action on Wood Fire (Total Extinction)

Compound ^a	Magirus (26)	Metz (23)	Tyner (24)	Bryan & Smith (25)
Ammonium chloride - NH_4Cl	-	*	-	-
Diammonium hydrogen phosphate - $(\text{NH}_4)_2\text{HPO}_4$	-	*	*(L) ^b	*
Ammonium dihydrogen phosphate - $\text{NH}_4\text{H}_2\text{PO}_4$	-	-	*(L)	*
Ammonium sulphate - $(\text{NH}_4)_2\text{SO}_4$	-	*	*(H) ^c	-
Ammonium salts in general	-	-	-	*
Boric acid - H_3BO_4	-	-	*(L)	-
Calcium chloride - CaCl_2	*	*	*	*
Lithium chloride - LiCl	-	-	*(H)	-
Magnesium chloride - MgCl_2	-	-	*(H)	-
Phosphoric acid - H_3PO_4	-	-	*(L)	-
Potassium acetate - $\text{KC}_2\text{H}_3\text{O}_2$	-	-	*(H)	-
Potassium carbonate - K_2CO_3	*	-	*(H)	-
Potassium oxalate - KHC_2O_4	*	-	-	-
Water glass	*	-	-	-
Zinc chloride - ZnCl_2	-	-	*(H)	-
Number of compounds investigated:	8	10	33	15

NOTES:

- a. Asterisk denotes compound reported effective.
- b. L = low concentration, 2 to 5 percent.
- c. H = high concentration, 25 percent.

appears to be no correlation between ions and effectiveness, but the experimental programs reported in the literature were not established in such a manner as to reveal any such correlation.

(3) It appears that almost any inorganic salt in the concentration range of about 20 percent will increase the effectiveness of water in extinguishing wood fires.

(4) No conclusions can be reached concerning organic compounds and their derivatives. Although Tyner's data shows that some organic acids and their salts (an exception being potassium acetate) were generally less effective than water alone, it is doubtful because of the small number employed that this finding can be extended to all organic acids (and compounds) and their salt derivatives. Various organic compounds have been reported as constituents in patented fire charges and fire-preventing solutions to be applied to wood.

(5) Although Metz, Tyner, and Bryan and Smith chose their chemical solutions with the requirements for an ideal additive in mind, it is possible that some compound deviating greatly from these requirements could be found which is even more efficient than the ammonium phosphates; however, such a compound would not be applicable for general usage.

c. Variables. The following variables have been found to affect the efficiency of an additive:

(1) Concentration of Chemical. Both Tyner and Bryan and Smith investigated concentration of the chemical completely. Their results agree and show that for the more efficient additives the greatest percentage of the increase in effectiveness occurs in solutions more dilute than 5 percent. The superiority factor, however, seems to decrease below the maximum value at high salt concentrations. Evidently, a concentration is reached where the increase in fire-fighting ability by the addition of a salt is counterbalanced by the loss in evaporative cooling resulting from the displacement of water.

(2) Rate of Application. Rate of application is extremely important. Tyner indicated and Bryan and Smith determined the relationship between rate of application and the effectiveness of any agent. For any given fire and at a relatively high spraying rate, there will be little difference in effectiveness between water and salt solution. However, as the rate of delivery is decreased, a much greater increase in the total amount of water is required than for the salt solution, thereby increasing the superiority factor. Finally, a rate of

application is reached where the solution will never extinguish the fire. It is at the lower rates of application where additives show their maximum effectiveness.

(3) Wind Velocity. Tyner found that the superiority of an ammonium dihydrogen phosphate solution over water is greater with moderate wind velocities than at zero wind velocity. This relationship may be extended to all extinguisher solutions.

d. Effect on Wood. The effect of these additives on the wood itself was not determined (nor even mentioned) by the above investigators. It has been reported that dry-rot can be caused by the hygroscopic properties of calcium chloride when impregnated in wood (19). It is also known that many inorganic salts (i.e., zinc chloride) embrittle wood and cause serious deterioration in strength. The more concentrated the solution applied, the greater the effect. It is believed, however, that the agents employed in fire retardants have no appreciable effect on wood (28).

It is possible that further investigation along this line would show that the adverse effect of an agent on wood would be enough to discourage its use. Unfavorable action on wood becomes more important as the size of the equipment increases or as the delivery efficiency (the ratio of total solution pumped to that which reaches the flammable area) becomes less.

e. General. The German authors seem to believe that it is not economical to employ additives. Metz concludes that unless there is a shortage of water, additives are not worth the increased expense and the extra effort required to inhibit corrosion. No large-scale tests have been reported, however, from Germany.

To obtain a broader picture, the American Forest Products Laboratory employed the better agents found by Tyner to extend his laboratory work to fairly large-scale outdoor fires involving various types of wood and brush. This work is described by Truax (29), who presents the following conclusions:

Whenever there is an abundant supply of water, chemicals are not considered to have any worthwhile application, but if there is a scarcity of water, chemical additives may yield important advantages. The use of these agents is probably applicable in the early stages or initial stages of attack on forest or brush fires, lumber yard fires, etc., through the use of back packs and small tankers. They have little, if any, application to large fires.

The British also extended their laboratory research. E. H. Coleman (30) described observations of the effect of ammonium-dihydrogen-phosphate solution on model large-scale fires and conventional fires fought with regular fire equipment. Because of variable conditions (such as wind velocity, type and arrangement of material, size of fire, and method of spraying), the determination of conclusions was difficult. Coleman concluded that the most important and practical application of additives is their use in small appliances where the rate of delivery is generally low relative to the size of the fire and where the effective delivery is large. Since the ability of small fire extinguishers often determines whether a small fire is extinguished or whether it continues on to become a major one, increasing of the capacity of these appliances by salt additions would be economical particularly in those instances where the maximum capability of the existing water is approached. Since in large fires the rate of delivery is always at a maximum and great wastage is present, additives give no advantage over water. Construction features such as brickwork and steel beams also decrease the relative effectiveness. Any shortage of water may enable the use of additives when they would not otherwise be used.

Metz (23), Tyner (24), and Bryan and Smith (25) described apparatus that was used in determining the effectiveness of additives to water for the extinguishment of cellulosic fires. Folke, et al (31) also reported a test procedure for investigating the factors involved in the extinction of wood fires with water. The primary requirement is a standard reproducible fire burning under controllable conditions.

8. Theoretical Aspects of Freezing-Point Depression.

a. Anion and Cation Effects. The effects of the anion and cation on solubility and freezing-point depression are arranged by Traube (32) in the following manner:

(1) Solubility.

Nitrate > Chlorate > Iodide > Bromide > Chloride
Hydroxide > Sulfate > Carbonate

Hydrogen > Cesium > Rubidium > Ammonium
Lithium > Potassium > Sodium

(2) Freezing-Point Depression.

Nitrate < Thiocyanate < Chloride < Bromide < Iodide
Cesium < Rubidium < Potassium < Sodium < Lithium

Since this arrangement is only general, it cannot be used to predict the actual freezing point of any given compound dissolved in water. This listing does, however, indicate those combinations of chemicals that have been tried in the past and, more or less, the freezing-point lowering to be expected upon employing them in the future.

b. Surface-Tension Correlation. A correlation between freezing-point depression and change in surface tension was noted by S. C. Bradford (33) as a result of development of his molecular theory of solution. On analysis, it appears that Bradford's contribution was mainly to emphasize the broad importance of inter- and intra-molecular forces in determining properties of solutions. The equations developed can be applied in a qualitative way to explain some general aspects of freezing behavior and, as shown, surprisingly good correlations are observed in the case of relatively dilute solutions. There is no obvious method of even qualitatively extending Bradford's theory to the present case of very concentrated solutions of three or more components.

c. Observations of E. Kordes. E. Kordes (34) attacked the more general problem of correlating eutectic behavior of mixtures by grouping together data from the following classes of substances: molecular compounds, ternary electrolytes, binary electrolytes, and monatomic elements. He defined the following quantities:

T_a = fusion temperature of higher melting component.

T_b = fusion temperature of lower melting component.

T_e = eutectic temperature.

$\frac{T_b - T_e}{T_b}$ = eutectic freezing-point lowering for component b.

$\frac{T_a - T_e}{T_b}$ = eutectic freezing-point lowering for component a.

$\frac{T_b - T_e}{T_a}$ = common eutectic freezing-point lowering.

Kordes was able to plot a series of curves using as ordinate and abscissa $\frac{T_e}{T_a}$ and $\frac{T_b}{T_a}$, respectively. These parameters from each class of substances defined above were found to fall, roughly, on characteristic curves with separate curves for mixtures of electrolytes showing dissociation of one or both components. The following empirical equation was derived and summarizes the information contained in the above-mentioned plots:

$$\log \frac{T_b - T_e}{T_a} = k' \log \frac{T_b}{T_a} = \log k \quad (1)$$

where: k' is a constant characteristic of the class of substances being considered.

k is a constant, actually the eutectic lowering which would be found as T_b approached T_a .

An even more useful relationship defined by Kordes is the following:

$$\frac{T_a - T_e}{T_b - T_e} = 1.5 \left(\frac{N_a}{N_b} - 1 \right)^{+1} \quad (2)$$

where: N_a and N_b are the mole fractions of components a and b, respectively, in the eutectic mixture.

It should be noted that equation 2 is independent of whether two metals, two electrolytes, or two molecular compounds are mixed; for equation 1, however, the physico-chemical character of the pure substances must be known. However, the author points out that both equations are restricted to use for systems from whose fusions pure components crystallize, which show no association or inclination for the formation of compounds, and that consist of ideal mixtures in the liquid state. In the case of greatest interest, aqueous salt solutions, the equations developed by Kordes are of the least applicability. This is, in general, because of association effects and tendency toward hydrate formation. Even in the case of real mixtures approaching ideal solutions in behavior, the correlation is not exact and deviations of small amounts are common while large deviations would not be altogether uncommon. In 24 examples of the application of Kordes' equations to salt and water mixtures, it was shown that errors of 1 to 14° F were encountered and in the specific cases of silver chloride and silver bromide which (as is well known) are quantitatively insoluble, a eutectic composition of 2 percent salt and a eutectic lowering of 5° F were calculated.

d. Observations of E. Tezner. E. Tezner (35) reported the results of some experimental work from which he concluded that in aqueous solutions of mixtures of electrolytes and nonelectrolytes, the net freezing-point depression would be expected to be less than the sum of the parts. This fact was attributed to the dissociation of electrolytes being less than normal which was perhaps partly due to an increase in viscosity. The difference increased with increasing concentration of nonelectrolytes. The evidence was based on experiments using sodium chloride and sodium sulphate as electrolytes and phenol, resorcinol, and glucose as nonelectrolytes.

e. Observations of O. Klein and O. Svanberg. O. Klein and O. Svanberg (36) studied the freezing-point lowering of aqueous solutions of two salts. They defined the quantity $d = S - s$

where: S = the observed depression of the mixture.

s = the sum of the individual depressions.

d = the difference between the two.

A quantity K is then $K = \frac{d}{C_1 C_2}$

where: C_1 and C_2 are the concentrations of the two salts.

K , which then always has the sign of d , was originally supposed to be a constant. However, as the experimental work accompanying the article showed, K may vary either positively or negatively depending on the concentrations and the nature of the compounds in question. All experimental values given by the authors were for aqueous solutions of compounds having a common ion. Their results, however, are limited to ternary systems. The compounds studied were: nitric, hydrochloric, hydrobromic, and hydriodic acids; sodium and potassium bromide; iodide; nitrate and oxalate; sodium nitrate; sulfate and acetate; calcium chloride; strontium chloride; and copper sulfate. Following is a summary of the conclusions presented:

(1) There appears to be no general rule in regard to the sign of the effect of a salt. In several cases, the freezing-point lowering is smaller and in others larger than the sum of the individual lowerings. In the case of most electrolytes, the effect is positive. A negative effect is found in sulfates, nitrates, and alkalis.

(2) In mixtures of halogen acids and alkali halogens, $K = \frac{d}{C_1 C_2}$ and is positive and fairly constant.

(3) For alkaline earth salts, K is also positive but increases with concentration.

f. Thermodynamic Consideration. Certain aspects of the present problem are clarified in a paper by G. N. Lewis (37) in which he considers the equilibrium between liquid and solid phases at the freezing point of solutions in the light of activity relationships and points out that a eutectic mixture of two components would behave like a pure solvent on addition of a third component to the freezing solutions. He indicates the derivation of the following

special equation for this case:

$$dt = \frac{RT^2}{\Delta H} dN_1 \quad (3)$$

where: dN_1 = differential amount of solute added to eutectic.

dt = change in freezing point of eutectic on addition of dN_1 mols of solute.

R = gas constant.

T = freezing temperature.

ΔH = heat of fusion of eutectic solid.

This general equation is valid for addition of another component to eutectics of any number of components. This equation, similar in form to the well-known law of freezing-point depressions for dilute binary solutions, is integrable only under certain conditions. The variation of heat of fusion with liquid composition and with temperature must be taken into account. Furthermore, it must not be forgotten that one is limited by the solubility of the additive in the original eutectic mixture as a solvent. This equation also assumes that the true activity of the solute can be replaced by its mol fraction for calculation. None of these assumptions hold true in concentrated solutions; therefore, no information concerning the ultimate freezing-point depression achievable is obtainable from equation 3.

The following points, based on the above discussion, are of interest for the freezing-point investigation:

(1) The eutectic temperature of binary systems can be lowered (at least theoretically) by an amount initially proportional to the mol fraction of solute added to the eutectic mixture, but one is not able to ascertain from purely thermodynamic factors the limiting solubility or the final lowering achieved.

(2) Using the theory of molecular cohesion and adhesion, one is able to arrange ions according to their relative lowering of freezing points of pure substances by comparing their solubility, effect on surface tension, and other properties of solutions. The proper arrangement, however, implies a knowledge of relative cohesions and adhesions of all components in the mixture in question. Furthermore, ideal solution behavior is a requirement for the use of Bradford's equations

even in the simple (and not applicable) case of dilute binary solutions.

(3) The equations which have been found by Kordes to connect melting points and eutectic composition and temperature do not extend to cases of interest to this research.

(4) Although it was reported that in mixtures of electrolytes and nonelectrolytes the total depression is less than the sum of the parts, in mixtures of two electrolytes in ternary systems the depression may be either greater or less than the sum of the individual lowerings.

9. Theoretical Aspects of Fire Extinction. Before a discussion on the mechanism of additives is presented, a brief description of the combustion of wood and the action of water in extinguishing fires will be given in order to promote a better understanding of the subject.

The following description of the combustion of wood is based on information presented by Wise and Jahn (28) and Coleman (30):

Because the ignition temperature is higher than the charring or decomposition temperature, the combustion of wood, in reality, is the burning of the products from thermal decomposition. These products fall into three categories: volatile flammables (combustible gases, light and heavy vapors, and tar mists); volatile nonflammables (steam and carbon dioxide); and nonvolatile flammables (charcoal). After the initial stages of burning, the cross-section of a piece of burning wood (or cellulosic material) can be divided into three sections. The first layer consists primarily of charcoal from which a small volume of gases is distilled. The temperature decreases from the ignition temperature of charcoal (or above) at the surface to about 320°C at the interface between this and the second layer in which most of the destructive decomposition occurs. The temperature of the inner boundary is approximately 250°C , or the temperature at which thermal decomposition begins. The volatile products pass through the charcoal layer where they are heated, mixed with the gases distilled in this section, and finally ignited with air. They generally burn some distance from the surface where there is sufficient air for complete combustion. In the third layer, the moisture in the wood is vaporized. Since most of the heat of combustion from the volatiles is not available to the wood and the charcoal burns very slowly and dissipates the majority of its heat by radiation, burning wood is rarely able to maintain its ignition temperature against the diffusion of heat inward. Therefore, the combustion of wood requires constant or repeated application of heat from some outside source, usually other burning objects. The combustion of wood depends on many variables such as

size, shape, position, moisture content, specific gravity, arrangement, air supply, and confining walls.

Bryan and Smith concluded that the resistance of burning wood to extinction depends more on its temperature than on the rate at which it is generating heat. They found that although the rate of burning or heat generation is the greatest during the initial stages of burning, the time required for extinguishing increased as the time of burning increased. The following explanation was proposed: The major part of the heat evolved in the initial stages of combustion is due to the burning of volatiles distilled from the surface layer. Because these volatiles burn at a distance away from the wood, most of their heat of combustion is dissipated by convection, although in a typical propagating fire this combustion aids in supporting the combustion of another piece of material. Therefore, the burning material is still at a low temperature level and can easily be extinguished. The small amount of heat which is absorbed (or the heat from another burning area) gradually diffuses into the wood, liberating more volatiles, but at a diminishing rate because of the slowness in the conduction of heat. This decrease in the production of combustible volatiles causes the intensity of flaming and the liberation of heat to diminish slowly with time. During this period, the resistance to extinction increases slightly because of the slow rise in temperature. When the decrease in flaming allows access of air to the charcoal, the charcoal begins to glow. The calorific value of charcoal is much higher than that of the volatile substances and, moreover, its heat of combustion is liberated directly in the surface layers. Therefore, at this point in the combustion process, a greater proportion of the heat being evolved is absorbed by the wood and the temperature of the charcoal layer is raised rapidly. Not only does the extinction resistance rapidly increase because of the increase in the sensible heat content, but the increase in the mean temperature of the material also promotes regeneration or rekindling of any portion of the fire temporarily extinguished because of the higher rate of radiant heat transfer from elements at the higher temperatures. Therefore, the resistance of a fire to extinction depends on its heat content, the absolute temperature, and the ignition temperature of the burning material. The results of another investigation, Folke, et al (31), indicate that the resistance increases rapidly during the first stage of combustion and then levels out to some constant value. It was reported that the resistance of a laboratory wood crib remained more or less constant between 50 and 75 percent of the crib burned.

a. Fire Extinguishment. The following factors cause water to be effective in extinguishing cellulosic fires:

- (1) The cooling of the fire and surroundings to below the ignition temperature by the removal of heat necessary for vaporization of the water.

(2) The oxygen replacing action of the generated steam.

(3) The increasing of the ignition temperature of the evolved combustible gases because of their dilution by the water vapor.

The first factor is by far the most important; it is very doubtful that the latter two have any appreciable effect. If the fire could be covered completely with a stream of water, the amount required for extinction would be thermally equivalent to some fraction of the heat content of the burning wood, and cooling of the whole mass to just below the ignition temperature would be sufficient. Generally, fires are too large to be completely covered; therefore, only a portion of the fire is being extinguished at any one time. The charcoal must be cooled to a temperature lower than its ignition temperature because the areas temporarily extinguished at any one time are able to receive radiant and convected heat. The consequence is that more water is required than when the fire can be simultaneously covered completely with water. With decrease in the rate of application, the time necessary for cooling of any given area is increased, allowing an even greater time for heat transfer. The result is that still more water is necessary for extinguishment than that amount based on a fraction of the burning wood heat content. When the delivery rate is below a critical value, the rate of cooling is never large enough to counterbalance the rate of heat generation. For this reason the spraying rate relative to the size of the fire is very important in extinguishing fires.

b. Fire Retardancy. In 1821, Gay-Lussac (38) proposed that the effectiveness of fireproofing agents or, since there is a parallelism, fire-extinguishing agents in regarding the rate of combustion is due to either one or both of the following mechanisms:

(1) The dilution of the combustible gases with non-combustible gases or decomposition products.

(2) The formation of a protective glaze over the surface of the fuel.

The first proposal has been discounted by Tyner because of the large amounts of steam and carbon dioxide already present. (The smothering action of the noncombustible gases is generally considered of secondary importance anyway.) The second mechanism appears to be fairly important in some cases since the effectiveness appears to have some relationship with the melting point as shown in Table IV. Although there is some apparent correlation, there does not appear to be any simple relationship involved. Also, the fact that the most effective agents cannot be explained by this mechanism has turned investigators to other proposals.

Table IV. Correlation Between Effectiveness
and Melting Point for Chloride Salts

Compound	Melting Point (°C)	Tyner (24)	
		Percent by Weight	Superiority Factor
Sodium Chloride	804	25	1.00
Potassium Chloride	690	25	1.20
Calcium Chloride	772	26	1.50
Magnesium Chloride	712	25	1.70
Lithium Chloride	614	27	1.80
Zinc Chloride	365	25	1.65
Ammonium Chloride	350*	28	1.50

* Decomposes.

Metz and Tyner indicate that additives, especially in low concentrations, would not be expected to alter greatly the cooling capacity of water. Metz also indicates that a large concentration of salts might cause a decrease in the thermal capacity because of the displacement of water.

Metz first expressed the opinion that for many salts, the action of the salts on the combustion of wood determines the effectiveness. He suggested that the acidic nature of the decomposition products, in particular those from the salts of ammonia (these salts easily break down into ammonia and an acid), cause the formation of a carbonaceous layer. This layer, which to begin with is less readily combustible, tends to slow down the thermal decomposition of the wood underneath it. Although Metz only applied this reasoning to explain the effectiveness of ammonia compounds, acidic salts (such as zinc chloride) might be expected to show such a favorable alteration of the combustion mechanism. Tyner believed that the explanation for the effectiveness of many salts is their influence on the ratio of charcoal to volatile combustibles which more or less agrees with Metz. When the ratio of charcoal to volatile combustibles is higher, the rate of combustion is slowed down because a charcoal surface layer is less readily combustible than are gases and tars. He also cited the work of Palmer (39) and Richardson (40) to support this approach. They found in studying the effect of chemicals on the destructive distillation of wood that certain chemicals (especially phosphoric acid and salts of ammonia) greatly reduced the yield of the gases and tars while giving an increased yield of charcoal. Bryan and Smith made no reference to any mechanism other than the one concerning the combustion action, while Metz and Tyner did discuss other possible mechanisms. They indicated

that additives not only affect the charcoal yield but also, in many instances, increase the ignition temperature of the charcoal. Their explanation for the reason salt solutions can be applied at lower rates of delivery is that before any temporarily extinguished area will be rekindled, it must receive more heat as the result of the formation of this relatively combustion-resistant charcoal surface layer. According to Bryan and Smith, the distinction between the actions of a flame retardant and a glow retardant rests upon whether the additive increases the charcoal yield only or also increases the ignition temperature of the charcoal (inhibits glowing). A few salts (for example, the ammonium phosphates) show both properties, and this is the apparent reason for their excellent effectiveness.

A survey of the results and theories reported in the literature indicates that the effectiveness of additives is related to both their physical and chemical properties. For the effective agents presented, possession of one or more of the following capabilities appears to be important: (a) increase in the proportion of charcoal formed, thereby decreasing the rate of combustion by reducing the amount of the readily combustible gases, (b) increase in the ignition temperature of the surface charcoal, and (c) formation of molten inactive protecting layer upon the surface of the wood. Although the cooling and smothering action of the liberated, inert gases and the catalytic action of these gases may be contributing factors, their importance appears to be only secondary.

III. LABORATORY INVESTIGATION

10. Basis of Experimental Investigation in the Laboratory. From the study of the literature and theoretical correlations, it became apparent that salts (for example, ammonium salts) which render maximum fire-extinguishing effect on Class A combustible fires were poor freezing-point depressants. Consequently, it was decided that emphasis should be placed on the development of an antifreeze formulation, particularly in view of the observation that, in general, a 20 percent concentration of an inorganic salt in water generally improved the fire-extinguishing effect of water. Since no precise predictions could be made from theoretical relationships, laboratory testing was deemed necessary. Reported literature indicated that the following salts should be considered in this study: calcium/zinc chloride systems; zinc chloride, sodium lactate, ferric chloride, aluminum chloride, lithium chloride, lithium bromide, and lithium iodide.

The following salts were considered as the major salt component for an antifreeze charge.

a. Calcium Chloride. The calcium chloride/water system has a eutectic temperature of minus 60° F. Calcium chloride's non-toxicity and availability are desirable as characteristics of an ingredient of a nonfreezing fire-extinguishing solution. Investigation of systems containing calcium chloride was directed to lowering the freezing point of the eutectic calcium chloride/water system to such an extent that a concentration variation of plus or minus 2 percent could be tolerated in making up the solution.

b. Zinc Chloride. Although the zinc chloride/water system can meet the freezing-point requirements, the high salt content required (51 percent) and high viscosity of concentrated zinc-chloride solutions suggest that these properties might be improved if one or more components were added to the system. Another disadvantage of zinc chloride is that it is an internal poison in doses of over 0.02 gram and should be labeled "Poison" (C.F. Merck's index).

c. Lithium Chloride. A 32 percent aqueous solution of lithium chloride was cooled to minus 130° F without any precipitation of solid. Below minus 65° F, however, the solution was quite viscous and crystallization may have been inhibited. Compared to some of the other depressants, lithium chloride is relatively costly. Attention, therefore, was directed to minimizing the lithium-chloride content of systems containing lithium chloride as one component.

d. Ferric Chloride. The eutectic point in the ferric chloride/water system is minus 68° F, and 33 percent ferric chloride was directed toward extending the liquid area so that the salt concentration could be varied plus or minus 2 percent without precipitation of solid at minus 65° F.

e. Aluminum Chloride. The eutectic point in the aluminum chloride/water system is at minus 68° F and 25.4 percent aluminum chloride by weight. As in the case of ferric chloride, research was directed to enlargement of the liquid area at minus 65° F so that the salt concentration of the fire-extinguishing formulation could be varied plus or minus 2 percent without precipitation of solid at minus 65° F.

11. Experimental Procedures for Freezing-Point Depression and Viscosity. There are two different basic methods for the determination of freezing points. One is the equilibrium method (41). With this method, solid solvent is brought into contact with the pre-cooled solution in either an insulated flask (37) or temperature-controlled bath (42). When equilibrium between solid and solution has been reached, the solution is analyzed. The freezing point of a solution of this composition is the temperature of the system from which it was removed.

The second method for the determination of freezing points of concentrated solutions involves use of a modified Beckman molecular weight apparatus (Fig. 1) for the determination of cooling or warming curves (11, 43-44). A tube containing the solution to be studied is immersed in a bath kept below the freezing point of the solution. An air jacket may be provided around the tube of solution to lower the cooling rate. Temperatures are taken at various time intervals. When solid solute or solvent begins to separate from solution, the accompanying heat effects alter the rate of cooling. Thus, the temperature at which the cooling rate changes sharply is

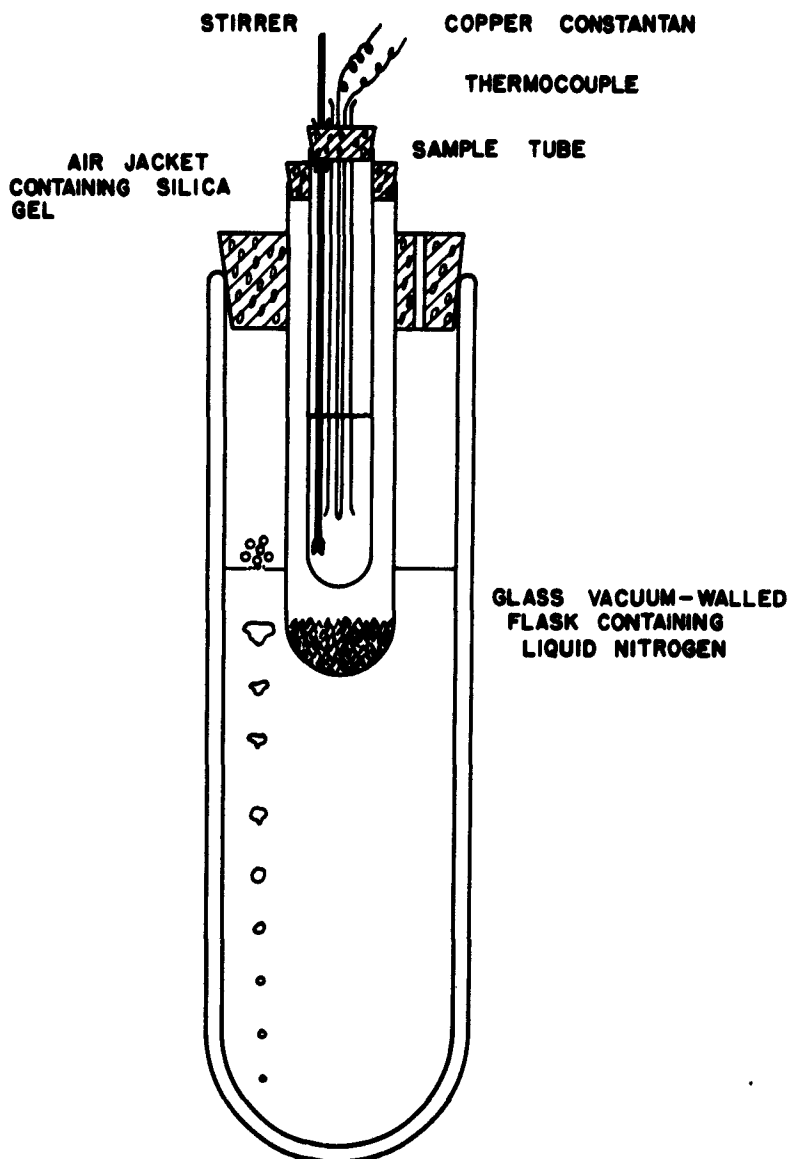


Fig. 1. Apparatus for determination of eutectic temperatures.

the temperature at which solid begins to separate from solution. Whenever a eutectic composition is present, there is no change in temperature during solidification. Therefore, on a plot of temperature of solution versus time, a change in slope indicates separation of solid from solution and a plateau indicates solidification of the eutectic composition.

a. Disadvantages of Equilibrium Method. The disadvantages in using the equilibrium method for determining the composition and freezing points of antifreeze fire-extinguishing compositions are as follows:

(1) In order to arrive at a eutectic composition and temperature for a given system, construction of a phase diagram is desirable. This requires the making of many experiments on a given system and the analysis of the solution in each experiment. Theoretically, it is possible to determine eutectic temperature by placement of excess solute and excess ice in contact with solution. However, it has been said that the concentration of solute obtainable in the presence of ice is limited by the slow rate of solution of solute in nearly saturated solution and by heat leaks which are inherent at low temperatures and which melt ice.

(2) Only the simplest systems can be readily analyzed. The tedious quantitative analysis of complex systems restricts the number of systems that can be studied over a reasonable period of time.

b. Advantages of Beckman-Type Apparatus. Since the disadvantages inherent in the use of a modified Beckman apparatus for obtaining cooling or warming curves are more easily overcome, it was decided not to use the method of equilibrium for determination of freezing points. The advantages of the Beckman-type apparatus are as follows:

(1) A solution can be made from known solutions or weights of solute. This makes further analysis unnecessary. Thus, complex systems may be studied without tedious analysis.

(2) Smaller quantities of solutes are required since heat leaks will not affect the phase composition of the system. A small heat leak in the equilibrium method must be offset by selection of a system of such a size that heat leaks are a negligible part of the total heat effects.

(3) Since the composition of liquid approaches that of the eutectic as solid is frozen or precipitated from solution, analysis of liquid present when a plateau is recorded on

the temperature-time curve gives the eutectic composition. This involves one analysis per system and is advantageous where the system is too complex to be represented by a phase diagram.

(4) Both the temperature at which solid begins to separate from solution and the eutectic temperature may be observed from a single cooling or warming curve. Only one or two other curves at various composition are required to confirm the eutectic temperature.

c. Disadvantage of Beckman Method. The paramount disadvantage in use of the Beckman method is supercooling of the solution. Means by which this disadvantage may be overcome are as follows:

(1) The solution may be seeded with minute crystals of solute or drops of liquid air (44).

(2) The straight-line portions of the cooling curve before supercooling is encountered and after crystallization has started may be extrapolated to an intersection from which the temperature at which solid would have first separated from solution may be read (45).

(3) The sample may be partially or completely frozen and then warmed. LaLande (42) describes a very sensitive method in which the rate of temperature rise in a partially frozen sample is controlled by an electrical-resistance heater in the solution and a controlled-temperature bath around the sample tube. The rate of temperature rise can be adjusted to a value as low as 0.001°C per minute using this technique.

d. Cooling-Curve Method. Since the purpose of determining the eutectic temperatures was to reject those systems which do not depress the freezing point to minus 65°F , it was necessary to use a method that would permit the examination of many systems in a short period of time. This objective was best realized by the cooling-curve method described above. Those systems which passed this preliminary screening test were subsequently investigated for the extent of the liquid area at minus 65°F .

Stock solutions of binary compositions were mixed in various proportions to obtain samples of solution for use in determination of the eutectic temperature. This method of preparing samples allows the possible coverage of every conceivable composition in a ternary system; however, in these screening experiments, compositions lying along the line connecting the eutectic compositions in the two binary systems were the main object of investigation.

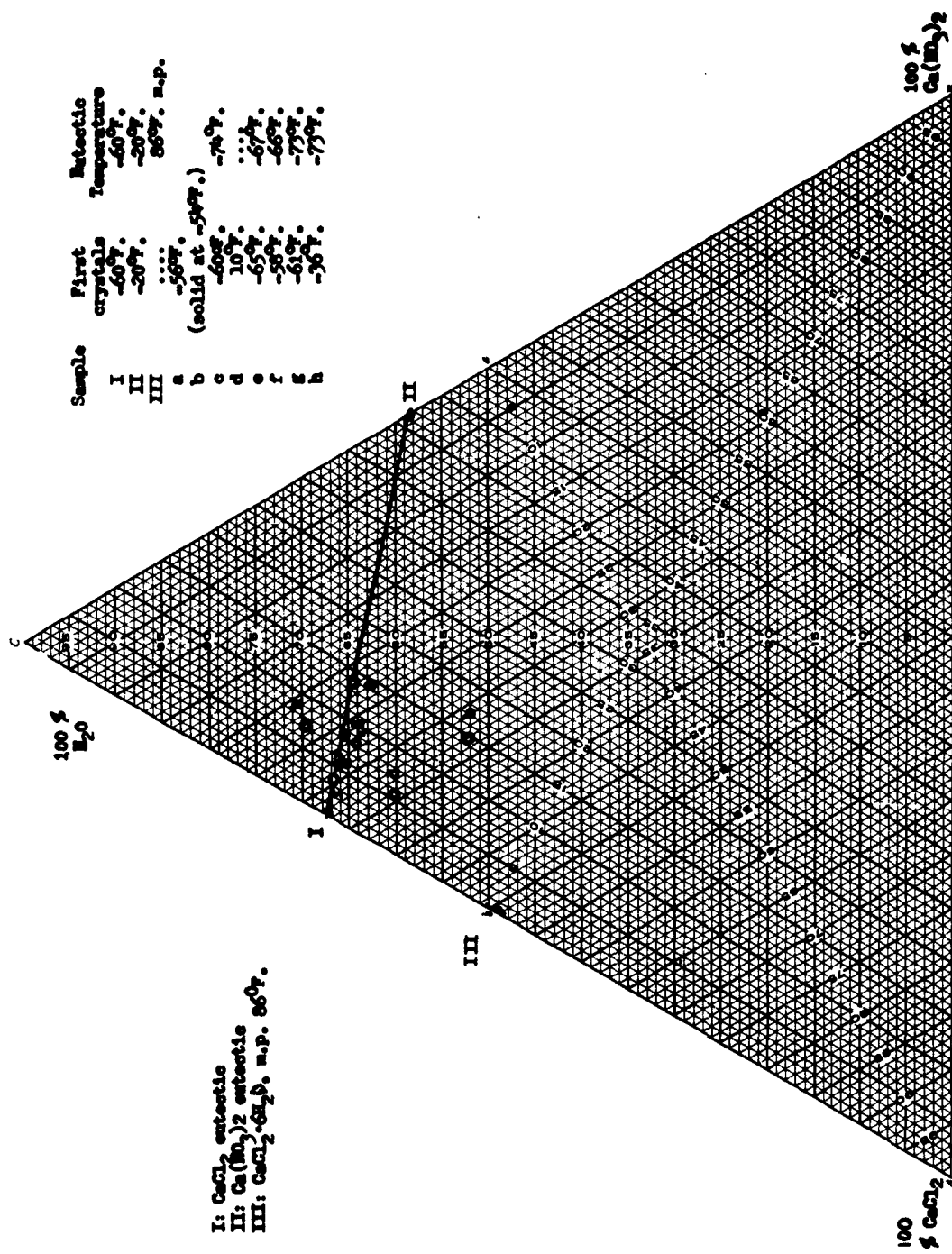


Fig. 2. Eutectic temperatures in the ternary, calcium chloride/calcium nitrate/water system.

A triangular composition diagram for the ternary system calcium chloride/calcium nitrate/water is shown in Fig. 2. Point I represents the binary eutectic composition of calcium nitrate/water. When various proportions of these two solutions are mixed, compositions lying along line I-II are obtained. The results of cooling-curve analyses of the samples prepared in this manner are also shown in Fig. 2. A eutectic temperature of minus 73° F was observed for samples a, g, and h whereas only minus 67° F was observed for samples e and f. This difference was attributed to either the possible formation of a compound in the region separating these two groups of samples or a peritectic reaction in the particular region investigated.

In this particular system, samples b, d, and h were investigated. They did not fall on the line connecting the binary eutectic compositions. It was found that these samples did not show a eutectic temperature lower than that of the samples falling on line I-II.

Samples for analysis of quaternary systems were similarly formed by mixing of solutions of binary eutectic compositions. However, such complex systems cannot be completely represented by a planar phase isotherm; four binary systems are involved, and an "isotherm" is a three-dimensional figure. The "quaternary" systems formed from mixtures of binary eutectics are, in actuality, pseudo-ternary systems in which all compositions can be represented on a planar, triangular composition diagram.

A sample of thirty milliliters made up by the method described above was placed in the sample tube of the apparatus shown in Fig. 1. The sample tube was surrounded by an air jacket containing silica gel to prevent condensation of moisture on the wall of the tube. The air jacket was immersed in liquid nitrogen and served as heat-transfer resistance to give a low cooling rate. The sample was agitated, and the temperature was recorded every minute. The appearance of crystals could be noted and, consequently, compared with the freezing point or limit of solubility obtained from change of slope of the cooling curve. A definite plateau in the cooling curve was taken as the eutectic temperature. A sample of different composition from the same system was then used to check the eutectic temperature, repeating the procedure. Where the two samples were of different eutectic temperatures, other samples of different compositions were used until reproducibility was obtained. Where two or more eutectics were found, the lowest was reported. Systems that did not exhibit a eutectic temperature below minus 65° F were rejected.

A cooling curve for the calcium chloride/calcium nitrate/water system is shown in Fig. 3. The ordinates are the millivolts registered by the copper-constantan couple and are

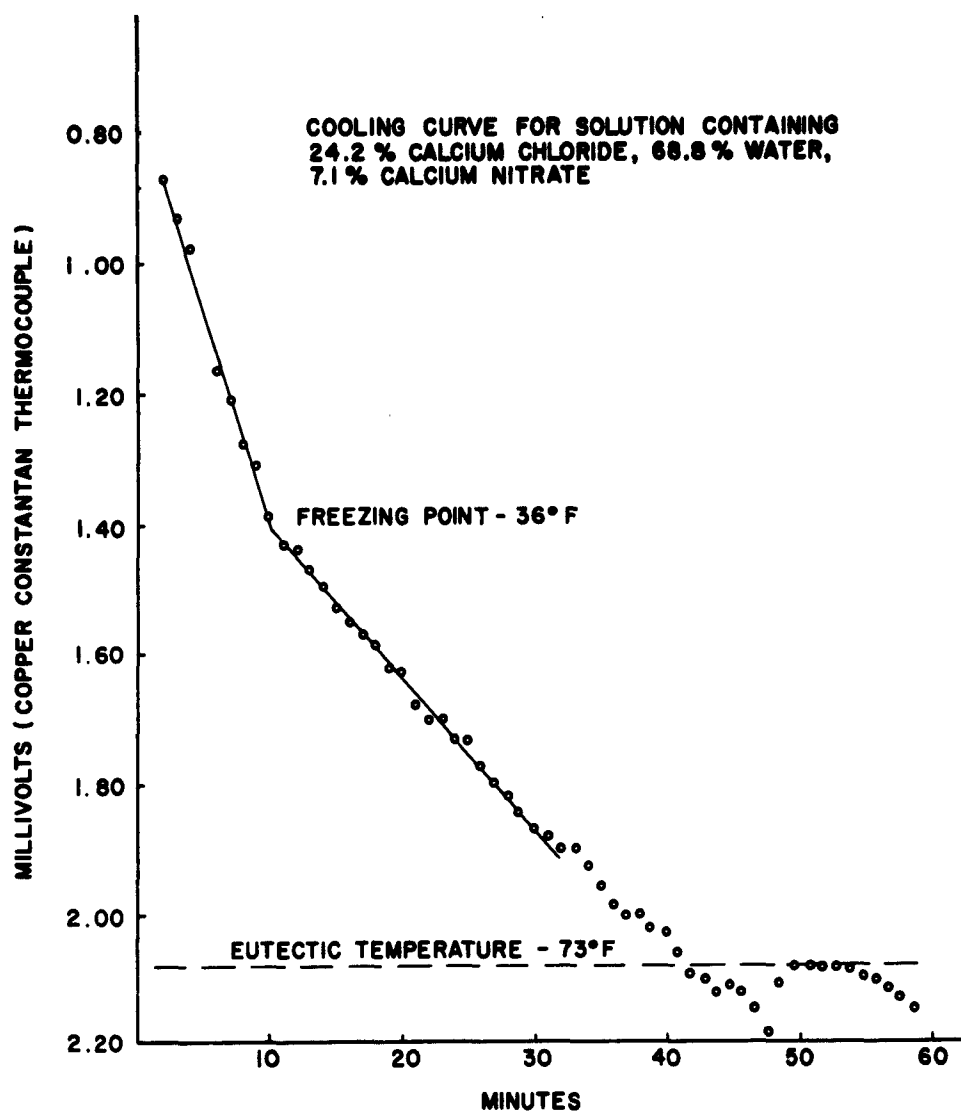


Fig. 3. Cooling curve for solution containing 24.2 percent calcium chloride, 68.8 percent water, and 7.1 percent calcium nitrate.

converted to degrees Fahrenheit at the freezing point and eutectic point of the sample. Freezing points were determined by extrapolation of the straight-line portions of the cooling curve.

The procedure used was proved reliable by comparison of the experimental value obtained for the eutectic temperature of the calcium chloride/water system (minus 60.3° F) with the minus 59.8° F value reported in the International Critical Tables (3).

The second phase of the freezing-point investigation called for definition of the boundary between the liquid and solid regions for selected systems at minus 65° F. It is possible to do this by the use of cooling-curve data in an ideal situation. Two factors militating against the use of the method, however, are the often slow establishment of equilibrium between phases and the large number of separate runs required to detail the boundary sufficiently. The simplest and most straightforward way to achieve the desired result is to maintain a sufficient number of samples of various compositions taken from the system under study at the temperature desired (in this case, minus 65° F) long enough to establish equilibrium. Examination of the samples then reveals areas of solid, liquid, and two-phase content.

The desirability of the initial screening by means of cooling-curve experiments is apparent when one considers that a period of several days is required to achieve a close enough approach to equilibrium for each run. Thus, the system and area of interest in the gross composition diagram must be pinpointed as much as possible beforehand.

The isothermal bath consisted of a reservoir of methanol cooled to minus 100° F by indirect contact with dry ice. Methanol was pumped through heat-transfer coils in the bath in which the test tubes were immersed. A thermostatic switch set for minus 65° F started and stopped the pump to maintain the desired temperature.

The procedure for the tests was as follows:

- (1) Thirty to fifty compositions were selected covering the eutectic region of the system selected for study.
- (2) Four-milliliter samples each of a different composition were made up and placed in a small rimmed test tube.
- (3) The tubes were placed in the rack, chilled to minus 65° F, and maintained there for a period of about 4 days.
- (4) The tubes were then examined. The presence or absence of solid and the density of solid relative to the solution were noted.
- (5) From results of the above examination, charts (not necessarily phase diagrams) were prepared from which it was possible to choose selected compositions meeting the freezing-point requirements.

The preparation of samples of known composition for use in defining the solid-liquid area at minus 65° F is best

explained by reference to a specific example. The preparation of samples for the investigation of the calcium chloride/zinc chloride/water system is described below.

Solutions of reagent-grade zinc chloride were prepared, and the composition was determined from specific-gravity measurements made with a Westphal balance. Similarly, the exact composition of calcium-chloride solution was found after it was determined that analysis by specific gravity and volumetric analysis for chloride gave the same results. Zinc-chloride and calcium-chloride solutions of known compositions and densities were mixed in various proportions to obtain samples of various known compositions.

The composition of all samples formed by mixing two solutions in various proportions must fall on a straight line connecting the compositions of these two solutions on the phase diagram. Thus, by varying the composition of the stock solutions and the proportions in which they were mixed, the entire area of the phase diagram which was of interest could be investigated to determine nonfreezing compositions. Samples in all systems investigated were prepared in this manner (that is, by mixing solutions of known compositions and densities in definite proportions). Reagent-grade chemicals and distilled water were used in preparation of these samples. The effect of sea water and impurities was treated as a separate phase of this research.

Aqueous salt solutions were analyzed by measurement of specific gravity with a Westphal balance. By this method, the composition of the solution could be determined with an accuracy of 0.1 percent. The densities for aqueous solution given in the Handbook of Chemistry and Physics were those from which compositions corresponding to measured density were read. Volumetric analyses of calcium-chloride solutions for chloride were made and were found to give the same compositions as those determined by density measurements. Information on the densities of lithium-chloride solutions was not available in the literature, and it was necessary to prepare a density-concentration chart for this salt. This chart, shown in Fig. 4, was prepared by titration of lithium-chloride solutions of known densities with standard silver-nitrate solution.

To determine solution viscosity, a glass apparatus as shown in Fig. 5 was selected. Since close temperature control was required, the previously described low-temperature bath was used, in which the liquid compositions at minus 65° F (minus 53.9° C) were determined. The procedure was as follows: The breathing tube was stoppered and liquid was poured in the filling bulb until it was above the mark above the tube. The filling bulb was then stoppered, and the breathing tube was unstopped. The slight vacuum above the

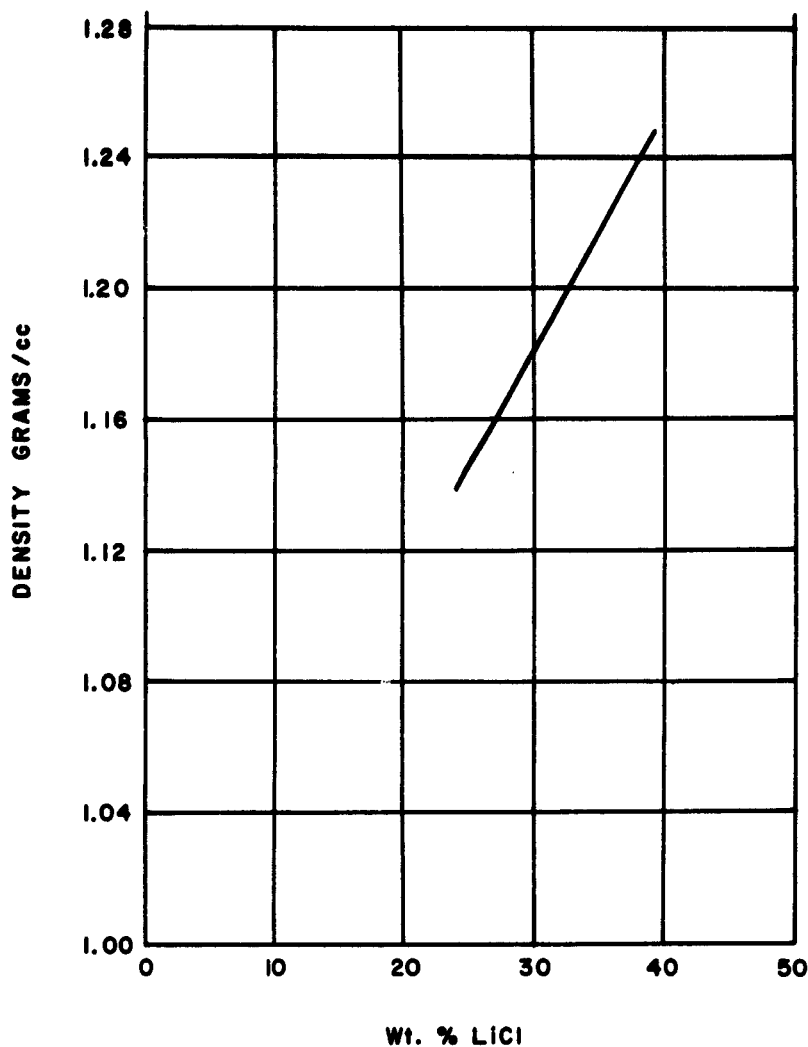


Fig. 4. Densities of aqueous lithium-chloride solutions, 24° C.

liquid prevented liquid discharge through the orifice. The apparatus was then immersed in the minus 65° F bath for 20 to 25 minutes to allow the bulb and contents to come to temperature. This time was found to be long enough so that reproducible results were obtained. The filling bulb was unstoppered, and the liquid was timed between the upper and lower marks. In this procedure during a trial run, the bulb is withdrawn from the bath from time to time to observe the progress of the liquid. In subsequent runs, the approximate time of efflux is known and the bulb only needs to be drawn out of the bath for a few seconds at the time start and at the end of the run. Since the air space above the methanol is still within the

insulated cold chamber, it is thought that the two brief exposures do not affect the results. Experimentally, the efflux times were found to be reproducible to within better than 1 percent, whether the bulb is withdrawn once or several times.

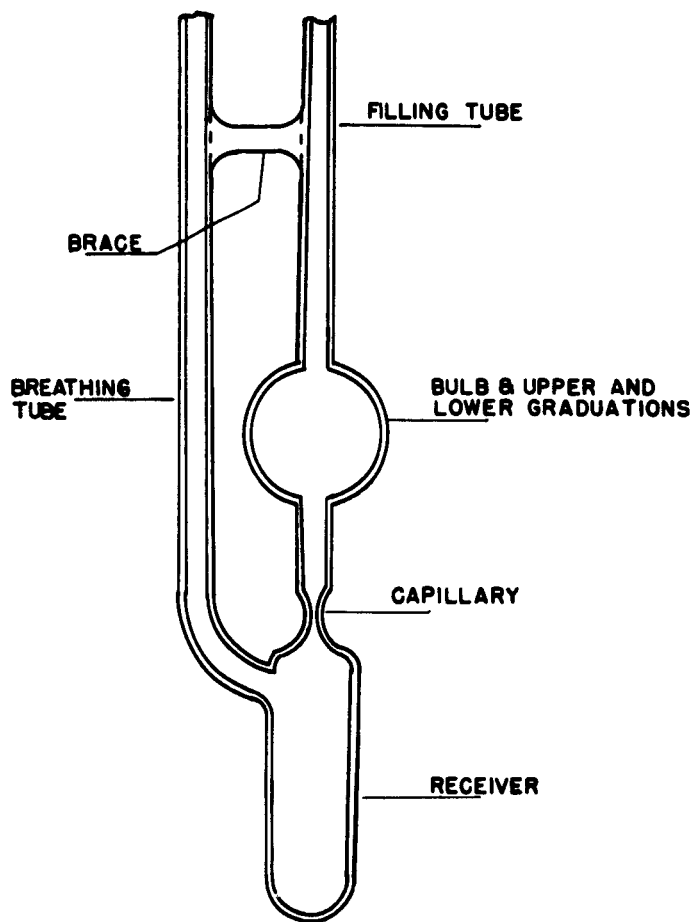


Fig. 5. Viscosimeter tube for use at minus 65° F.

To convert efflux time to kinematic viscosity units, it was necessary to calibrate the viscosimeter with a fluid of known viscosity. Information was available in the technical literature on the absolute viscosity (46) and the density (3) of n-butyl alcohol. From the data, the kinematic viscosity of n-butyl alcohol at minus 65° F was calculated to be 52 centistokes. The efflux time for n-butyl alcohol was found to be 79 seconds as the average of a number of runs. The constant for the instrument was, therefore:

$$k = \frac{52}{79} = 0.66$$

and $= 0.66t$
 $=$ kinematic viscosity, centistokes
 t = efflux time, seconds.

It was assumed that, over the range of viscosities involved, Poiseuille's Law for liquid flow through capillaries was followed, from which efflux time is proportional to kinematic viscosity.

12. Test Procedures for Corrosion Inhibition. The use of salts as antifreeze agents is analogous to use of brine solutions in the refrigeration industry. The recommendations of the American Society of Refrigeration Engineers (47) are presented in Table V.

Table V. Treatment of Refrigeration Brines

Inhibitor	Calcium Chloride (grams per liter)	Calcium/ Magnesium Chloride (grams per liter)	Sodium Chloride (grams per liter)
Sodium dichromate ¹ ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$)	1.6	3.2	3.2
Disodium phosphate ² ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$)	-	-	1.6

1. Enough sodium hydroxide added to convert dichromate to neutral chromate, and pH maintained at 8.5 (slightly lower for galvanized pipe).
2. Brine neutralized or made slightly acidic, pH = 6.8 to 7.5.

The salt content of the brines is 20 percent and greater. The metals being protected are iron, steel, and galvanized iron. The disodium-phosphate treatment is not considered as effective as the sodium-dichromate treatment; the phosphate also has to be renewed every month, while the chromate only needs renewing every year. The sodium dichromate may be replaced by an equivalent amount of sodium chromate which amounts to 1.75 grams per liter for the calcium-chloride system and 3.50 grams per liter for the calcium/magnesium chloride and sodium-chloride systems.

In the USAERDL Materials Branch preliminary study (1) to determine the feasibility of using a 20 to 30 percent lithium-chloride

solution (pH = 7.5 to 8.5) as a low-temperature engine antifreeze, it was found that this solution was less corrosive (at room temperature and 160° F) to cast iron, lead-tin solder, copper, and brass than was distilled water (pH = 7.5) with aluminum as the only exception. The addition of 3.5 grams of sodium chromate per liter tended to inhibit the attack of lithium chloride.

Army and Navy specifications (48) for the 28-percent-calcium-chloride, fire-extinguisher solutions for use to minus 40° F required that the solutions contain approximately 15 grams of sodium chromate per liter to inhibit the corrosion of iron and copper.

Sodium dichromate (49), if added in sufficient quantity, may be used for the practically complete protection of iron and steel in sodium-chloride solutions of all concentrations at all temperatures and for the protection of aluminum in dilute salt solutions at room temperature. It may also be used for partial protection of copper, brass, lead, zinc, and galvanized iron in sodium-chloride solutions at room temperature.

Although chromates in proper amount might reduce galvanic contact effects materially (50), it is recommended (47) that the contact of dissimilar metals in brine solution be avoided. Corrosion arising from such a contact is one of the main factors for the failure of engine antifreeze brines (51).

Sodium chromate with a small amount of sodium metasilicate has been found effective for refrigerating brines in aluminum and aluminum-iron systems (50). Sodium silicate does not reduce corrosion in chloride solutions sufficiently to warrant its use in refrigeration brines. When sodium silicate is added along with sodium chromate, however, the combined effect seems to be more beneficial than with the chromate alone (47). Zinc dust has been employed for reducing corrosion by salt solutions, but it is probably not useful except for open brine tanks using calcium chloride where the dust can be added a little at a time onto the brine surface (52). Organic colloids, notably dextrin, have been found as ingredients of commercial inhibitive mixtures for brines, but it seems doubtful that they would give satisfactory protection to ordinary metals without the sodium chromate being present (52).

Salt solutions are considered to be very corrosive. The literature survey, however, indicated that the solutions being investigated (which for the most part contain calcium chloride and lithium chloride) could probably be inhibited. Fortunately, the particular use of these brines favors inhibition because of the associated temperature ranging from room to minus 65° F, high concentration (or specific gravity), little agitation (if any) with air, low surface area to volume ratio, and no dissimilar metallic contacts.

The pH values that are reported for the solutions derive from the use of reagent-grade chemicals. Specifications for the actual materials should be written to exclude any acidic impurities which might decrease these values. Naturally, acidic waters (which in themselves are corrosive) should never be used.

a. Selection of Inhibitor. Sodium chromate was selected as the inhibitor in the study of corrosion primarily because from the literature search it appeared to be the most effective inhibitor for brines. Secondary considerations were as follows:

(1) Cathodic inhibitors are rather specific in their use.

(2) High molecular weight or colloidal absorption inhibitors would probably increase the brine viscosity which is already relatively high at minus 65° F. Although elements such as aldehydes are good acid pickling inhibitors, the survey of the literature does not indicate that they have been extended to brine solutions.

(3) The chromate salts are more soluble than the carbonates, phosphates, and silicates; hence, enough sodium chromate can be added to retard corrosion. Also, since the solubility of the chromates varies inversely with temperature, a saturated chromate solution at room temperature will not throw out a precipitate at minus 65° F.

(4) A solid inhibitor is desirable from the standpoint of ease in packaging.

b. Specific Details. In the development of the corrosion test, reference was made to the following publications:

ASTM A 224-46, Conducting Plant Corrosion Tests.

ASTM B 185-43T, Total Immersion Corrosion Test of Nonferrous Metals.

ASTM A 279-44T, Total Immersion Corrosion Test of Stainless Steels.

These outline general principles to be followed in corrosion testing although specific test conditions are left up to the laboratory making the test. Specific conditions chosen, as discussed below, seem to approach service conditions as closely as possible.

(1) Temperature. A temperature of 95° F (35° C) was chosen for two reasons:

(a) It is the highest ambient temperature likely to be encountered at which the water additive solution is in contact with metallic containers.

(b) It is a convenient, controllable temperature for maintaining the corrosion bath.

(2) Metal Specimens. The metals chosen were as shown in Table VI.

Table VI. Metals Used in Corrosion Test

Metal	Type	Thickness (in.)	Source
Brass	Alloy, 6, ASTM B36-49T (Nom. 60 Cu, 30 Zn)	1/16	Chase Brass & Copper Co.
Zinc	Commercially pure	0.016	-
Copper	Electrolytic copper	1/16	USAERDL
Steel	SAE 1020	1/16	USAERDL
Aluminum	61S	1/16	USAERDL
Magnesium	3S	1/16	USAERDL

Individual specimens tested were coupons $\frac{1}{2}$ by 3 inches in size, weighed to 0.1 milligram on an analytical balance after filing, polishing on a buffing wheel, washing, rinsing in acetone, and drying.

(3) Duplication of Samples. It was felt that duplication of individual samples would insure sufficient accuracy for the purpose of this research since the expected error of the average corrosion rate from statistical considerations under these conditions would be plus or minus 9.7 percent. To obtain an expected error less than plus or minus 5 percent would require eight samples per individual metal for every composition.

(4) Arrangement of Specimens. Each specimen was held in an individual square glass bottle about 4 inches high and of about 100-ml capacity. To each bottle was added exactly 60 ml of the solution under study. The specimen was consequently immersed about 2 inches in the electrolyte, leaving 1 inch exposed to the air above the solution. This method of partial immersion introduces the effect of the interface into the results and, it is thought, corresponds more closely to conditions likely to be encountered in practice than would a total-immersion method. The metal screw caps of the bottles were left quite loose to allow access of air to the solutions.

The actual area of contact of the specimen was determined by inspection of the sample at the end of the test.

(5) Constant Temperature Bath. The sample bottles were placed on the false bottom of a rectangular tank of a size large enough to hold about 80 bottles. Bath water was added to immerse the bottles up to their necks. A heater and thermoswitch combination maintained the bath temperature at 35°C plus or minus 1°C . A circulating pump helped minimize temperature gradients in the bath.

(6) Formulations Studied. The number of different formulations to be tested for corrosiveness (Table VII) was limited to the three otherwise most desirable selections after salt content, viscosity, pH, and toxicity were considered and to the calcium chloride/iron chloride solution which was known to have a low pH but had a fairly high water content. Where possible, each formulation was prepared in both inhibited and uninhibited form.

Table VII. Composition of Formulations
Selected for Corrosion Test

Formulation	Composition	Inhibitor
1a	24% lithium chloride 76% water	-
1b (inhibited)	Same	Na_2CrO_4 (unsaturated) 3500 mg per liter
2c	5% lithium chloride 69% water 26% calcium chloride	-
2d (inhibited)	Same	Saturated with Na_2CrO_4 1050 mg per liter
3a	10% calcium nitrate 27% calcium chloride 63% water	-
3b (inhibited)	Same	Saturated with Na_2CrO_4 84 mg per liter
4	5% ferric chloride 29% calcium chloride 66% water	-
Control*	28% calcium chloride 72% water	Saturated with Na_2CrO_4 3850 mg per liter

* Made up to specifications of JAN-C-344.

The technical literature on corrosion by refrigeration brines indicated that the optimum concentration of sodium-chromate inhibitor in salt solutions similar to the ones developed here as fire extinguishers is about 3,500 milligrams per liter. It was possible to obtain this concentration only in Formulation 1 which does not contain calcium chloride. In Formulations 2 and 3, the high concentrations of calcium ion and the low solubility product of calcium chromate limit the concentrations to the lower values shown. Formulation 4, from the iron/calcium chloride system, is incapable of holding any appreciable quantity of chromate, and this system was tested only in uninhibited form. The chromate-containing solutions are saturated with chromate at room temperature, except Formulation 1. Because the solubilities of chromates increase with decreasing temperature, it was expected (and checked by experiment) that no solids would freeze out of the inhibited formulations even at minus 65° F.

(7) Combination of Metals and Formulations. Each of the six metals was studied in contact with each of the seven formulations, and every sample was duplicated. In addition, two copper and two steel specimens were in contact with the control solution. Thus, the total number of samples was 88.

13. Fire Test Procedures.

a. Test Parameters. In devising a fire test, on the model scale, a number of test parameters must be considered.

The use of a standard crib of constant weight is a very definite requirement for a reproducible fire. The wood used by each investigator was a species which was considered quite homogeneous in nature and was conditioned to a constant moisture content before usage. The size of the individual sticks must not be so small as to cause too rapid burning nor so large as to present too small a surface for combustion. The crib arrangement should be in such a pattern as to allow sufficient air for complete combustion and access to the surface of the wood for extinction by a spray.

The platform should allow any excess extinguishing solution and the air for combustion to pass through. Bryan and Smith (25) found that to keep their 100-pound crib from collapsing before extinction, steel rods passing up through each stick were necessary. The other investigators did not mention this problem.

In all the various systems reported, attempts were made to ignite the crib sufficiently in a constant and short period of time.

The constancy of the draft is very important in maintaining a reproducible fire. Metz used forced draft to impart a greater extinction resistance to his crib, thereby securing better results.

Two methods denoting the time of solution application were used: (1) Application of the solution after a definite time of burning (including ignition period); and (2) application after a definite proportion of the wood had been burned. If ignition material is used, the time when spraying is started must be after the complete burning of the ignition material.

Perhaps the largest error in the procedures of Folke (31), Metz (23), and Tyner (24) arose from the manual method which was employed to extinguish the fire. The procedure required the operator to walk around the fire and spray first those areas which appeared to need extinguishing the most. It is to be expected that this technique would depend not only upon the operator but also on his judgment concerning a particular fire. Bryan and Smith employed a rotating platform and a fixed nozzle; thus, the crib was always exposed to a constant spray pattern. Although an intermittent spray was initially used by Bryan and Smith to increase the resistance to extinction, it was found to be unnecessary and undesirable from the standpoint of ease of operation.

Both the time and the quantity of solution required for total, or ember, extinction were measured, and the rate of application was known in all of the outlined procedures. When necessary, the weight of the crib was also measured. Except for Bryan and Smith, the point where extinction occurred was determined visually. Bryan and Smith used a hydraulic system which continuously recorded the crib weight in relation to time of combustion. The time required for extinction was then read from the chart.

b. Superiority Factors. The results in the literature are expressed (or can easily be expressed) in terms of superiority factors. The result reported most is calculated by dividing the amount of water required for extinguishment by the amount of salt solution necessary at a given rate of application. It is probably best to consider this factor as the ratio of time necessary to extinguish the crib by the solution to that required by water when applied at the same rate of application. According to Bryan and Smith, this superiority factor has the following disadvantages:

- (1) Because the resistance to extinction is not the same during at least most of the burning time, this ratio does not represent a constant extinguishing resistance for the solution and water. Water, as a general rule, will take longer to extinguish a fire; hence, it will encounter a greater resistance.

(2) The ratio varies greatly with the relative rate of delivery from unity at very high rates to infinity at extremely low rates. Because of this variation, the results of different investigators cannot be compared directly.

(3) The ratio depends greatly on the actual apparatus and procedure employed.

Bryan and Smith proposed a new superiority factor that apparently completely overcomes the first two disadvantages and partially overcomes the third. It is the ratio between the volume of water and the volume of solution (or the ratio between the two delivery rates) necessary to extinguish a fire in the same time. The value of this factor ranges from unity at high spraying rates to some maximum value at low rates. This limiting value, therefore, represents the maximum potential fire-fighting effectiveness of the solution. The authors stated that a comparison of these maximum values results in a more accurate estimate of the relative efficiencies of different additives and that fire-extinction effectiveness as found by different investigators can be compared when expressed in terms of superiority factor.

The density, viscosity, and surface tension affect the size of drops from a spray nozzle. Thus, the diameter of drops of solutions may be either larger or smaller than the diameter of drops of water. Although the magnitude of change would probably be negligible for dilute solutions, it may become fairly large for very concentrated solutions. Even though the exact effect of variations in the diameter of spray droplets on the extinction of a fire is not known, both of these superiority factors automatically include this effect, if present.

The reproducibility was not reported in any of the articles. While Metz used the results from only two runs to determine the fire-fighting capacity of a salt, Tyner and Bryan and Smith averaged between five and ten determinations per chemical. Obviously, precise reproducibility is not inherent in a test of this type.

c. Test Apparatus. The test apparatus used in the fire tests included a crib platform, means for igniting a wood crib placed on the platform, draft control, and means of application of the salt solutions to the crib fire.

(1) Crib Specifications. "C-select" white pine (knot free and kiln dried), which is readily available and fairly homogeneous, was found to be a satisfactory crib material. The crib weighed approximately 2.2 pounds (1 kg) and was not large enough to necessitate bracing. It consisted of 21 conditioned sticks; each 7-7/8 inches by 1 inch by 3/4 inch

and weighing between 41.0 and 53.0 grams. Seven layers of three sticks were disposed in a shape of a triangle having gaps of about 2 inches at the corners. Alternate layers were rotated 60 degrees. This arrangement allowed sufficient air for combustion and space for the spray to reach all parts of the wood.

(2) Crib Platform. A 12-inch-diameter, variable-speed, rotating platform was used. The platform was of an open construction to allow free passage of the solution and combustion air. A rotation speed of 10 rpm was found satisfactory.

(3) Ignition Means. Four winged-top, Bunsen burners arranged as the corners of a rectangle composed the ignition system. The rate of burning was controlled by a governor in the gas line with a pressure of 4 inches of water being maintained at all times.

(4) Draft Control. The amount of draft was controlled by a damper in the exhaust hood. A forced draft of approximately 400 feet per minute (measured at the top of the crib) was found necessary to increase the extinction resistance of the crib, thereby producing better fire-extinction effectiveness.

(5) Application of Solution. The solutions and water were sprayed at 40 psig through nozzles procured from the Monarch Manufacturing Works, Inc., Philadelphia. Ten nozzles were employed which gave a spraying-rate range of 1.1 to 4.0 gallons per hour. The crib was small enough so that the nozzle did not have to move up and down.

d. Construction and Assembly of Small Fire Test. A small, low-voltage, direct-current motor and the rotating platform were mounted on the pan of a laboratory balance (maximum capacity of 25 pounds) having a five-pound, dial-reading scale. The platform extended several inches away from the balance in order to allow the interposition of a galvanized iron sheet that protected components such as the balance table from the solution and heat. The weight of items such as the platform and motor was counterbalanced so that the dial-reading scale read zero (or slightly above) before the addition of the crib. The rotating speed of the circular platform could be varied by using different voltages across the motor. The converted balance was placed on a table which held the pressure regulators, valves and lines for the compressed air and natural gas, container holding the spraying material, and the nozzle mount. The nozzle mount was constructed so that the position of the nozzle could be easily mounted to any desired position. The ignition system was movable so that it could be moved away from under the crib

after ignition. An exhaust hood with an adjustable damper for draft control covered the rotating platform and crib.

After the "C-select" white pine was sawed into 7-7/8-inch-length sticks, it was stored in a constant-temperature, measured-humidity, insulated storage chamber until the relative humidity in the chamber dropped to a value of about 2 percent. This usually required a week. Thereafter, water was added to maintain the humidity at this value. After the humidity reached 2 percent, the sticks were removed and weighed and only those falling within the range of 41.0 to 53.0 grams were returned to the chamber where they remained until burned.

The spraying rate of water and formulations through various nozzles was determined by collecting the spray in a suitable graduated cylinder in a measured time. The spraying pressure of 40 psig was carefully maintained.

Twenty-one sticks of conditioned wood were made into a crib weighing approximately 2.2 pounds (1 kg). (Since the crib platform was also a balance platform, its weight was automatically measured.) After the correct platform rotating speed of 10 rpm was obtained, the Bunsen burner ignition system was moved under the crib. Adequate ignition was accomplished in 85 seconds, and the burners were removed. The forced draft (exhaust hood) fan was then turned on to create the necessary draft. Spraying was initiated after 40 percent of the crib had been burned. This point was determined based on the loss of weight recorded on the balance reading-dial. The time required for total extinction (or all glowing to disappear) was determined visually.

The volume superiority factor proposed by Bryan and Smith was determined, since it is believed that their arguments are correct in that this factor presents a more accurate record of effectiveness. Calibrated nozzles were used to develop plots of the rates of application of water and solutions versus extinction time. From these plots, the superiority of the formulations over water was calculated.

The reproducibility of the crib weight was within plus or minus 5 percent (Table VIII). This deviation seems quite reasonable. The higher weight range, which resulted in a slightly higher crib weight, was adopted to equalize the number of heavier and lighter sticks discarded. Table VIII also shows the effect of the relative humidity in the storage box on the weight of the crib. As would be expected, the crib is heavier when the relative humidity is higher since a larger moisture content is present in the wood. To eliminate this variation, the wood was always conditioned at a relative humidity of about 2 percent.

Table VIII. Reproducibility of Crib Weight

Run No.	Storage Chamber Humidity (%)	Average Crib Weight		Mean Deviation (%)
		(lb)	(kg)	
2 through 6 ^a	9.5	2.25	1.02	± 3
7 through 12 ^a	3.0	2.12	0.964	± 2
13 through 16 ^a	5.0	2.20	1.00	± 2
17 through 29 ^a	2.0	2.08	0.945	± 5
30 through 43 ^b	2.0	2.20	1.00	± 5

a. Stick tolerance: 40.0 to 52.0 grams.

b. Stick tolerance: 41.0 to 53.0 grams.

Table IX shows that the maximum mean deviation for the time required to burn 50 percent of the crib weight was about plus or minus 10 percent. This value is considered good for the commercial grade of wood used.

Table IX. Reproducibility of Combustion

Run No.	Average Crib Weight (lb)	Average Weight Burned (lb)	Percent Burned	Average Time (sec)	Mean Deviation (%)
3 through 6 ^a	2.25	1.12	50	263	± 8
7 through 12 ^b	2.12	1.06	50	222	± 10

a. Draft = approximately 100 ft/min.

b. Draft = approximately 400 ft/min.

The literature review revealed that the extinction resistance of any fire depends on the percent burned or the time of combustion before spraying is started. The results in Table X agree and also show that this resistance tends to approach a constant value at the higher percents of crib burned. An optimum percentage is one where slight variations in operation result in only a small change in the resistance and where, at the same time, the crib will hold together until combustion ceases. At the final nozzle position, this value was around 40 percent.

After the first series of runs, it was found that it would be desirable to increase the resistance to extinction. In addition to the increase of time before spraying (which has limitations

Table X. Effect of Time Burned
Before Spraying on Extinction

Run No.	Nozzle Position	Percent Crib Burned before Spraying	Average Time for Total Extinction (seconds)
14, 22, 23	A	20	561
15	A	25	690
13, 24	A	30	719
40, 41	Final	30	545
42, 43	Final	40	603

as explained in the previous subparagraph), there are two other possible methods of increasing the resistance. These include use of a larger crib and use of a stronger draft. The latter solution was employed because the size of the crib was limited by the spray pattern of the nozzle which was mounted in a fixed position. Table XI shows that the increasing of the draft by the enlargement of the hood nearly doubled the spraying time.

Table XI. Effect of Draft on Extinction

Run No.	Draft (ft/min)	Nozzle No.	Percent Crib Burned before Spraying	Average Time for Total Extinction (sec)
3, 5, 6	100	5.50	50	148
7 through 10	400	5.50	50	280

As shown in Table XII, the time required for extinction can be very sensitive to the position of the nozzle.

Table XII. Effect of Nozzle Position on Extinction

Run No.*	Nozzle Position	Average Time for Total Extinction (sec)
13, 24	A	719
26, 27, 29	B	648
30, 31, 34	C	586
36 through 39	D	638
40, 41	Final	545

* All runs made with nozzle No. 3.50 and 30 percent of crib burned before spraying.

Although Position B resulted from loosening of the nozzle mount, the last three positions were planned to see exactly what this effect would be. The reason for the high sensitivity is that the different positions changed the amount of the spray which reached the crib. It is believed that any movement of the nozzle which does not alter the amount of water reaching the crib will not affect the time for extinction to such an extent.

The effect of room humidity and temperature, if any, was not apparent in the standardization runs. The literature (53) reports that in centrifugal nozzles of the type being used the flow rate increases slightly and the spray cone angle decreases with an increase in viscosity. Apparently, the change in viscosity of water over a room temperature range of about 10 degrees does not cause rate and angle changes which are noticeable in extinguishment of the fire. These results are shown in Table XIII.

Table XIII. Reproducibility of Total Extinction

Run No.	Nozzle No.	Nozzle Position	Percent Crib Burned Before Spraying	Average Time for Total Extinction (sec)	Mean Deviation (%)
3, 5, 6 ^a	5.50	A	50	148	± 6
7 through 10 ^b	5.50	A	50	280	± 8
17, 18, 19 ^b	4.50	A	25	192	± 9
26, 27, 29 ^b	3.50	B	30	648	± 3
36 through 39 ^b	3.50	D	30	638	± 10
40, 41 ^b	3.50	Final	30	545	± 9

a. Draft approximately 100 ft/min.

b. Draft approximately 400 ft/min.

The maximum mean deviation of 10 percent in this series of runs is considered reasonable for a test of this type; it is believed that any value up to 15 percent would be satisfactory. In all series of runs made, the reproducibility of total extinction was always below 15 percent.

14. Proof Tests for Application of Antifreeze Charges. The laboratory tests described in the preceding sections concern the physical-chemical properties of salt solutions. From these properties, a formulation was selected having the following composition: 8.8 percent lithium chloride, 20.0 percent calcium chloride, and 71.2 percent water (balance).

For packaging purposes, lithium chloride is conveniently handled as an anhydrous salt. Calcium chloride is usually available as the dihydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in which the concentration of the salt is approximately 75 percent with the balance being water. Since lithium chloride is strongly deliquescent, it was necessary to determine if LiCl_2 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ would be compatible in the same package. Migration of the water of hydration could result in caking of the mixture of salt granules. To determine this compatibility, sample charges were made up (1/3 gallon or approximately 1.3 liter in size for properly mixed charge and water) and placed into polyethylene bags weighing 6.5 to 6.7 grams each. The bags were sealed by fusing of the open end. Two units were subjected to high-humidity exposure (approximately 95 percent at 90°F), one to low temperature and the other to high temperature.

Another test procedure used was as follows. The proposed antifreeze charge made up with fresh water was placed in two 4-gallon, back-pack, pump-type extinguishers. One extinguisher was then stored in normal room temperature, and the other was stored in a tropical test chamber at approximately 90°F 95 percent relative humidity.

IV. TEST RESULTS

15. Freezing-Point-Depression Study and Low-Temperature Viscosity. The experimental results are presented in Appendix B and are summarized in the figures as noted below for the systems having a eutectic point below minus 65°F .

Calcium chloride/lithium chloride/water, Fig. 6.

Lithium chloride/water, Fig. 7.

Calcium nitrate/calcium chloride/water, Fig. 8.

Calcium chloride/aluminum chloride/water, Fig. 9.

Zinc chloride/calcium chloride/water, Fig. 10.

Zinc chloride/water, Fig. 11.

Experimental results are presented in Appendix B.

Results of over 100 determinations of eutectic temperatures by cooling curves are given in Appendix C. In these studies, the eutectics at which the concentration of the freezing-point depressants was the lowest were of prime interest, since it was observed that these would be generally the lowest and would correspond to the minimum requirement for weight of depressants to antifreeze a given

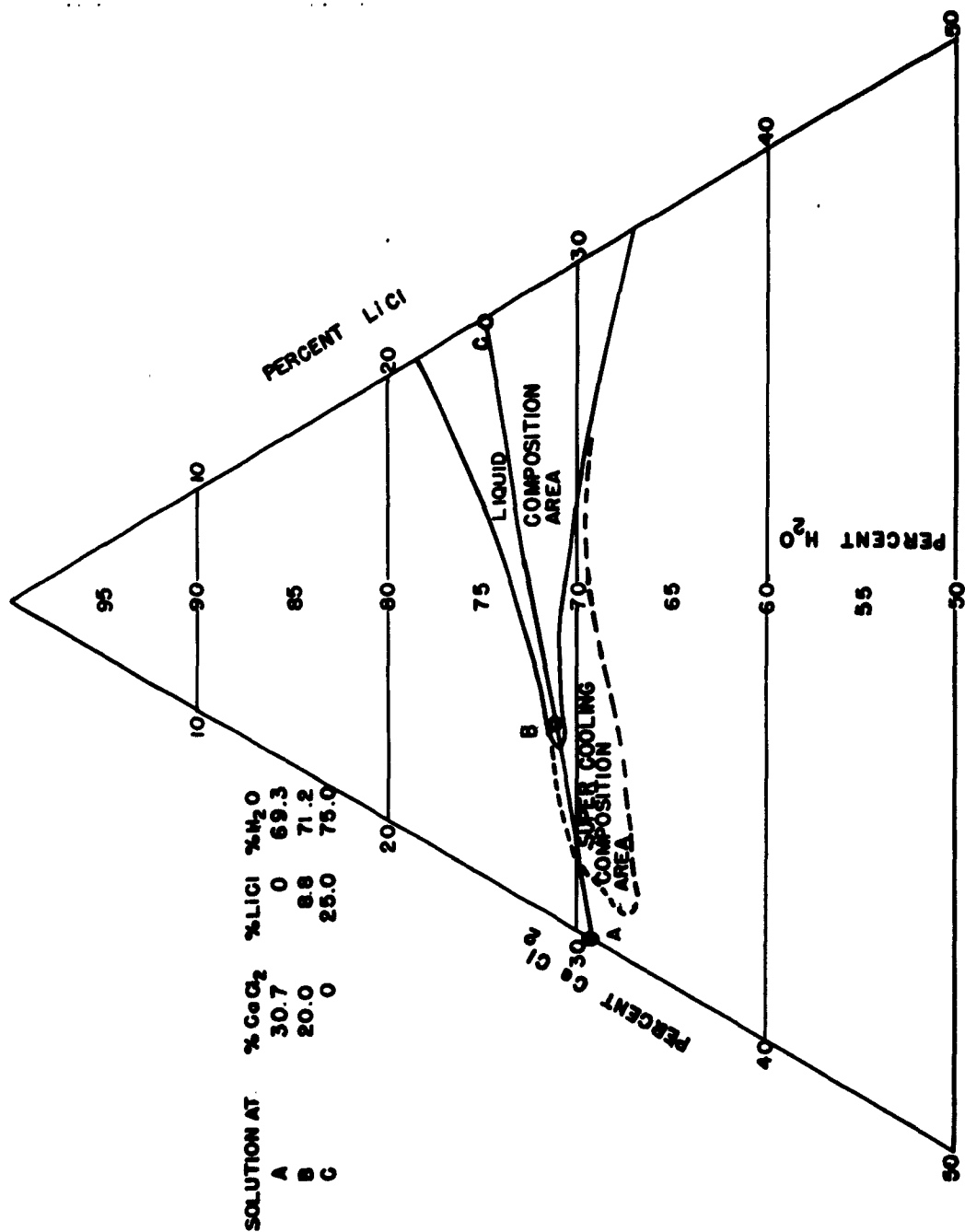


Fig. 6. System diagram for $\text{CaCl}_2/\text{LiCl}/\text{H}_2\text{O}$ at minus 65°F .

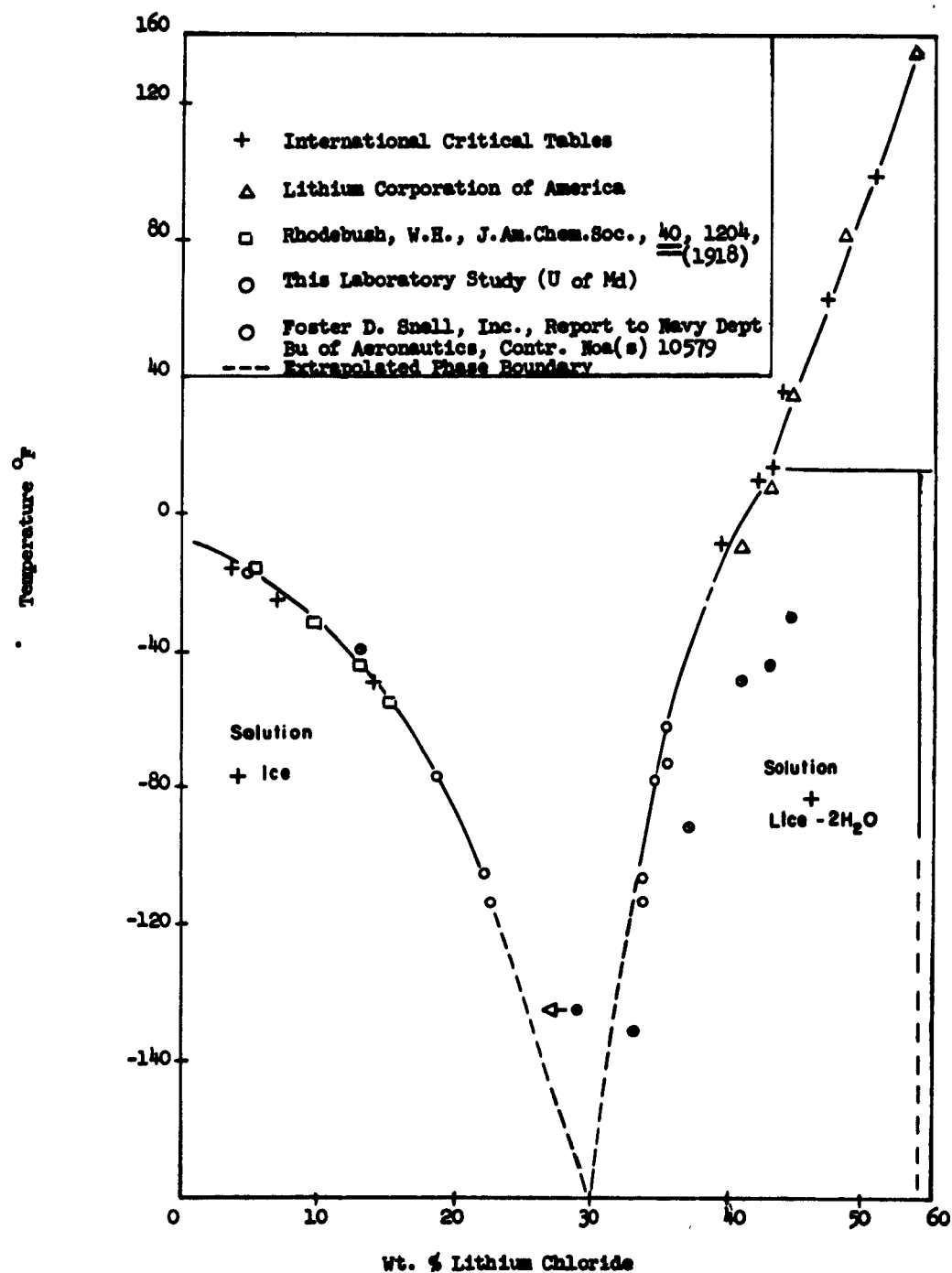


Fig. 7. Phase diagram for lithium chloride/water system.

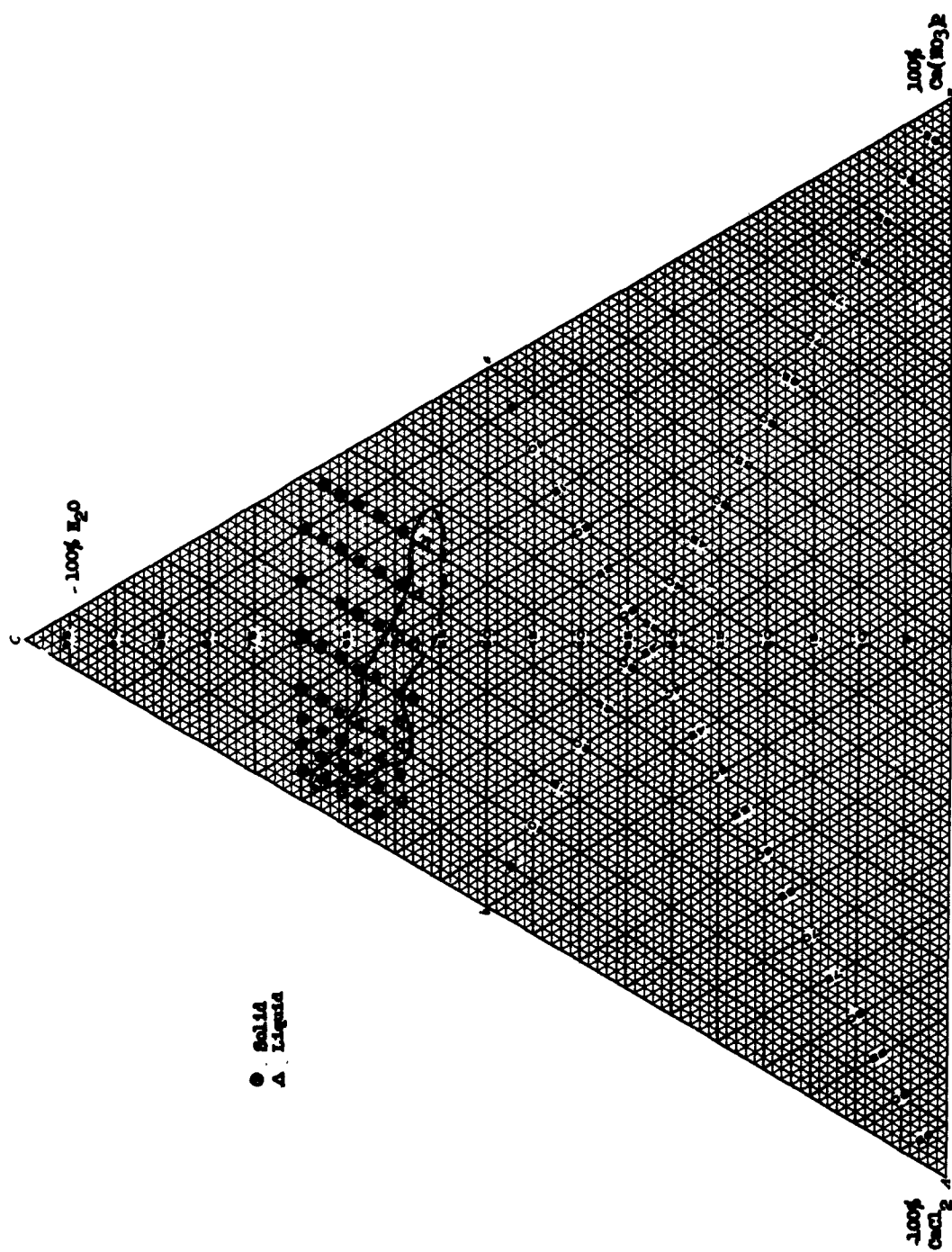


Fig. 8. Proven liquid area at minus 65° F in calcium nitrate/calcium chloride/water system.

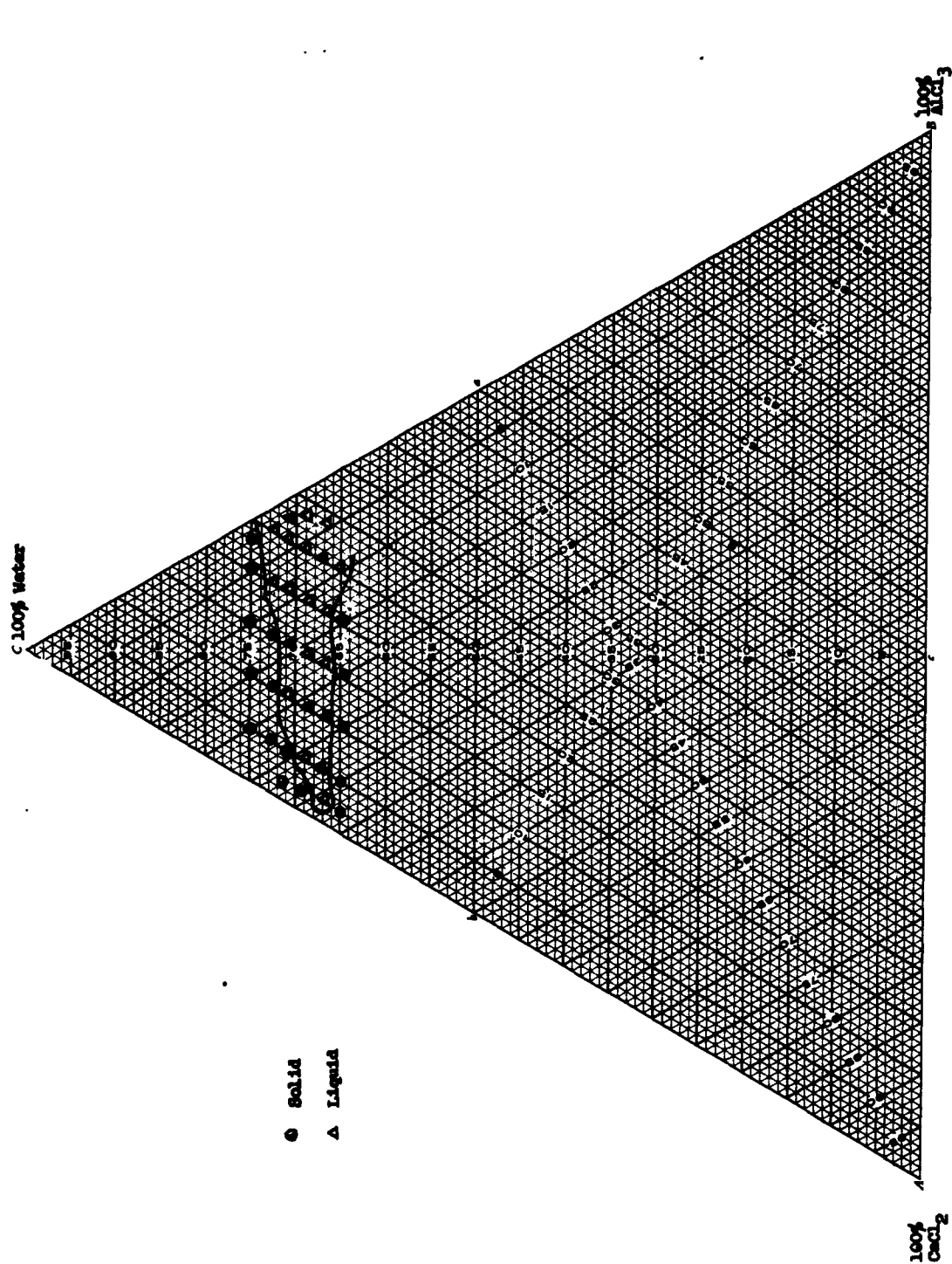


Fig. 9. Proven liquid area at minus 65° F in calcium chloride/aluminum chloride/water system.

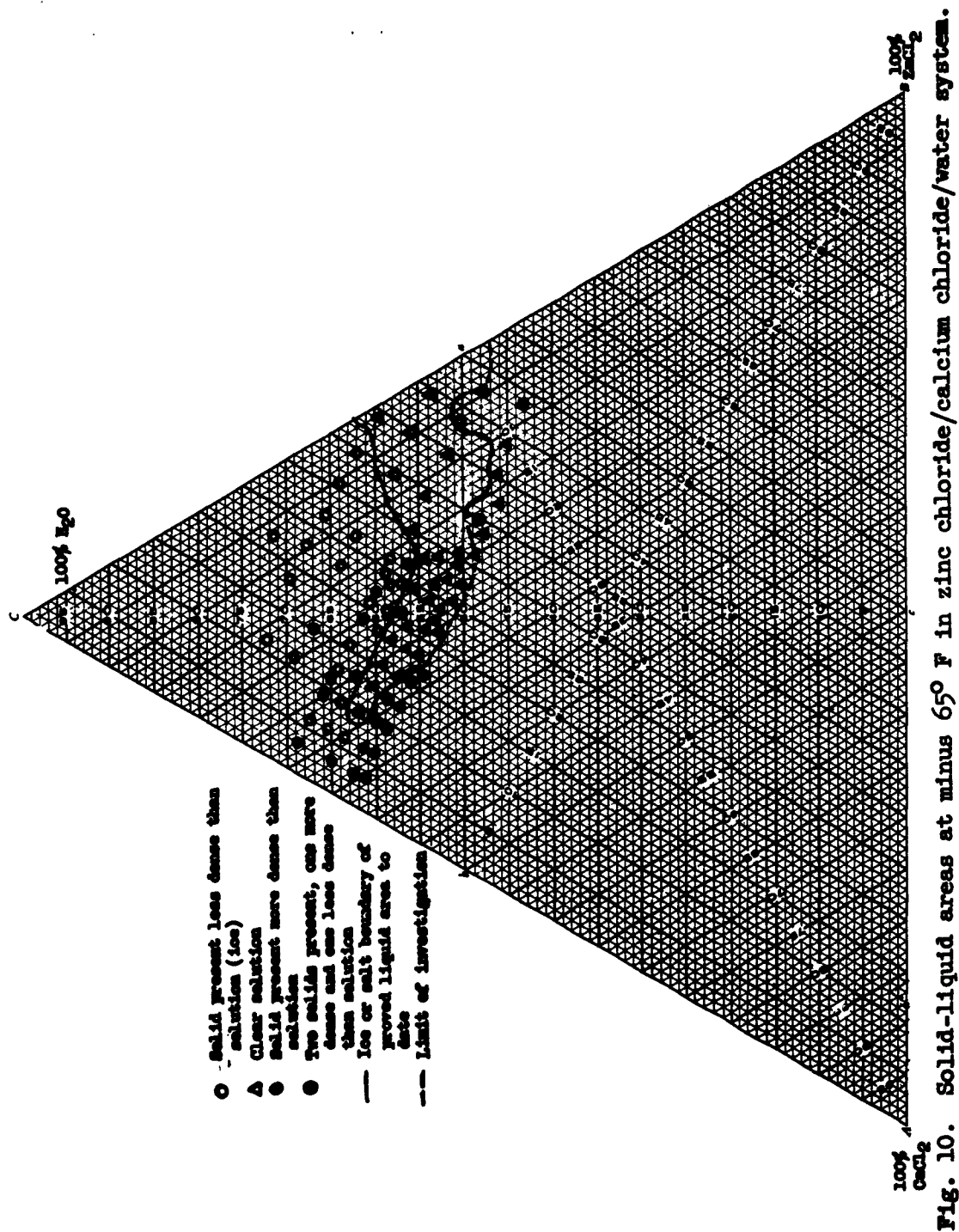


Fig. 10. Solid-liquid areas at minus 65° F in zinc chloride/calcium chloride/water system.

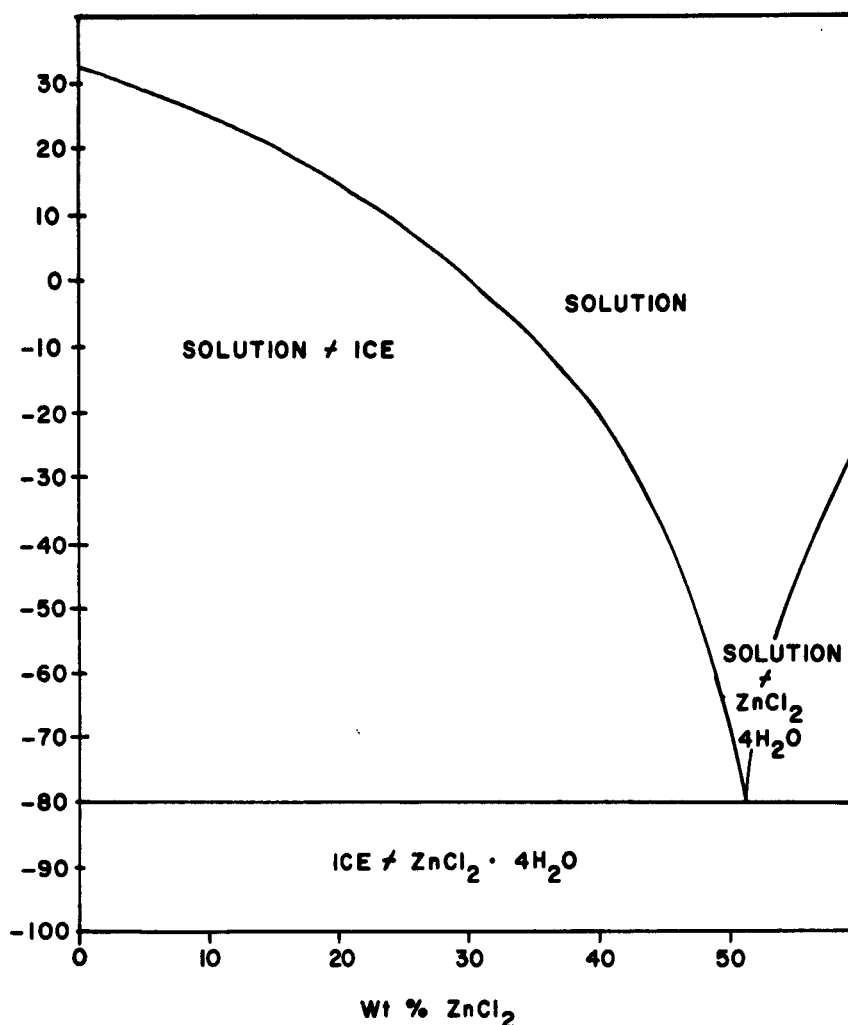


Fig. 11. Phase diagram for zinc chloride/water system.

quantity of water. Where multiple eutectic points were observed, it was found that the lowest ternary eutectic temperature was in a region close to the lowest binary eutectic temperature. Based on the eutectic points which were determined to be less than minus 65° F in temperature, the systems were selected for phase-diagram development at minus 65° F (minus 53.9° C). From the phase diagrams developed, it is seen that the two systems presenting eutectic points corresponding to solids concentrations less than 30 percent by weight are lithium chloride/water and calcium-chloride/lithium chloride/water. In addition to the freezing point of a system, the viscosity is important and must not be greater than the range of 120 to 150 centistokes at minus 65° F (minus 53.9° C). Table XIV gives the result of the viscosity determinations.

Table XIV. Results of Viscosity Tests at Minus 65° F

Formulation	Composition	Average Efflux Time (sec)	Kinematic Viscosity (centi- stokes)	Mean Deviation (centi- stokes)
1	24% lithium chloride 76% water	106	71	± 1
2b	8.8% lithium chloride 20.0% calcium chloride 71.2% water 1050 mg/liter Na ₂ CrO ₄		106.5*	
2b (sea water)	8.8% lithium chloride 20.0% calcium chloride 71.2% sea water 1050 mg/liter Na ₂ CrO ₄		123.6*	
3	10% calcium nitrate 27% calcium chloride 63% water	420	276	± 2
4	5% ferric chloride 29% calcium chloride 66% water	174	115	± 2
5	8% aluminum chloride 24% calcium chloride 68% water	247	163	± 2
6	20% zinc chloride 25% calcium chloride 55% water	126	83	± 1
7	51% zinc chloride 49% water	306	202	± 2

* USAERDL data; other data from University of Maryland study.

16. Corrosion Tests. Table XV summarizes all the results obtained in the corrosion study. Figure 12 represents these same results graphically. Complete results are given in Table XXVI, Appendix D. Two conclusions are evident from the results. The first is that Formulation 2 is the least corrosive of all four of the formulations tested. The corrosion rates obtained in Formulation 4

Table XV. Corrosion of Various Metals in Formulations

Formu- lation	Initial pH	Time of Test (days)	Average Corrosion Rate per Year x 10 ⁴ (mean percent deviation from average of two rates beside each value)			
			Steel	Copper	Brass	Aluminum Zinc Magnesium
1	6.6	33	1.37 (17)	1.53 (3.3)	1.22 (2.0)	0.78 (5.1) 2.11 (0.5) 62.1 (30)
1*	6.7	33	0.7 (43)	1.07 (14)	0.26 (9.6)	0.07 (0) 0.41 (41) 0.73 (48)
2	5.0	33	0.97 (13)	1.22 (5.7)	0.94 (7.5)	0.42 (2.5) 2.44 (1.4) 1.81 (37)
2*	5.2	33	0.43 (2.3)	0.54 (7.4)	0.35 (8.6)	0.02 (100) 0.26 (0) 0.44 (5.7)
3	4.8	21	1.73 (12)	1.03 (7.8)	1.09 (1.8)	1.47 (10) 10.7 (50) Very high
3*	4.8	21	1.17 (15)	0.78 (9.0)	0.84 (6.0)	0.09 (100) 5.19 (20) 17.9 (30)
4	0.5	6	141.5 (0.4)	292 (0.5)	209 (0.5)	288 (14) Extremely high Extremely high
Control	5.6	33	2.32 (26)	0.09 (0.5)	---	---

*Inhibited.

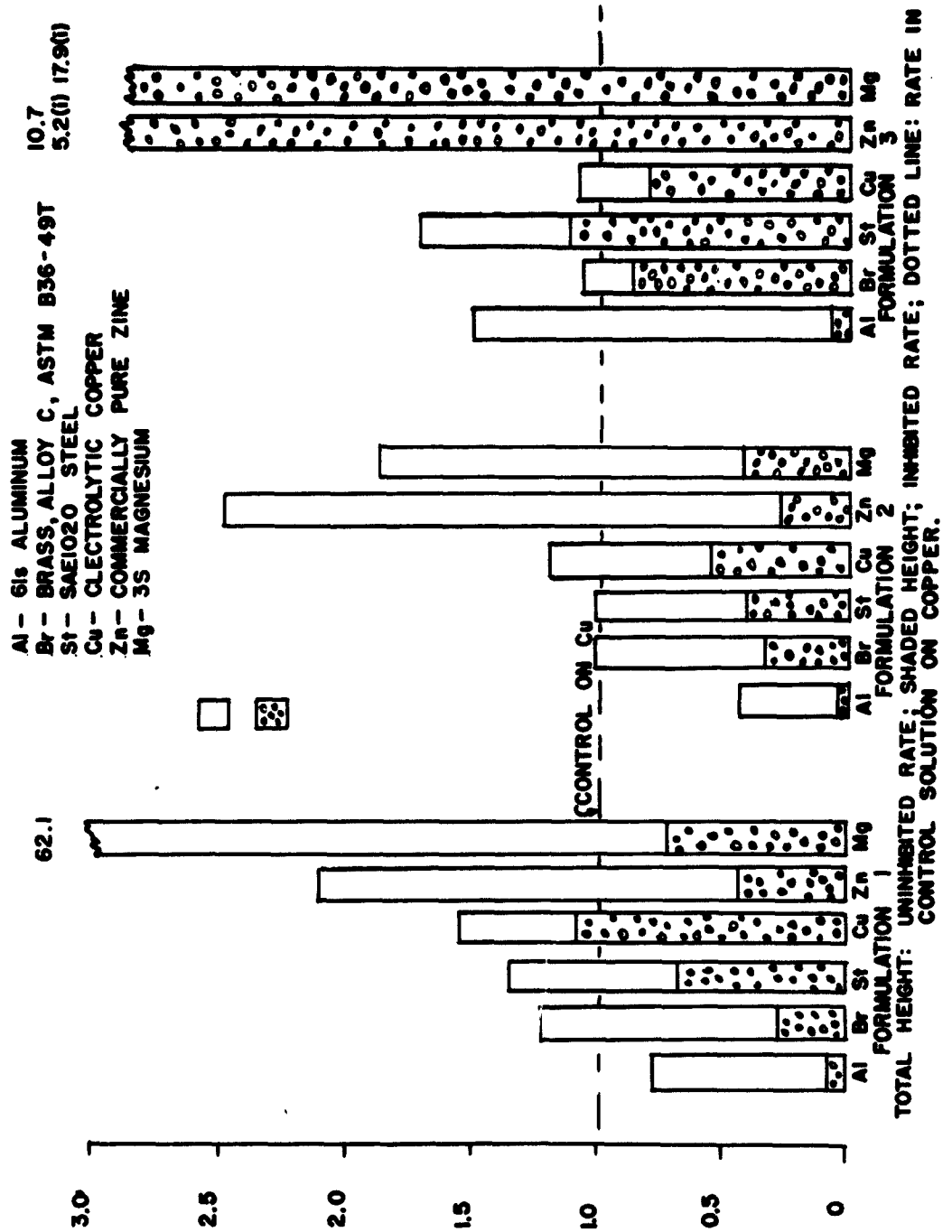


Fig. 12. Corrosion of various metals in formulations.

(5 percent ferric chloride, 27 percent calcium chloride, 66 percent water) were so much greater than those obtained in the other formulations that they could not be represented in Fig. 12. The order of increasing corrosiveness for the formulations is: 2, 1, 3, and 4; Formulation 1 is only slightly less corrosive than Formulation 3. The second conclusion to be drawn is that sodium chromate was a fairly effective inhibitor in nearly every case where it was used, although it appears to be relatively more effective in Formulation 2 than in the others. This is particularly remarkable in view of the fact that this formulation contained less chromate than Formulation 1 (Table VII). It is probable that the chromate would have been more effective in Formulation 3 if it were not limited to such a low concentration by its solubility in this mixture. No excess chromate was present in either of the inhibited formulations (2 and 3) which were saturated with it. A large excess would result in the metathetical reaction $\text{Na}_2\text{CrO}_4 + \text{CaCl}_2(\text{sol.}) = \text{CaCrO}_4(\text{insol.}) + 2\text{NaCl}(\text{sol.})$ displacing enough calcium from the formulations to cause precipitation at minus 65° F. A slight excess, however, could probably be tolerated in practice.

The results obtained with steel in the control solutions are not considered a fair basis for comparison with the other formulations. That part of the metal exposed to the air appeared to have been accidentally wetted and dried alternately at least once. This caused greater total corrosion of these specimens than of the specimens in the experimental solutions. The copper specimens in the control solution appeared to give satisfactory and reproducible results, and the value obtained with this combination (0.00099 inch per year) may be compared with those of the other solutions. It should be recalled that these results are for partial immersion in quiescent solutions with the solution surface exposed to air. Those metals which, in the various formulations, equaled or exceeded the resistance of copper in the control solution are listed in Table XVI.

Table XVI. Metals Passing Corrosion Test

Formulation	Metals Corroding Less Than 0.001 inch per year ^a
1	Aluminum
1 ^b	Aluminum, brass, steel, zinc, magnesium
2	Aluminum, brass, steel
2 ^b	Aluminum, brass, steel, copper, zinc, magnesium
3	Copper
3 ^b	Aluminum, brass, copper
4	None

a. Corrosion rate of copper in control (28% CaCl_2 , JAN-C-344) solution = 0.00099 inch per year.

b. Inhibited.

In reaction to all the inhibited formulations, aluminum is by far the least corroded of the six metals. It is also the metal most susceptible to the action of the inhibitor. Zinc and magnesium were the most corroded in all the uninhibited solutions. None of the metals withstood Formulation 4 to any reasonable degree. In this solution also, zinc and magnesium were attacked so quickly that no rate could be calculated because the samples disintegrated. The attack on the magnesium in all solutions was a pitting type in which laceworks of channels were formed on the surface. The calculated corrosion rates were based on the superficial area exposed, however. Brass, steel, and copper had intermediate rates in the various solutions and were very nearly the same in Formulation 2.

In connection with the excellent resistance of aluminum obtained in this study, it should be noted that the previous investigation at USAERDL (1) into the corrosion of aluminum, copper, lead-tin solder, brass, and cast iron by lithium-chloride solutions indicated that aluminum was the most readily attacked metal at a pH of 7.5 and was even more so at a pH of 8.5. The pH of the 24 percent lithium-chloride solutions (Formulation 1) studied was 6.6 to 6.7. Two other important differences between the previous test conditions (1) and those used here are:

a. Previously, the different specimens apparently were in electrical contact; galvanic couples were, therefore, formed accelerating the attack on the aluminum in comparison with the other metals. The specimens in this investigation were in isolated sample bottles.

b. Previously, the specimens were in agitated solutions; those used in the test described were in quiescent solutions.

The most desirable formulation from the standpoint of corrosion is number 2. Judged by its (inhibited) attack on electrolytic copper, it is only slightly more than half as corrosive as the control solution. The inhibited attack on aluminum, brass, steel, zinc, and magnesium is even less than that on copper. Without inhibitor, the corrosiveness could be considered excessive only to zinc and magnesium. Formulations 1 and 3 are somewhat more corrosive than 2; however, when Formulation 1 is inhibited, it is about equal in corrosiveness to the comparison control solution, whereas Formulation 3 cannot be inhibited to the same degree and is excessively corrosive to zinc and magnesium even when saturated with sodium chromate (87 mg. per l.). Formulation 4 is more corrosive than Formulations 1, 2, and 3 by two orders of magnitude. It is doubtful that any adjustment of the composition of this solution within the limits prescribed by the freezing-point requirements could improve it enough to make it acceptable.

The excellent performance of aluminum has already been pointed out, but it should be mentioned that aluminum in bimetallic contact with less active metals would probably not show this superiority. Brass, steel, and copper had intermediate rates in the various formulations, but the best choice of a construction material depends on the formulation under consideration. Zinc and magnesium are too active to withstand the attack of the various formulations except 1 and 2 inhibited. Because of the pitting attack on the magnesium, the effective penetration of this metal is actually greater than that indicated in Table XV and Fig. 12.

Sodium chromate is an effective inhibitor even where used in less than the recommended quantity (3,500 mg per liter).

It is probable that the corrosiveness of Formulations 1, 2, and 3 could be lessened even more by addition of some alkaline ingredient to raise the pH. Judging from the results with Formulation 4, Formulation 4 and the other proposed formulations which contain zinc, iron, and aluminum chlorides would probably not be susceptible to this remedy since insoluble basic chlorides or hydroxides would be formed before the pH was high enough to lower the corrosion rate to an acceptable point.

17. Fire Tests. Figure 13 summarizes the results of the fire tests. Appendix E presents the test results in greater detail. Volume superiority factors as proposed by Bryan and Smith (25) are

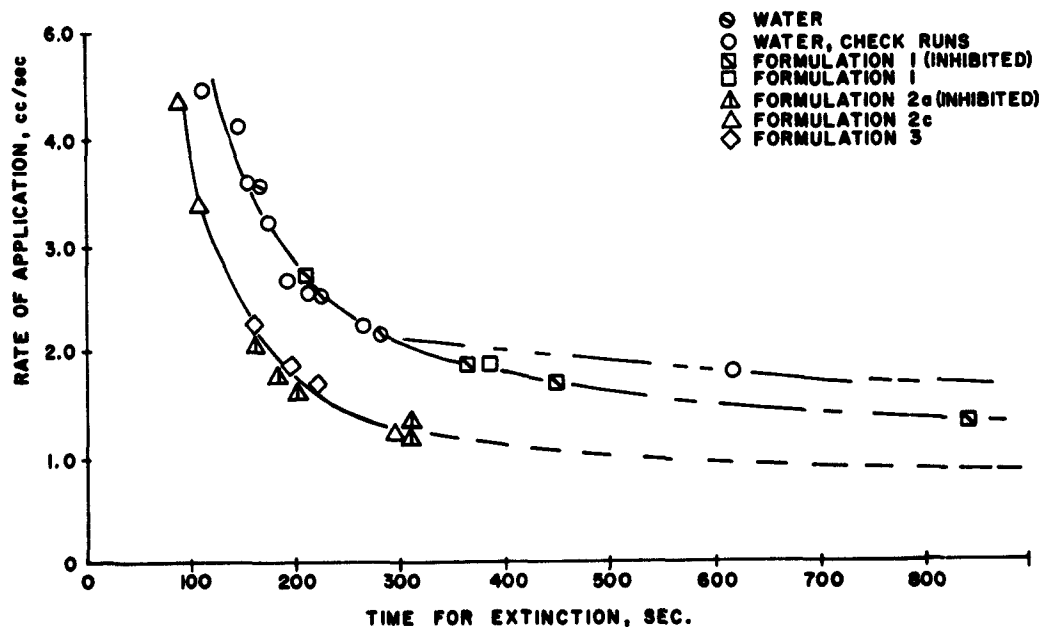
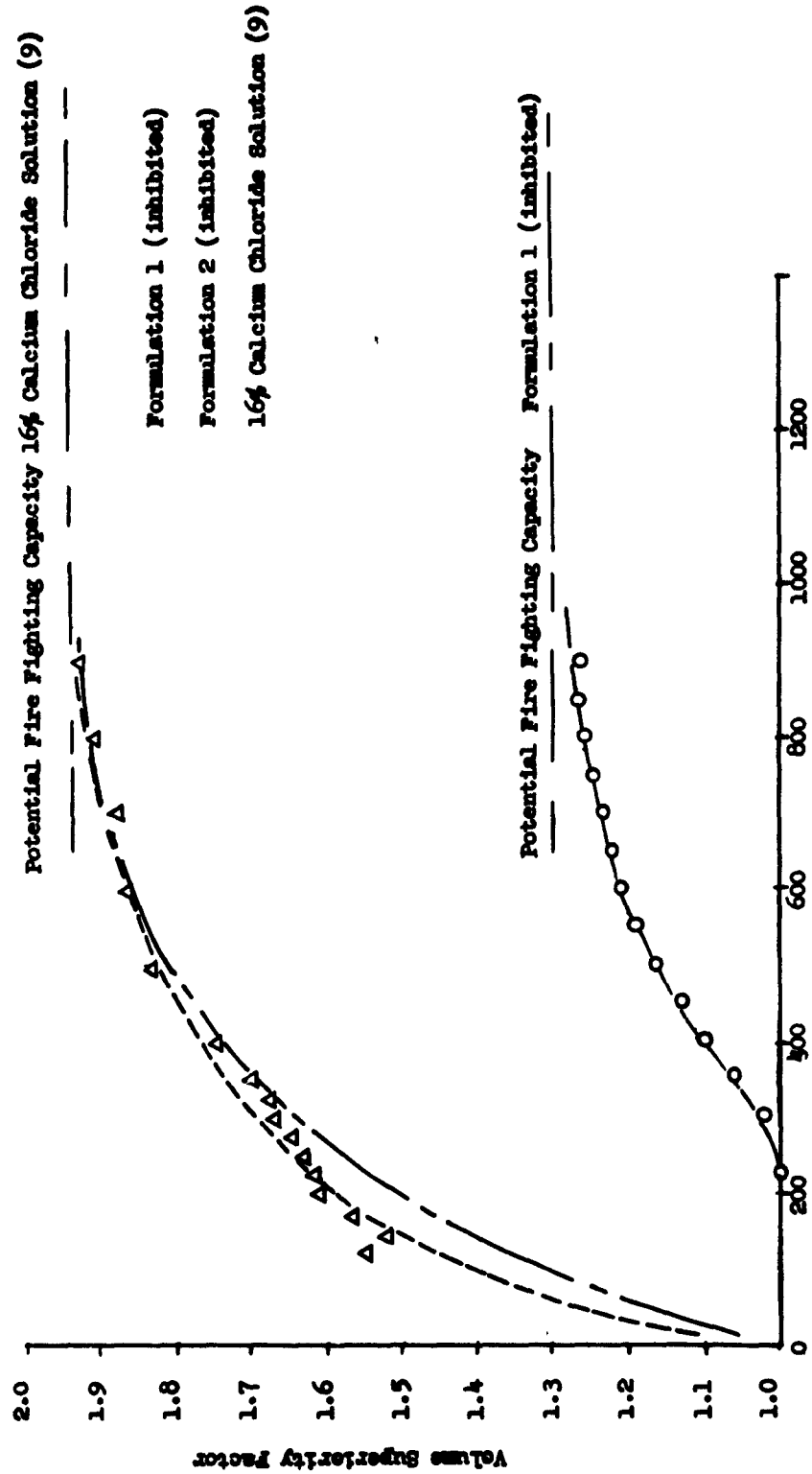


Fig. 13. Fire extinction effectiveness.



Time for Total Extinction, Sec.

Fig. 14. Volume superiority factor.

plotted in Fig. 14. In Figs. 13 and 14, superiority of the LiCl CaCl_2 formulation over LiCl is shown.

18. Proof Tests. From the preceding tests, it is seen that for minus 65° F (minus 53.9° C) service, the formulation of inhibited 8.8 percent LiCl $_2$, 20.0 percent CaCl $_2$, and 71.2 percent water appears most suited from the standpoint of fire-fighting effectiveness, low-temperature fluidity, corrosive effect, and toxicity (zinc-chloride base formulations are considered undesirable since zinc chloride is classed as a "poison"). Proof tests of the packaging based on the above formulation were undertaken. The results of these tests are summarized in Table XVII.

Table XVII. Results of Three Weeks of Storage at High and Low Temperature*

Temperature	Result
-65° F	No change in crystals No change in bags
+150° F	No change in crystals No change in bags
+170° F	No change in crystals Polyethylene bag ruptured
+90° F, 95% R.H.	No change in crystals No deterioration of bag

* Charges in polyethylene bags.

There was no noticeable effect of storage of the charged, 4-gallon, pump-type extinguishers at either normal storage or tropical temperature and high humidity storage.

V. CONCLUSIONS

19. Conclusions. It is concluded that:

a. A solution having 20.0 percent calcium chloride (CaCl $_2$), 8.8 percent lithium chloride (LiCl), and 71.2 percent water (H $_2$ O) composition on a weight basis and having a density of 1.2265 at 68° F (20° C) (54) is satisfactory as a candidate antifreeze salt for winterizing water to minus 65° F.

b. Sodium chromate at a concentration of 1,050 mg per liter of solution effectively inhibits the corrosive effect of the above salt solution on aluminum, steel, brass, zinc, magnesium, and copper.

c. Lithium-chloride solutions (approximately 23 percent LiCl by weight in water) are effectively nonfreezing to below minus 65° F and except for higher cost are as applicable for application in antifreeze charges as the CaCl_2 LiCl mixture in solution with water.

d. Dry packaging of salt charges including the inhibitor is feasible.

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APPENDICES

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APPENDIX A

AUTHORITY

SUBPROJECT OF PROJECT 8-76-04-100

R&D PROJECT CARD		TYPE OF REPORT PROGRESS		REPORT CONTROL SYMBOL CSCRD-1	
1. PROJECT TITLE WATER ADDITIVES, FIRE FIGHTING (u)		3. SECURITY OF PROJECT U		2. PROJECT NO. 8-76-04-109	
		4. CEIC NO. 2004/228		5. REPORT DATE 31 Dec 56	
6. BASIC FIELD OR SUBJECT Fire Fighting		7. SUB FIELD OR SUBJECT SUB GROUP Fighting, Fire		7A. TECH. ORL 80-9	
8. COORDINATING AGENCY Corps of Engineers		12. CONTRACTOR AND/OR LABORATORY Engr Res & Dev Lab		CONTRACT/WORK NO.	
9. DIRECTING AGENCY Engr Res & Dev Div, TO, OCE					
10. REQUESTING AGENCY Office, Chief of Engineers					
11. PARTICIPATING AND/OR COORDINATING AGENCIES Dept of the Air Force (C) Dept of the Navy (C)		13. RELATED PROJECTS NR-407-050 NS-041-007 AF (WADC) 6075		17. EST. COMPLETION DATES DES. Jul 57 DEV. Oct 57 TEST Feb 58 OP. EVAL. Jul 58	
		14. DATE APPROVED 18 January 1952 by GSUSA		18. FISCAL ESTIMATES	
		15. FUNDING			
16.					
Supersedes project card dated 31 December 1955.					
19. DOCUMENT AND/OR JUSTIFICATION There is a requirement for superior water additive for combating Class A (solid combustible) and Class B (liquid fuel) fires. Water and water fog are used for combating Class A fires. Independent investigations have shown that certain salts enhance the effectiveness of water in extinguishing this type fire, and may render water more effective against Class B fires. In addition a superior foam-producing compound is desired for extinguishing Class B fires. Protein base foams now in use do not possess a sufficient water retention with respect to the elapsed time after application to provide the best possible fire extinguishing effect. It is anticipated that the development will result in items of such marked superiority over existing items that complete replacement will be justified.					
21. BRIEF OF PROJECT AND OBJECTIVE:					
a. Brief:					
(1) Objective:					
Development of a superior water additive or additives for use with water in combating Class A and B fires.					
(2) Military Characteristics:					
(a) The water additive or additives shall:					
1. Render water more effective in extinguishing Class A fires.					
2. Render water effective against Class B fires.					
22. DOC	23. ORL	24. ORL	25. P	26. L	27. C
DD FORM 613			PAGE 1 OF 4		
REPLACES DD FORM 1A WHICH MAY BE USED.					

R&D PROJECT CARD
CONTINUATION SHEET

SO-9

1. PROJECT TITLE WATER ADDITIVES, FIRE FIGHTING (U)	2. SECURITY OF PROJECT U 4. CORPS OF ENGINEERS	3. PROJECT NO. 8-76-04-109 5. REPORT DATE 31 December 56
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Block 21 a continued

3. Insofar as possible render water effective against military liquid fuel fires in addition to hydrocarbon base fuel fires.
 4. Be more effective than protein base foam and superior to such foam in the physical and/or chemical properties which are critical from the standpoint of fire extinguishment.
 - (b) The water additive or additives shall be suitable for use in water at temperatures from ± 32 F to ± 160 F, shall be stable, and not affected by 5 years storage at temperatures from -80 F to ± 160 F and shall not be adversely affected by freezing up to 50 cycles of freeze and thaw.
 - (c) The water additive or additives shall be easily admixed with water at the point of use, and shall be effective in concentrations not exceeding 6 percent by volume of the admixed component.
 - (d) The water additive or additives shall be more corrosive than protein base foam (Type 5, JAN-C-266).
 - (e) The water additive or additives shall be easily produced, and shall be of such nature that performance of the item shall not be dependent on minor process variables, or techniques of different manufacturers.
 - (f) The water additive or additives shall be produced from non-critical materials.
 - (g) Air Transportability is not required.
- b. Approach:
- (1) Conduct studies and extensive literature search on use of salts, foams, and emulsions in formulation of more effective fire fighting solutions.
 - (2) Conduct literature and laboratory research on current effective water mechanisms involved in their activity.
 - (3) Make correlations of chemical structures of the various additives used or proposed in the past and determine, if possible, by which mechanisms the fire extinguishing performance of water can be significantly augmented, using experimental methods to verify observations of conclusions where necessary.
 - (4) Examine the relationship of water additives to other agents such as dry powders, flame retardants, and vaporizing liquids to determine if chemical components of the latter classes of agents may be advantageously incorporated into experimental water additives for subsequent tests.
 - (5) Conduct engineering tests on various classes of water additives to determine relative merits of each class.
 - (6) Select most promising class, or classes, for further development and tests.
 - (7) Recommend service test of most effective item or items meeting all the military requirements.

R&D PROJECT CARD
CONTINUATION SHEET

SC-9

1. PROJECT TITLE WATER ADDITIVES, FIRE FIGHTING (U)	2. SECURITY OF PROJECT U	3. PROJECT NO. 8-76-04-109
	4. CORPS OF ENGINEERS	5. REPORT DATE 31 December 56

Block 21 continued

c. Subtasks:

- (1) The related project 8-76-04-002, Fuel Storage Fire Protection, will result in the development of techniques and equipment for combating liquid fuel fires. It is anticipated that such techniques and equipment shall be applicable to the use of any improved water additive.
- (2) Evaluation of mechanisms of action of vaporizing liquid agents in flame extinguishment, under project 8-76-04-003, Fire Extinguishing Agent, Improved, Self-Contained, may provide basis for investigation of a new class of water additives.
- (3) Project NR 407-050 has resulted in laboratory foam test methods which have been used in ERDL studies involving foam application. Data on fire tests conducted under this project will be of value in formulating the program of investigation.
- (4) Project NS 041-007 has resulted in stability data for existing protein base foam. It is anticipated that these data, and test experience will be utilized in further investigation.
- (5) Project (AF) 664-800 covers work on agents suitable for non-hydrocarbon fuel fires. Liaison will be maintained so that advantage may be made of the development under the project.

d. Other Information:

- (1) References:
Thomas and Hochwalt (Industrial Engineering Chemistry, Vol. 20, p 575-7, 1918) reported the positive effect of alkali salts on extinguishing oil fires.
- (2) Discussion:
 - (a) Much work has been done, on the use of salts in fighting Class A fires (Forestry Service) and in compounding flame retardants for Class A material. Industry is currently engaged in research on protein base foam liquid to make up to 3 percent solution. Outside of the fire fighting industry a synthetic foam with a methylated cellulose base has been proposed, which could be effective at 2 percent concentration in water. Current protein base foam does not possess a sufficient water retention with respect to time elapsed after application to provide the best possible fire extinguishing effect. At the best water retentions obtainable, the fluidity of the foam is reduced as indicated in NRL Report on Foam Standardization Methods dated 26 April 1948. Current chemical powder foams are not as adaptable to military operations since they require greater care in handling and utilization.
 - (b) The previously reported effects and promising avenues of development indicate that production of a superior end item is feasible. In the development of an end item cognizance shall be taken of new military liquid fuels and the relative difficulty of fire extinguishment where these fuels are involved.

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R&D PROJECT CARD
CONTINUATION SHEET

80-9

1. PROJECT TITLE WATER ADDITIVES, FIRE FIGHTING (U)	2. SECURITY OF PROJECT U	3. PROJECT NO. 8-76-04-109
Klook 21d Continued (c) Agencies interested in this project, in addition to the Corps of Engineers, with which liaison will be maintained, and which will be furnished copies of reports on the project, are the Department of the Navy and Department of the Air Force.	4. COFE	5. REPORT DATE 31 Dec 56

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1 FEB 56.

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APPENDIX B

EXPERIMENTAL RESULTS

Table XVIII. Results of Freezing-Point Experiments

System No.	System	Lowest Eutectic Temperature Observed ($^{\circ}\text{F}$)	Remarks
1	Lithium chloride/ water	-	No eutectic temperature observed or high viscosity of solution at low temperature. A 32% lithium chloride was cooled to -100°F without precipitation of solid.
2	Calcium chloride/ lithium chloride/ water		Clear solutions observed below -65°F . The high viscosity of these solutions below -70°F seems to prevent crystallization.
3	Calcium chloride/ calcium nitrate/ water	-73	-
4	Calcium chloride/ ferric chloride/ water		Clear solutions observed below -65°F . High viscosity at low temperature seems to prevent crystallization in solutions containing more iron than calcium.
5	Calcium chloride/ aluminum chloride/ water	-68	-
6	Calcium chloride/ zinc chloride/water	below -65	Solid-liquid areas of this system at -100°F are available in the literature (6).

Table XVIII (cont'd)

7	Zinc chloride/water		Eutectic temperature reported in International Critical Tables at -81° F.
8	Calcium chloride/ aluminum nitrate/ water	-72	-
9	Calcium nitrate/ ferric chloride/ water	-	Clear solutions observed below -65° F. Eutectic temperature could not be determined because of high viscosity of solution.
10	Calcium chloride/ lithium bromide/ water	-74	Bromide less desirable than chloride which subsequently proved satisfactory.
11	Calcium chloride/ magnesium bromide/ water	-68	Rejected because systems containing bromide were believed to be less desirable than other accepted systems.
12	Calcium chloride/ magnesium nitrate/ water	-68	-
13	Calcium chloride/ sodium iodide/water	-68	Iodide less desirable than chloride which subsequently proved satisfactory.
14	Calcium chloride/ ferric nitrate/water	-66	-
15	Calcium chloride/ zinc nitrate/water	-66	-
16	Calcium chloride/ cupric nitrate/water	-65	-
17	Sodium lactate/water Potassium lactate/ water	-	Solution very viscous at -65° F. No eutectic temperature observed on solidification of a sample of solution.

Table XVIII (cont'd)

18	Calcium chloride/ sodium lactate/ water	-	High viscosity seems to prevent crystallization. Gel observed on cooling below -65° F.
19	Calcium iodide/ water	-	Aqueous solution changes to an orange color on standing.
20	Calcium chloride/ calcium bromide/ water	-64	-
21	Calcium chloride/ cupric chloride/ water	-64	-
22	Calcium chloride/ zinc bromide/water	-63	This eutectic was observed near the calcium chloride eutectic composition.
23	Calcium chloride/ magnesium chloride/ water	-62	-
24	Calcium chloride/ sodium chloride/ water	-61	-
25	Aluminum bromide/ water	-	Aluminum bromide hydrolyzes to form an insoluble product.
26	Calcium lactate/water Magnesium lactate/ water	-	Both salts are relatively insoluble.

Table XIX. Data for Phase Diagram,
Lithium Chloride/Water

Temperature	LiCl Content of Solutions Which Contained Ice (Wt % LiCl)	LiCl Content of Solutions Which Were Liquid (Wt % LiCl)	LiCl Content of Solution Containing Precipitated Salt (Wt % LiCl)
-72	0 through 22	23 through 33	34 through 38
-65	0 through 21	22 through 33	34 through 38
-35	0 through 18	19 through 34	35 through 38
-32	-	35	36 through 38
-21	-	35	36 through 38

Table XX. Data for Zinc Chloride/Calcium Chloride/Water System

Sample No.	H ₂ O (%)	CaCl ₂ (%)	ZnCl ₂ (%)	Description of Sample at -65° F With Estimated % of Sample Which was Solid
1	73	16.2	10.8	Solid
2	71.5	7.0	21.5	75% solid on top
3	71.0	14.0	15.0	Partially solid
4	69.8	5.0	25.2	80% solid
5	69.3	12.3	18.4	90% solid on top
6	68.8	20.2	11.0	90% solid on top
7	68.6	28.2	3.2	Solid
8	68.2	26.9	4.9	90% solid on top
9	67.7	3.0	29.3	Partially solid
10	67.5	10.3	22.2	90% solid on top
11	67.0	18.0	15.0	90% solid on top
12	65.9	25.1	9.0	90% solid on top
13	65.8	8.2	26.0	90% solid on top
14	65.2	28.8	6.0	15% solid on top
15	65.2	16.2	18.6	90% solid on top
16	65.0	24.0	11.0	90% solid on top
17	64.6	32.3	3.1	Partially solid
18	64.3	23.7	12.0	80% solid on top
19	64.0	27.0	9.0	40% solid on top
20	63.8	6.1	30.1	85% solid on top
21	63.5	14.1	22.4	90% solid on top
22	63.2	30.8	6.0	15% solid on top
23	63.0	22.0	15.0	80% solid on top
24	63.0	22.0	15.0	70% solid on top
25	62.8	34.2	3.0	50% solid on bottom, 10% solid on top
26	62.8	25.5	11.7	60% solid on top
27	62.2	28.9	8.9	Clear liquid
28	61.8	12.1	26.1	60% solid on top
29	61.8	4.1	34.1	3% solid on top
30	61.7	35.2	3.1	60% solid on bottom, 20% solid on top
31	61.6	20.5	17.9	Partially solid
32	61.4	32.5	6.1	50% solid on bottom
33	61.3	23.8	14.9	80% solid on top
34	61.3	20.2	18.5	60% solid on top
35	60.8	27.1	12.1	Clear liquid
36	60.2	33.8	6.0	Partially solid
37	60.2	30.8	9.0	Partially solid
38	60.2	18.8	21.0	80% solid on top
39	60.0	22.0	18.0	90% solid on top
40	59.9	18.2	21.9	15% solid on top
41	59.8	29.0	11.2	80% solid on bottom
42	59.8	9.8	30.4	2% solid on top
43	59.5	25.5	15.0	Clear liquid
44	59.5	1.8	28.7	Clear liquid
45	59.0	32.0	9.0	Partially solid

Table XX (cont'd)

46	58.8	17.2	24.0	80% solid on top
47	58.6	20.5	20.9	70% solid on top
48	58.1	23.8	18.1	Clear liquid
49	58.0	31.0	11.0	Clear liquid
50	58.0	16.1	25.9	5% solid on top
51	57.8	30.3	11.9	Partially solid
52	57.8	27.2	15.0	Clear liquid
53	57.8	7.8	34.4	Clear liquid
54	57.2	18.8	24.0	60% solid on top
55	57.0	22.0	79.0	Clear liquid
56	56.5	25.5	18.0	Clear liquid
57	56.3	28.8	14.9	Clear liquid
58	56.3	28.7	15.0	Partially solid
59	56.0	28.0	16.0	Clear liquid
60	56.0	14.1	29.9	Clear liquid
61	55.5	20.2	24.3	Clear liquid
62	55.5	52.0	39.3	Clear liquid
63	55.0	23.8	21.2	Clear liquid
64	54.2	11.9	33.9	Clear liquid
65	54.0	22.0	24.0	Clear liquid
66	53.9	25.1	21.0	Clear liquid
67	53.6	24.7	21.7	Clear liquid
68	53.3	2.8	43.9	Clear liquid
69	52.5	23.5	24.0	Clear liquid
70	52.0	9.2	38.8	80% solid on bottom
71	50.8	20.3	28.9	Clear liquid
72	50.2	29.0	29.8	Clear liquid
73	50.0	6.9	43.1	5% solid on bottom
74	48.7	17.2	34.1	8% solid on bottom
75	48.0	4.6	47.4	Clear liquid
76	46.3	14.0	39.7	Clear liquid
77	44.8	11.8	44.4	Clear liquid
78	42.9	8.8	48.3	10% solid on bottom
79	58.0	18.5	23.5	Solid
80	56.5	23.5	20.0	Clear liquid
81	56.0	17.5	26.5	Solid
82	55.5	20.0	24.5	Clear liquid
83	54.5	29.0	16.5	Solid
84	54.5	24.5	21.0	Clear liquid
85	54.0	18.0	28.0	Clear liquid
86	53.0	21.0	26.0	Clear liquid
87	52.5	26.0	21.5	Clear liquid
88	52.5	19.0	28.5	Clear liquid
89	51.5	24.0	24.5	Clear liquid
90	51.5	21.5	27.0	Clear liquid
91	50	22.5	27.5	Clear liquid
92	50	20.0	30.0	Clear liquid
93	48.5	20.5	31.0	Clear liquid
94	47.5	19.0	33.5	Clear liquid
95	45.5	17.0	37.5	Clear liquid

Table XXI. Data for Lithium Chloride/Calcium Chloride/Water

Sample No.	H ₂ O (%)	CaCl ₂ (%)	LiCl (%)	Description of Sample at -65° F with Estimated % of Sample Which was Solid
101	82	15	3	Solid
102	82	12	6	Solid
103	82	9	9	Solid
104	82	6	12	Solid
105	82	3	15	Solid
106	80	17	3	Solid
107	80	14	6	Solid
108	80	11	9	Solid
109	80	8	12	Solid
110	80	5	15	95% solid on top of solution
111	80	2	18	Solid
112	78	19	3	Solid
113	78	16	6	Solid
114	78	13	9	95% solid on top
115	78	10	12	95% solid on top
116	78	7	15	Solid
117	78	4	18	Clear solution (metastable)
118	76	21	3	Solid
119	76	18	6	Solid
120	76	15	9	95% solid on top
121	76	12	12	Solid
122	76	9	15	90% solid on top
123	76	6	18	Clear solution
124	76	3	21	Clear solution
125	74	23	3	95% solid on top
126	74	20	6	95% solid on top
127	74	17	9	50% solid on top
128	74	14	12	50% solid on top
129	74	11	15	Clear liquid
130	74	8	18	Clear liquid
131	74	5	21	Clear liquid
132	72	25	3	95% solid on top
133	72	22	6	50% solid on top
134	72	19	9	Clear liquid
135	72	16	12	Clear liquid
136	72	13	15	Clear liquid
137	72	10	18	Clear liquid
138	72	7	21	Clear liquid
139	72	4	24	Clear liquid
140	72	16	12	Clear liquid
141	72	13	15	Clear liquid
142	72	10	18	Clear liquid
143	72	7	21	Clear liquid

Table XXI (cont'd)

144	72	4	24	Clear liquid
145	70	24	6	Clear liquid (metastable)
146	70	21	9	Clear liquid
147	70	18	12	Clear liquid
148	70	15	15	Clear liquid
149	70	12	18	Clear liquid
150	70	9	21	Clear liquid
151	70	6	24	Clear liquid
152	68	29	3	Clear liquid (metastable)
153	68	26	6	40% solid on bottom
154	68	23	9	Clear liquid (metastable)
155	68	20	12	60% solid on bottom
156	68	17	15	40% solid on bottom
157	68	14	18	40% solid on bottom
158	68	11	21	40% solid on bottom
159	68	8	24	25% solid on bottom
160	66	31	3	Solid
161	66	28	6	Solid
162	66	25	9	Solid
163	66	22	12	Solid
164	66	19	15	Solid
165	66	16	18	Solid
166	66	13	21	Solid
167	66	10	24	Solid
168	64	33	3	Solid
169	64	30	6	Solid
170	64	27	9	Solid
171	64	24	12	Solid
172	64	21	15	Solid
173	64	18	18	Solid
174	64	15	21	Solid
175	64	12	24	Solid
176	62	35	3	Solid
177	62	32	6	Solid
178	62	29	9	Solid
179	62	26	12	Solid
180	62	23	15	Solid
181	62	20	18	Solid
182	62	17	21	Solid
183	62	14	24	Solid
184	68	29	3	Clear liquid (metastable)
185	68	28	4	Clear liquid (metastable)
186	68	27	5	50% solid
187	68	26	6	Clear liquid (metastable)
188	68	25	7	Clear liquid (metastable)
189	68	24	8	Clear liquid (metastable)

Table XXI (cont'd)

190	68	23	9	5% solid on bottom
191	68	22	10	Clear liquid
192	68	21	11	50% solid on bottom
193	68	20	12	15% solid on bottom
194	68	19	13	45% solid on bottom
195	68	18	14	40% solid on bottom
196	68	17	15	40% solid on bottom
197	73	22	5	Solid
198	73	21	6	Solid
199	73	20	7	60% solid on top
200	73	19	8	40% solid on top
201	73	18	9	70% solid on top
202	73	18	10	60% solid on top
203	73	16	11	10% solid on top
204	73	15	12	Clear
205	72	23	5	90% solid on top
206	72	22	6	80% solid on top
207	72	21	7	40% solid on top
208	72	20	8	20% solid on top
209	72	19	9	Clear liquid
210	72	18	10	Clear liquid
211	72	17	11	Clear liquid
212	72	16	12	Clear liquid
213	71	24	5	Clear liquid (metastable)
214	71	23	6	Clear liquid (metastable)
215	71	22	7	Clear liquid (metastable)
216	71	21	8	Clear liquid
217	71	20	9	Clear liquid
218	71	19	10	Clear liquid
219	71	18	11	Clear liquid
220	71	17	12	Clear liquid
221	70	25	5	Clear liquid (metastable)
222	70	24	6	Clear liquid (metastable)
223	70	23	7	Clear liquid (metastable)
224	70	22	8	Clear liquid (boundary point)
225	70	21	9	Clear liquid
226	70	20	10	Clear liquid
227	70	19	11	Clear liquid
228	70	18	12	Clear liquid
229	69	26	5	Clear liquid (metastable)
230	69	25	6	Clear liquid (metastable)
231	69	25	6	Clear liquid (metastable)
232	69	23	8	Clear liquid (metastable)
233	69	22	9	Clear liquid (metastable)
234	69	21	10	Clear liquid (metastable)
235	69	20	11	Clear liquid (metastable)

Table XXI (cont'd)

236	69	19	12	Clear liquid (metastable)
237	68	27	5	Clear liquid (metastable)
238	68	26	6	30% solid on bottom
239	68	25	7	Clear liquid (metastable)
240	68	24	8	Clear liquid (metastable)
241	68	23	9	Clear liquid (metastable)
242	68	22	10	Clear liquid (metastable)
243	68	21	11	Clear liquid (metastable)
244	68	20	12	30% solid on bottom
245	72.5	25.0	2.5	Solid
246	72.5	24.5	3.0	Solid
247	72.5	24.0	3.5	Solid
248	72.5	23.5	4.0	Solid
249	72.5	23.0	4.5	Solid
250	72.5	22.5	5.0	Solid
251	72.5	22.0	5.5	Solid
252	71.5	26.0	2.5	99% solid on top
253	71.5	25.5	3.0	95% solid on top
254	71.5	25.0	3.5	90% solid on top
255	71.5	24.5	4.0	80% solid on top
256	71.5	24.0	4.5	60% solid on top
257	71.5	23.5	5.0	20% solid on top
258	71.5	23.0	5.5	5% solid on top
259	70.5	27.0	2.5	10% solid on top
260	70.5	26.5	3.0	5% solid on top
261	70.5	26.0	3.5	Clear liquid (metastable)
262	70.5	25.5	4.0	Clear liquid (metastable)
263	70.5	25.0	4.5	Clear liquid (metastable)
264	70.5	24.5	5.0	Clear liquid (metastable)
265	70.5	24.0	5.5	Clear liquid (metastable)
266	69.5	28.0	2.5	Clear liquid (metastable)
267	69.5	27.5	3.0	Clear liquid (metastable)
268	69.5	27.0	3.5	Clear liquid (metastable)
269	69.5	26.5	4.0	Clear liquid (metastable)
270	69.5	26.0	4.5	Clear liquid (metastable)
271	69.5	25.5	5.0	Clear liquid (metastable)
272	69.5	25.0	5.5	Clear liquid (metastable)
273	68.5	29.0	2.5	Clear liquid (metastable)
274	68.5	28.5	3.0	Clear liquid (metastable)
275	68.5	28.0	3.5	Clear liquid (metastable)
276	68.5	27.5	4.0	Clear liquid (metastable)
277	68.5	27.0	4.5	Clear liquid (metastable)
278	68.5	26.5	5.0	Clear liquid (metastable)
279	68.5	26.0	5.5	Clear liquid (metastable)
280	67.5	30.0	2.5	Clear liquid (metastable)
281	67.5	29.5	3.0	Clear liquid (metastable)

Table XXI (cont'd)

282	67.5	29.0	3.5	Clear liquid (metastable)
283	67.5	28.5	4.0	Clear liquid (metastable)
284	67.5	28.0	4.5	Clear liquid (metastable)
285	67.5	28.5	5.0	Clear liquid (metastable)
286	67.5	27.0	5.5	Clear liquid (metastable)
287	68.0	31.0	1.0	Solid
288	68.0	30.0	2.0	50% solid on bottom
289	67.0	32.0	1.0	80% solid on bottom
290	67.0	31.0	2.0	Clear liquid (metastable)
291	67.0	30.0	3.0	Clear liquid (metastable)
292	67.0	29.0	4.0	Clear liquid (metastable)
293	67.0	28.0	5.0	Clear liquid (metastable)
294	67.0	27.0	6.0	Clear liquid (metastable)
295	67.0	26.0	7.0	Clear liquid (metastable)
296	67.0	25.0	8.0	Clear liquid (metastable)
297	66.0	33.0	1.0	Solid
298	66.0	32.0	2.0	Solid
299	66.0	31.0	3.0	Solid
300	66.0	30.0	4.0	Solid
301	66.0	29.0	5.0	Solid
302	66.0	28.0	6.0	Solid
303	66.0	27.0	7.0	Solid
304	66.0	26.0	8.0	Solid
305	63.5	30.5	6.0	Solid on bottom
306	65.0	29.2	5.8	Solid on bottom
307	66.0	28.5	5.5	Clear liquid (metastable)
308	67.5	27.3	5.2	Clear liquid (metastable)
309	68.5	26.5	5.0	Clear liquid (metastable)
310	70.0	25.0	5.0	Clear liquid (metastable)
311	71.5	23.7	4.8	Clear liquid (metastable)
312	72.5	22.9	4.6	Solid on top
313	73.5	22.1	4.9	Solid on top
314	75.0	20.8	4.2	Solid on top

Table XXII. Data for Calcium Nitrate/
Calcium Chloride/Water System

Sample No.	H ₂ O (%)	CaCl ₂ (%)	Ca(NO ₃) ₂ (%)	Description of Solution at -65° F
400	70.0	28.0	2.0	95% solid on top
401	70.0	25.0	5.0	95% solid on top
402	70.0	22.5	7.5	95% solid on top
403	70.0	20.0	10.0	Solid
404	70.0	15.0	15.0	Solid
405	70.0	10.0	20.0	Solid
406	70.0	5.0	25.0	Solid
407	68.0	30.0	2.	Clear liquid
408	68.0	27.0	5.0	90% solid on top
409	68.0	24.5	7.5	95% solid on top
410	68.0	22.0	10.0	Solid
411	68.0	17.0	15.0	Solid
412	68.0	12.	20.0	Solid
413	68.0	7.0	25.0	Solid
415	68.0	2.0	30.0	Solid
416	66.0	32.0	2.0	Solid
417	66.0	29.0	5.0	Clear
418	66.0	26.5	7.5	5% solid on top
419	66.0	24.0	10.0	90% solid on top
420	66.0	19.0	15.0	95% solid on top
421	66.0	14.0	20.0	Solid
422	66.0	9.0	25.0	Solid
423	66.0	4.0	30.0	Solid
424	64.0	34.0	2.0	Solid
425	64.0	31.0	5.0	Clear liquid
426	64.0	28.5	7.5	Clear liquid
427	64.0	26.0	10.0	Clear liquid
428	64.0	21.0	15.0	95% solid on top
429	64.0	16.0	20.0	95% solid on top
430	64.0	11.0	25.0	Solid
431	64.0	6.0	30.0	Solid
432	62.0	36.0	2.0	Solid
433	62.0	33.0	5.0	Solid
434	62.0	30.5	7.5	Clear liquid
435	62.0	23.0	15.0	Clear liquid
436	62.0	18.0	20.0	95% solid on top
437	62.0	13.0	25.0	95% solid on top
438	62.0	8.0	30.0	Solid
439	59.5	35.5	5.0	Solid
440	59.5	33.0	7.5	Solid
441	59.5	30.5	10.0	Clear liquid
442	59.5	28.0	12.5	Clear liquid
443	59.5	25.5	15.0	Clear liquid

Table XXII (cont'd)

444	59.5	20.5	20.0	Clear liquid
445	59.5	15.5	25.0	95% solid on top
446	59.5	10.5	30.0	Solid
447	58.5	26.5	15.0	Solid
448	58.0	22.0	20.0	Clear liquid

Table XXIII. Data for Ferric Chloride/
Calcium Chloride/Water System

Sample No.	H ₂ O (%)	CaCl ₂ (%)	FeCl ₃ (%)	Description of Solution at -65° F
449	70.0	27.5	2.5	80% solid on top
450	70.0	25.0	5.0	80% solid on top
451	70.0	20.0	10.0	Solid
452	70.0	15.0	15.0	Solid
453	70.0	10.0	20.0	Solid
454	70.0	5.0	25.0	Solid
455	68.0	29.5	2.5	Clear liquid
456	68.0	27.0	5.0	Clear liquid
457	68.0	22.0	10.0	3% solid on top
458	68.0	17.0	15.0	80% solid on top
459	68.0	12.0	20.0	90% solid on top
460	68.0	7.0	25.0	Solid
461	66.0	31.5	2.5	Clear liquid
462	66.0	29.0	5.0	Clear liquid
463	66.0	24.0	10.0	Clear liquid
464	66.0	19.0	15.0	Clear liquid
465	66.0	14.0	20.0	10% solid on top
466	66.0	9.0	25.0	50% solid on top
467	64.0	33.5	2.5	Solid
468	64.0	31.0	5.0	Clear liquid
469	64.0	26.0	10.0	Clear liquid .
470	64.0	21.0	15.0	Clear liquid
471	64.0	16.0	20.0	Clear liquid
472	64.0	11.0	25.0	Clear liquid
473	62.0	35.5	2.5	Solid
474	62.0	33.0	5.0	Solid
475	62.0	28.0	10.0	Clear liquid
476	62.0	23.0	15.0	Solid
477	62.0	18.0	20.0	Clear liquid
478	62.0	13.0	25.0	Clear liquid

Table XXIV. Data for Aluminum Chloride/
Calcium Chloride/Water System

Sample No.	H ₂ O (%)	CaCl ₂ (%)	Al ₂ Cl ₃ (%)	Description of Sample at -65° F
501	75.0	20.0	5.0	Solid
502	75.0	15.0	10.0	Solid
503	75.0	10.0	15.0	Solid
504	75.0	5.0	20.0	Solid
505	75.0	2.0	23.0	Solid
506	73.0	22.0	5.0	Solid
507	73.0	17.0	10.0	Solid
508	73.0	12.0	15.0	Solid
509	73.0	7.0	20.0	Clear liquid
510	73.0	2.0	25.0	Clear liquid
511	71.0	27.0	2.0	Solid
512	71.0	24.0	5.0	Solid
513	71.0	19.0	10.0	Clear liquid
514	71.0	14.0	15.0	Clear liquid
515	71.0	9.0	20.0	Clear liquid
516	71.0	4.0	25.0	Clear liquid
517	71.0	2.0	27.0	Clear liquid
518	69.0	29.0	2.0	Clear liquid
519	69.0	26.0	5.0	Clear liquid
520	69.0	21.0	10.0	Clear liquid
521	69.0	16.0	15.0	Clear liquid
522	69.0	11.0	20.0	Clear liquid
523	69.0	6.0	25.0	Clear liquid
524	69.0	3.0	28.0	Clear liquid
525	67.0	31.0	2.0	Clear liquid
526	67.0	28.0	5.0	Clear liquid
527	67.0	23.0	10.0	Clear liquid
528	67.0	18.0	15.0	Clear liquid
529	67.0	13.0	20.0	Clear liquid
530	67.0	8.0	25.0	Clear liquid
531	65.0	33.0	2.0	Solid
532	65.0	30.0	5.0	Clear liquid
533	65.0	25.0	10.0	Clear liquid
534	65.0	20.0	15.0	Solid
535	65.0	15.0	20.0	Solid
536	65.0	10.0	25.0	Liquid

APPENDIX C

COOLING-CURVE RESULTS

Table XXV. Intermediate Results on Screening of Systems by Cooling-Curve Analysis.

System	Run No.	CaCl ₂ (%)	Water (%)	Appearance of Crystals (° F)	Apparent Eutectic Temp. (° F)
Calcium chloride/ magnesium chloride/water	7A&7B	26.5	70.0	-44	-62
	12A	14.5	68.5	-10	
	13	8.0	82.5	+ 4	
	16	25.0	69.0	-43	-62
	45	21.0	71.5	-56	-61
Calcium chloride/ ferric chloride/ water	39	16.5	71.0	-46	
	40	4.0	74.0	-36	
	46	26.0	67.5	-60	-64
	41	0.0	74.5	-26	None observed
	47	13.0	67.5	-70	-70
	49	12.5	67.0	-67	None observed
	50	12.0	67.0	-67	None observed
	51	9.0	67.0	-66	
Calcium chloride/ sodium chloride/water	25	20.0	73.0		-61
Calcium chloride/ zinc chloride/water	22	20.0	50.0		None observed
Magnesium lactate/water	20				30
Calcium lactate/ water	21				30
Calcium chloride/ calcium nitrate/ water	31, 32	22.5	64.5	-56	
	28	33.5	52.0	Solid at -54	
	33	26.5	65.5	-60	-74
	34	34.5	60.0	+10	
	35	29.0	64.0	-65	-67
	36	30.0	66.5	-58	-66
	37	26.5	65.5	-61	-73
	38	23.5	69.5	-36	-73
Calcium chloride/ calcium bromide/water	52	28.5	65.0	-64	-64

Table XXV (cont'd)

Calcium chloride	17				No definite temperature of solidification. Very viscous at low temperature.
Sodium lactate/ water	18	0.0	40.0		None observed
Calcium chloride/ magnesium nitrate/ water	53 54 55 56 59	22.0 26.0 28.0 26.0 24.0	67.5 67.5 67.5 67.5 67.5	-42 -50 -61 -47 -44	-66 -76 -67.5 -68
Calcium chloride/ aluminum chloride/ water	60 61 64 77	22.5 25.5 22.5 25.5	72.0 70.5 70.5 69.5	-52 -60 -68 -63	-66 -63 -68 -63
Calcium chloride/ aluminum nitrate/ water	73 74 75 76 78	28.5 29.5 27.5 29.5 29.5	66.0 66.5 65.5 66.5 67.5	-65 -62 -65 -65 -56	73 74 75 76 78
Calcium chloride/ zinc nitrate/water	79 80	26.0 29.0	66.0 67.0	-28 -48	-66
Calcium chloride/ zinc bromide/water	81 82	28.0 30.0	64.0 65.5	-57 -60	-68 -63
Calcium chloride/ lithium chloride/ water	84 91 92	25.0 6.0 9.5	67.5 68.0 68.0	-68 None observed None observed	-68 None observed None observed
Calcium chloride/ lithium bromide/ water	85 86	26.0 26.0	66.0 66.0		-74 -73
Calcium chloride/ cupric nitrate/ water	87 88	26.0 28.5	67.0 67.0	-38 -48	-65
Lithium chloride/ water		0.0	70.0	None observed	None observed

APPENDIX D

CORROSION RESULTS

Table XXVI. Corrosion Data and Calculated Penetration Rate

Specimen No.	Formulation	pH	Corroded Area, in ²	Time of Contact (days)	Loss in Weight (Mg)	Mils Per Year*	Average
a. SAE 1020 Steel, Density 128 gm/cu in.							
1	1	6.6	2.00	33	26.4	1.14)	1.37
2	1	6.6	2.00	33	36.7	1.59)	
3	1(inh)	6.7	2.00	33	23.2	1.00)	0.7
4	1(inh)	6.7	2.00	33	9.2	0.4)	
5	2	5.0	2.00	33	19.6	0.84)	0.97
6	2	5.0	2.00	33	25.2	1.09)	
7	2(inh)	5.2	2.13	33	10.2	0.41)	0.43
8	2(inh)	5.2	2.13	33	10.8	0.44)	
9	3	4.8	2.00	21	22.4	1.53)	1.73
10	3	4.8	2.00	21	28.4	1.93)	
11	3(inh)	4.8	2.00	21	14.7	1.00)	1.17
12	3(inh)	4.8	2.00	21	19.7	1.34)	
13	Control	5.6	2.00	33	67.8	2.92)	2.32
14	Control	5.6	2.00	33	39.5	1.71)	
15	4	0.5	2.20	6	651.8	141)	141.5
16	4	0.5	2.20	6	656.2	142)	
b. Electrolytic Copper, Density 140 gm/cu in.							
1	1	6.6	2.00	33	40.2	1.58)	1.53
2	1	6.6	2.00	33	37.5	1.48)	
3	1(inh)*	6.7	2.00	33	23.2	0.92)	1.07
4	1(inh)	6.7	2.00	33	30.9	1.22)	
5	2	5.0	2.00	33	29.1	1.15)	1.22
6	2	5.0	2.00	33	32.5	1.28)	

Table XXVI (cont'd)

7	2(inh)	5.2	2.00	33	14.1	0.56)	.54
8	2(inh)	5.2	2.00	33	13.1	0.52)	
9	3	4.8	2.00	21	17.8	1.11)	1.03
10	3	4.8	2.00	21	15.3	0.95)	
11	3(inh)	4.8	2.00	21	13.7	0.85)	.78
12	3(inh)	4.8	2.00	21	11.5	0.71)	
13	Control	5.6	2.00	33	24.8	0.98)	.99 c
14	Control	5.6	2.00	33	25.0	0.99)	
15	4	0.5	2.00	6	1348.2	293.00)	291.50
16	4	0.5	2.00	6	1338.4	290.00)	

c. Brass (Alloy 6, ASTM B36-49T), Density 134 gm/cu in.

1	1	6.6	2.19	33	33.0	1.24)	1.22
2	1	6.6	1.80	33	25.8	1.19)	
3	1(inh)	6.7	2.00	33	5.5	0.23)	.26
4	1(inh)	6.7	2.00	33	6.8	0.28)	
5	2	5.0	2.06	33	24.9	1.00)	.94
6	2	5.0	2.06	33	21.8	0.87)	
7	2(inh)	5.2	2.00	33	7.8	0.32)	.35
8	2(inh)	5.2	2.00	33	9.3	0.38)	
9	3	4.8	2.00	21	16.4	1.07)	1.09
10	3	4.8	2.00	21	17.0	1.11)	
11	3(inh)	4.8	2.00	21	13.6	0.88)	.84
12	3(inh)	4.8	2.00	21	12.2	0.79)	
13	4	0.5	2.10	6	962.1	208.00)	209.00
14	4	0.5	2.10	6	968.5	210.00)	

d. 61S Aluminum, Density 44.3 gm/cu. in.

1	1	6.6	1.94	33	6.3	0.81)	.78
2	1	6.6	1.94	33	5.6	0.74)	
3	1(inh)	6.7	1.88	33	0.5	0.07)	.07
4	1(inh)	6.7	1.88	33	0.5	0.07)	

Table XXVI (cont'd)

5	2	5.0	2.00	33	3.4	4.3)	
6	2	5.0	2.00	33	3.3	4.1)	4.2
7	2(inh)	5.2	1.88	33	0.3	0.04)	
8	2(inh)	5.2	1.88	33	0.0	0.00)	.02
9	3	4.8	1.94	21	7.6	1.54)	
10	3	4.8	1.94	21	6.9	1.39)	1.47
11	3(inh)	4.8	1.94	21	0.0	0.00)	
12	3(inh)	4.8	1.94	21	0.9	0.18)	.09
13	4	0.5	2.13	6	384.4	248.00)	
14	4	0.5	2.13	6	507.1	327.00)	287.50

e. Commercially Pure Zinc, Density 110 gm/cu in.

1	1	6.6	1.88	33	39.7	2.12)	
2	1	6.6	1.88	33	39.4	2.10)	2.11
3	1(inh)	6.7	1.88	33	10.9	0.58)	
4	1(inh)	6.7	1.88	33	4.4	0.24)	0.41
5	2	5.0	1.94	33	46.2	2.40)	
6	2	5.0	1.88	33	46.1	2.47)	2.44
7	2(inh)	5.2	1.88	33	4.9	0.26)	
8	2(inh)	5.2	1.94	33	5.0	0.26)	0.26
9	3	4.8	2.00	21	66.9	5.28)	
10	3	4.8	1.94	21	197.3	16.10)	10.70
11	3(inh)	4.8	2.00	21	78.9	6.22)	
12	3(inh)	4.8	1.94	21	51.1	4.16)	5.19
13	4	0.5	-	6	-	-	very
14	4	0.5	-	6	-	-	high

f. 3S Magnesium, Density 28.8 gm/cu in.

1	1	6.6	2.00	33	425.3	81.0)	
2	1	6.6	super- ficial area	33	225.7	43.2)	62.1
3	1(inh)	6.7	"	33	55.8	1.08)	
4	1(inh)	6.7	"	33	19.5	0.38)	0.73

Table XXVI (cont'd)

5	2	5.0	super-	33	59.1	1.14)	1.81
6	2	5.0	ficial	33	129.1	2.48)	
			area				
7	2(inh)	5.2	"	33	21.2	0.41)	0.44
8	2(inh)	5.2	"	33	23.8	0.46)	
9	3	4.8	"	21	-	-	very
10	3	4.8	"	21	-	-	high
11	3(inh)	4.8	"	21	76.5	23.1)	17.9
12	3(inh)	4.8	"	21	41.6	12.6)	
13	4	0.5	"	6	-	-	very
14	4	0.5	"	6	-	-	high

NOTE:

$$* \text{mils per year} = \frac{(\text{loss in weight, mg.})}{\frac{(\text{time of contact, da.})(\text{corroded area, in}^2)(\text{density, gms/in}^3)}{365}}$$

APPENDIX E

SUMMARY OF SMALL FIRE TESTS

Investigator	Crib Specifications	Crib Support
Folke et al (31)	a. 88 pounds of 6- by 1- by 1-inch sticks dis- posed at random. b. 18 pieces of 6- by 1- by 1-inch (900 gram); six layers of three sticks.	a. Wire basket. b. Stationary platform.
Metz (23)	38 pieces of 24- by 1½- by 1½-inch (18.3 ± 0.7 kg); 14 layers of 2, 3, or 4 sticks.	Stationary platform (perforated iron drum).
Tyner (24)	18 pieces of 6- by 1- by 1-inch (990 gram, 55 g ± 10% per stick); six lay- ers of three sticks.	• Stationary platform (wire screen).
Bryan and Smith (25)	180 pieces of 24- by 2- by 2-inch (100 pounds); 60 layers of three sticks.	Rotating platform (10 rpm). Steel rods through sticks.
USAERDL	27 pieces of 7-7/8- by 1- by 3/4-inch (approx- imately 2.2 pounds); seven layers of three sticks.	Rotating platform (10 rpm).
Investigator	Ignition	Draft

Folke et al	Dish of benzene.	Natural.
Metz	Wood, wool, and petrol- eum. Burning time approximately 5 minutes.	Forced (10 ft/sec).
Tyner	Tirrill gas burners. Burning time 1 minute at constant gas pressure.	Natural and forced (up to 15 mph).

Bryan and Smith	Wood, wool, and small pieces of wood. Burning time < 4 minutes.	Natural.
USAERDL	Gas burners. Burning time 85 seconds at 4 inch H_2O gas pressure.	Forced (approximately 400 ft/min).

Investigator	Time of Solution Application	Application of Solution
Folke et al	After 50 to 75% of wood burned.	High and low pressure jets operated manually.
Metz	After 6 minutes of burning.	1 mm. glass nozzle at initial rate of 500 cc/min. Continuous spray operated manually at hand pump pressure.
Tyner	After 50% of wood burned.	Calibrated glass nozzles (usual rate - 26 cc/min). Continuous spray operated manually at 2 psig.
Bryan and Smith	After 4 and 6 minutes of burning.	Calibrated glass nozzle which moved up and down (rate from 0.05 to 0.5 gal./min.). Intermittent and continuous spray at 25 psig.
USAERDL	After 40% of wood burned.	Calibrated industrial-type nozzle (rates from 1.1 to 4.0 gal/hr). Continuous spray at 40 psig.

Investigator	Observation	Measurements
Folke et al	Ember extinction (visual).	Crib weight by balance; time and quantity of solution.
Metz	Ember extinction (visual).	Time and quantity of solution.

Tyner	Flame and ember extinction (visual).	Crib weight by balance; time and quantity of solution.
Bryan and Smith	Ember extinction (generally determined from the recording system chart).	Hydraulic system connected to a recording system (read time and crib weight off of chart); quantity of solution.
USAERDL	Ember extinction (visual).	Crib weight by balance; time and quantity of solution.

Investigator	Superiority Factor
Folke et al	None.
Metz	None (can determine ratio of volumes of water and solution required at given application rates from results given).
Tyner	Ratio of volumes of water and solution required at given application rate.
Bryan and Smith	a. Ratio of volumes of water and solution required at given application rate. b. Ratio of volumes required in a given time for extinction.
USAERDL	Ratio of volumes required in a given time.

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