

SHRP-W/UIR-92-603

Ice-Pavement Bond Prevention: Surface Modification

Bernard Baum

Roy White

Lynne Thoma

Springborn Laboratories, Inc.
Enfield, Connecticut



**Strategic Highway Research Program
National Research Council
Washington, DC 1992**

SHRP-W/UIR-92-603
Contract H-202
Program Manager: Don M. Harriott
Project Manager: L. David Minsk
Program Area Secretary: Lisa A. McNeil

February 1992

key words:
asphalt concrete
hydrophobic oils
ice
ice control
ice-pavement bond
ice removal
oils
organic compounds
surface friction
water-soluble oils
water-soluble salts

Strategic Highway Research Program
2101 Constitution Avenue, N.W.
Washington, DC 20418

(202) 334-3774

The publication of this article does not necessarily indicate approval or endorsement of the findings, opinions, conclusions, or recommendations either inferred or specifically expressed herein by the National Academy of Sciences, the United States Government, or the American Association of State Highway and Transportation Officials or its member states.

Acknowledgments

The research described herein was supported by the Strategic Highway Research Program (SHRP). SHRP is a unit of the National Research Council that was authorized by section 128 of the Surface Transportation and Uniform Relocation Assistance Act of 1987.

Table of Contents

SUMMARY.....	1
A. INTRODUCTION.....	1
1. The Problem.....	1
a. General.....	1
b. Specific.....	1
2. Objectives.....	1
3. Background.....	2
B. RESEARCH APPROACH.....	3
C. TECHNICAL DISCUSSION.....	5
1. Task 1: Literature and Information Search.....	5
2. Test Methods for Asphalt Concrete.....	16
a. Slush Test - Characteristics of Frozen Salt Solutions.....	16
b. Freezing Point Determination.....	17
c. Moisture Pick Up.....	17
d. Effect of Organic Liquids on Asphalt Concrete.....	21
e. Ice Adhesion Test.....	21
f. Friction Testing.....	24
g. Asphalt Concrete Mix Design and Briquette Preparation.....	27
h. Marshall Stability.....	36
i. Durability: Ice Adhesion After Continued Washing.....	36
j. Flake Formulation For Asphalt Additives.....	38
3. Additive Selection Criteria.....	38
4. Tasks 2 and 3: Chemical And Physical Modification.....	43
a. Slush Test and Freezing Point.....	43
b. Percent Moisture Pick Up.....	52
c. Effect of Organic Additives on Asphalt Concrete.....	58
d. Ice Adhesion.....	58
e. Friction.....	69
f. New Aggregate Design and Marshall Stability.....	69
g. Effect of Continued Washing of the AC Briquette on Ice Adhesion.....	74

h.	Additive Toxicology, Environmental	79
	Impact and Corrosivity.....	79
i.	Water Insoluble Additives.....	
j.	Replication Study of Best Ice Adhesion	82
	Lowering Additives in Asphalt Concrete.....	
k.	Preliminary Portland Cement	86
	Concrete Studies.....	
D.	STATISTICAL ANALYSIS.....	92
1.	Normal Probability Plots.....	92
2.	Analysis of Variance.....	99
E.	CONCLUSIONS.....	110
F.	RECOMMENDATIONS.....	114
	APPENDICES.....	115

List of Figures

1.	Apparatus For Freezing Point Depression Curves and Temperature Determinations.....	18
2.	Freezing Point Depression Curve for 20% CaCl_2 Solution in Deionized Water.....	19
3.	Freezing Point Depression Curve For 20% CaMg Acetate (Ice B Gon, Chevron) Solution in Deionized Water.....	20
4.	Ice Adhesion Test Apparatus.....	23
5.	Bicycle Wheel Friction Test Apparatus.....	25
6.	Tire Tread Marks.....	26
7.	Aggregate Gradation Chart.....	34
8.	Asphalt Solubility In Various Solvents.....	42
9.	Calcium Chloride Prills.....	55
10.	Ice B Gon Prills (Chevron).....	55
11.	Verglimit.....	55
12.	Sodium Formate (as rec'd).....	55
13.	Sodium Acetate.....	56
14.	Sodium Formate/Sodium Lignin Sulfonate.....	56
15.	Carbowax 300.....	56
16.	Sodium Chloride.....	56
17.	Poly G71-530 (Olin Chem.).....	57
18.	Formulation 25999-2.....	57
19.	Formulation 26000-1.....	57
20.	Normal Plot Of Shear Forces.....	93
21.	Normal Plot of Log (Shear + .01) Forces.....	95
22.	Normal Plot of Slush Ratings Scaled For Concentration.....	97
23.	British Pendulum Friction Scores, Wet Versus Dry Scores.....	100

List of Tables

1.	Rating Scale For Physical Characteristics Of Frozen Salt Solutions at -20°C	17
2.	Temperature Of Asphalt Concrete/Ice Interface Versus Time During Adhesion Testing.....	22
3.	Friction By The Bicycle Wheel Test.....	28
4.	Friction By The British Pendulum Test.....	29
5.	Comparison Of British Pendulum and Bicycle Wheel Friction Test.....	30
6.	Bicycle Wheel Friction Of Asphalt Concrete Briquette Surface Impregnated With Oil.....	31
7.	Friction On Asphalt Concrete Surface Impregnated With Various Oils: Comparing The Bicycle Wheel Test With The British Pendulum Test.....	32
8.	Aggregate Gradation Chart For Method A.....	35
9.	Formulation Based On Upper Curve Of The Aggregate Gradation Chart For Method B.....	37
10.	Flake Formulations.....	39
11.	Effective Additives and Their Solubility Parameters.....	41
12.	Effect Of Additives In Preventing Water From Freezing.....	44
13.	Effect Of Additives In Preventing Water From Freezing.....	47
14.	Promising Compounds.....	51
15.	Percent Weight Gain Of Selected Samples At 75 Percent Relative Humidity for 14 Days.....	53
16.	Percent Moisture Pick-Up Of Additive Versus Time At 75 Percent Relative Humidity.....	54
17.	Effect Of Plasticizers On Asphalt Concrete.....	59
18.	Effect Of Organic Liquids On Asphalt Concrete.....	60
19.	Ice Adhesion and Slush Rating Of Water Soluble Additives At -20°C : Oil and Salt Surface Coated Asphalt Concrete.....	61
20.	Ice Adhesion Of Inorganic Additives Surface Coated Onto Asphalt Concrete.....	62
21.	Ice Adhesion At -20°C Of Asphalt Concrete Surface Coated With Oils.....	63
22.	Effect Of Physical Form Of Additive and Test Temperature On Ice Adhesion Of Asphalt Concrete Briquettes Modified With Salts and Oils - Method A.....	65

23.	Ice Adhesion Of Briquettes Modified With Sodium Acetate and Sodium Formate - Method A.....	66
24.	Ice Adhesion Of Briquettes Modified With Fatty Amides - Method A.....	67
25.	Ice Adhesion Of Asphalt Concrete Briquettes Modified With Additional Oils - Method A.....	68
26.	Summary Of Best Systems: Ice Adhesion At -5°C Of Asphalt Concrete Briquettes Containing Additives - Method A.....	70
27.	British Pendulum Friction On Asphalt Concrete Coated With Various Oils.....	71
28.	Friction By The British Pendulum Number (BPN) Of Asphalt Concrete Briquettes Containing Additives - Method A.....	72
29.	Marshall Stability Of Oil Modified Briquettes - Method A.....	73
30.	Marshall Test Of Oil and Salt Modified Briquettes - Method A.....	75
31.	Marshall Tests Of Briquettes Using The Upper Curve Of The Aggregate Gradation Chart - Method B.....	76
32.	Marshall Stability Of Promising Additives.....	77
33.	Effect Of Washing The Asphalt Concrete Briquette Containing Additives On Ice Adhesion At -5°C - Method A.....	78
34.	Safety Of Selected Candidate Materials.....	80
35.	Replication Study Of Best Additives For Reducing Ice Adhesion To Asphalt Concrete.....	83
36.	Ice Adhesion: Replication Study On The Best Additives For Asphalt Concrete.....	84
37.	Friction By British Pendulum: Replication Study On The Best Additives For Asphalt Concrete.....	87
38.	Possible Deicing Additives In Portland Cement Concrete.....	89
39.	Condition Of PCC After Two Weeks Cure.....	90
40.	Ice Adhesion Of PCC Containing Possible Deicing Additives.....	91
41.	Ordered List Of Ice Adhesion Shear Forces.....	94
42.	Ordered List Of Ice Adhesion Shear Forces.....	96
43.	Physical Property Of Ice Crystals (Slush) Rating.....	98
44.	British Pendulum Friction Scores Wet Versus Dry Scores.....	101
45.	Analysis Of Ice Adhesion For Various Additives.....	102
46.	Analysis Of Ice Adhesion For Various Additives.....	103
47.	Analysis Of Ice Adhesion For Various Additives.....	104
48.	Analysis Of Friction - British Pendulum Test Five Replications.....	106
49.	Analysis Of Friction - British Pendulum Test Five Replications.....	107
50.	Analysis Of Friction - British Pendulum Test Five Replications - Dry.....	108

51.	Analysis Of Friction - British Pendulum Test	
	Five Replications - Wet.....	109
52.	Summary Of Best Additive Systems.....	113

Abstract

Studies were completed on the investigation of water-soluble inorganic and organic compounds, and of oils, to identify chemicals which could be placed in the wear course of asphalt concrete. The objective was to reduce the freezing point of surface accumulations of ice to weaken the ice-pavement bond or to prevent its formation. Tests were conducted to determine the persistence of additives and the effect on surface friction. Several promising candidate compounds were identified.

Executive Summary

There were two hypotheses originally postulated for choosing additives to be blended internally into asphalt concrete for the purpose of minimizing ice adhesion to the surface:

1. Water soluble salts and organic liquids* to lower freezing point,
2. Hydrophobic organic liquids* to weaken the bond to ice.

* The term "oil" will be used synonymously for "organic liquid".

All additives selected had to be low cost or at least potentially cost effective, non-halogenated, non-corrosive, non-toxic, environmentally safe and not volatile at the 300°F asphalt mix temperature.

Organic (water soluble and insoluble) liquids were first chosen based on polarity difference from the asphalt and later, more quantitatively, by calculated solubility parameter estimated from our knowledge of their structure. It was postulated that if the solubility parameter of the oil were too close to that of the asphalt, it would dissolve in and attack the asphalt. If it were too far removed from that of the asphalt, it would be so incompatible that it would separate and quickly diffuse out of the asphalt.

The solubility parameter criteria was later refined to mean a calculated solubility parameter greater than approximately 11.

It was proposed that the water soluble additives blended into the asphalt would become available at the surface by rain extraction and road wear.

It was proposed that the hydrophobic oils would become available at the pavement surface by exudation (diffusion) because of the difference in compatibility with the asphalt and through road wear. It was postulated that the oil must not become excessively viscous at low temperature or it would not "release" from the ice.

In first year of the program, the concept of blending water soluble additives (salts and oils) into asphalt concrete to effect reduction in ice adhesion has proven successful. Success is judged by reduction in ice adhesion to less than 10 psi, with no more than 10% loss in friction, and a Marshall Stability greater than 1200. Hydrophobic additives were not effective.

The following summarizes the pertinent data on the best additive systems to date. The psi ice adhesion should be as low as possible, the British Pendulum friction close to that of the unmodified control, the Marshall stability greater than 1200, and a Slush test rating close to 10. Sodium acetate, sodium formate, Ice-B-Gon (calcium magnesium acetate), and triethylene glycol give the lowest ice adhesion. However, all the other additives also show significant reductions. The final choices would depend on other future results, e.g., resistance to repeated washing, friction versus time, etc.

SUMMARY OF BEST ADDITIVE SYSTEMS

Additive (1)	Ice Adhesion (psi)	British Pendulum Friction (2) Dry/Wet	Marshall (2) Stability/ Flow	Price \$/lb.	Slush (3) Test Rating	Corrosivity (4)
Control	>64	49/35	3433/12	-	-	-
Verglimit	0.1	32/33	-	0.82	-	Y
Sodium Formate	0.1	46/34	3195/13.5	0.20	9	N
Sodium Acetate	0.2	38/32	1251/13.2	0.58	8	N
Sodium Chloride	0.1	45/34	-	0.03	10	Y
Ice-B-Gon (CMA) (5)	1.3	45/34	-	0.34	9	N
Propylene Glycol	12	47/32	1806/15.4	0.56	9	N
Dipropylene Glycol	6	46/32	-	0.57	8	N
Tetraethylene Glycol	4	34/35	945/14.8	0.88	8	N
Triethylene Glycol	0.8	36/35	1344/13.5	0.54	8	N
Carbowax 300	8	33/32	-	0.73	7	N
Poly G 71-530	12	45/33	1071/13.3	0.85	-	N
Connecticut Class I Specification	-	-	>1200/8-15	-	-	N

- (1) See Appendix B
- (2) Average of five tests
- (3) Water alone gives a rating of "0".
- (4) Y = yes; N = no.
- (5) Calcium-Magnesium Acetate, 91%, Chevron

There are several criteria for additive selection:

- o Water solubility.
- o Calculated solubility parameter greater than 11.
- o Lowering freezing point.
- o Non-toxic and non-corrosive.
- o Price.
- o Not volatile at 300°F asphalt mixing temperature.
- o Asphalt or Portland cement concrete.

Tentatively, pending testing on sections of roadway, we would recommend 5 - 6.5% sodium chloride for highway sections and 5 - 6.5% of Ice-B-Gon or sodium formate (powdered) for AC over the bridges. Three percent dipropylene glycol or Poly G 71-530 is also recommended for bridge AC sections.

A. INTRODUCTION

1. The Problem

a. General

Highway and bridges undergo accelerated deterioration when deicing salts penetrate the pavement, especially when they cause corrosion of embedded reinforcing steel. Accumulated corrosion products around the reinforcing steel cause cracks to develop allowing intrusion of more deleterious material thereby accelerating corrosion, causing spalling, and diminishing structural integrity. Salts also rust motor vehicles and may create an environmental hazard in nearby soils and water.

In addition, "snow and ice removal is expensive; equipment and labor costs of winter maintenance programs exceed one billion dollars".

b. Specific

Both physical and chemical modifications of the pavement surface are candidates for preventing the formation of ice or for reducing the strength of adhesion to a level that permits fast, complete, and low-force removal of ice or compacted snow. It is well-established that a low-energy surface will reduce the formation of strong bonds with ice or compacted snow. A freezing point depressant distributed in encapsulated form within the wearing course of asphalt concrete is one approach that is commercially available. A physical approach, also commercially available, uses rubber particles distributed in the asphalt concrete wear course to create a deformable surface which assists in dislodging ice when subjected to traffic loads. Hydrophobic coatings have been applied to pavements to create a low-energy surface. All these approaches have limitations that reduce their effectiveness to a narrow range of conditions. In some cases, pavement durability is adversely affected. Research is needed to extend the range of conditions over which pavement surface modifications are effective, and to improve their bond-inhibiting characteristics.

2. Objectives

The objectives of this program are to provide more cost-effective ways to prevent or minimize the buildup of snow and ice on highways and bridges during winter conditions, reduce the deterioration of bridges, pavement and vehicles, and mitigate adverse environmental consequences of the use of snow and ice control chemicals.

Specifically, the goals are to develop chemical or physical pavement modifications or chemical treatments which will reduce the bond strength of ice or compacted snow to the pavement. The pavement modification or treatment should be economical to manufacture, install, and maintain, not seriously affect the structural integrity, have a long service life, be non-toxic and non-corrosive, be effective over a wide range of climatic and traffic conditions, and not have an adverse effect on the coefficient of friction between rubber tires and pavement.

Another primary goal is to use a non-chlorine, preferably non-sulfate containing additive that will not cause metal corrosion. The use of salts, most commonly sodium chloride, to melt ice on highways is based on salt's ability to lower the freezing point of water. The main problems are impermanence (the salts wash away), uneven salt dispersion, corrosion (the salts are mainly chloride which catalyze corrosion of metal) and environmental pollution.

3. Background

To cause ice/snow to debond from pavement, requires one or more of the following:

- o Freezing point depressants
- o Deformability, i.e. lowering pavement modulus
- o Low energy surface

Throughout the world, the most common approach is the use of freezing point depressants, i.e. various salts, such as sodium and calcium chlorides. However, this is costly, corrosive to cars and the environment, and destructive to pavements.

Deformability, i.e. the use of rubber particles dispersed in the asphalt concrete wear surface, has been examined and may be useful as a subsidiary technique. The rubber lowers the modulus or stiffness of the surface and promotes cracking of the ice when subjected to traffic.

Creation of a low energy surface is an approach widely investigated for deicing of ships, dams and locks, train switches, leading edges of airplane wings, telephone lines and bare conductor wire.

Springborn Materials Science Division of Springborn Laboratories, Inc. has been investigating deicing of bare, overhead conductor wire for the Electric Power Research Institute (Palo Alto, CA) for several years. The primary approach is a coating of polyethylene containing exudable solid additives in combination with silicone or fluorocarbon oils to cover the conductor wire.

The reduction of the ice adhesion requires a decrease in substrate wettability, i.e. making it more hydrophobic.

It is well known that ice has an enormously high ability to bond to almost any surface, differing only in its bond strength. This may be due to mechanical penetration and interlocking ice at a rough surface; however, it is also

strongly dependent on molecular interactions resulting from surface free energy. In order to lower ice adhesion as much as possible, surface energy components must be made as small as possible. The lower the values of these components, the lower will be the overall forces that hold the ice to the surface, and the more easily it can be removed.

Liquids and solid surfaces vary widely in energies due to structural differences, resulting in the degree of intermolecular attraction. For certain hard inorganic surfaces, such as oxides, sulfides, etc., the surface energy may be as high as 500 dyne cm^{-1} . Water, due to its strong hydrogen bonding, is found to be 73 dyne cm^{-1} . Most organic surfaces, such as polymers, have surface energies in the order of $20\text{-}30 \text{ dyne cm}^{-1}$. Most liquids will wet surfaces of high energy because their internal forces are not as strong as those to the substrate. Surfaces that have the least affinity for other substances are typically very low in surface energy. Some of the lowest energy surfaces are found for the fluorine-containing polymers.

Observations, such as these, have been reported in the literature, and have given rise to the "constitutive law of wettability". This law states that, in general, the wettability of organic surfaces is determined by the nature and packing of the surface atoms and groups and is otherwise independent of the nature and arrangements of underlying molecules.

Another significant property is thought to be the glass transition temperature. This temperature (T_g) is the point at which long chain molecular motion ceases and the liquid-like movement of long segments of molecules, characteristic of the rubbery state, diminishes rapidly. Only small groups of atoms move against local restraints, and the polymer becomes stiff, hard and brittle. The extremely low T_g of silicone rubbers reflects their mobility at the atomic level, and indicates their ability to retain their flexibility at low winter temperatures.

Poly (dimethyl siloxane) silicone rubber is found to have a critical surface tension of 24 dyne cm^{-1} and yet is much more icephobic than a surface, such as Teflon FEP, with a surface tension of approximately 17 dyne cm^{-1} . This fact suggests that factors other than just surface energy are important in effective ice shedding. This difference in performance is thought to be due to the low modulus and high elongation of silicone elastomers, typically 120 psi modulus, 150% elongation. Flexible coatings have been noted to exhibit lower ice adhesion, and a degree of general flexibility can generate local stress and encourage crack initiation according to the Griffith-Irwin crack theory. On the basis of empirical observation, this flexibility appears to be a desirable property for adequate icephobic performance. One disadvantage to this fact is that low modulus materials are frequently soft, and poor abrasion resistance may preclude their use in situations where there may be high impact, rain erosion and mechanical wear.

B. RESEARCH APPROACH

Buildup of ice and hard-packed snow on asphalt and Portland cement highway surfaces is a recurring problem, and current ways of coping with it are far from satisfactory. It would be desirable to develop new and improved ways of

modifying the highway surface, to prevent or at least delay the buildup of ice, and to weaken the pavement-ice bond so that the ice which forms is easier to remove. New modifications should be permanent or at least longer-lasting than the present techniques.

In laying new pavement, these treatments could be included in the Portland cement concrete or in the surface layer of asphalt concrete; they could similarly be included in resurfacing material. For existing Portland cement pavement not to be resurfaced, impregnation treatments would be required; and this technique might also be desirable for existing asphalt pavement as well. For widespread common use, any such treatment would have to be economical to apply and maintain.

Another major requirement is that the treated pavement should have as good tire-pavement friction, particularly wet skid resistance, as present highway surfaces.

Other important requirements are that the treatment be safe to apply, and non-toxic, non-corrosive, and harmless to the environment when in use. It should be useful over a wide range of climate and traffic conditions.

Finally, such treatments should not decrease pavement durability and lifetime, and the paving material should be as recyclable as it is at present.

The overall general approach in this first year's program has been to incorporate two types of additives into asphalt concrete (AC):

- o Salts
- o Organic liquids (for convenience, henceforth called oils)

As a control, some work was carried out with Verglimit. This is calcium chloride coated with polymerized linseed oil to prevent moisture problems in the bag, and made alkaline with sodium hydroxide. This is compounded into the asphalt concrete and used, because of cost, only on bridge decks or on accident prone stretches of road. It is discussed further in the literature section.

Thus, Verglimit experience and Springborn's development of deicing oil-filled, polyethylene coatings for aluminum overhead conductors provide precedents for this program.

Investigative work was carried out at Springborn Materials Science Division of Springborn Laboratories, Inc., with some of the testing performed by our subcontractor, The University of Connecticut (UConn) Civil Engineering Laboratory. Our primary Civil Engineering consultant is Dr. Jack Stephens, Professor Emeritus, of UConn. Jack Postemski, formerly of the Connecticut Department of Transportation, has also been available as a consultant. Dr. Rudolph D. Deanin, Professor of Polymer Chemistry and Technology, at the University of Lowell, has been our chemical and polymer consultant. Recently, Dr. Uwe Koehn, Professor of Statistics at UConn, was taken on as a statistical consultant.

The first year program was divided primarily into three tasks:

- o Task 1: Literature and Information Search
- o Task 2: Develop Chemical Surface Modifications
- o Task 3: Develop Physical Surface Modifications

In the overall four year program, three additional tasks were scheduled:

- o Task 4: Formulation Modification
- o Task 5: Conduct Field Tests
- o Task 6: Prepare Reports and Manuals of Practice

C. TECHNICAL DISCUSSION

1. Task 1: Literature and Information Search

An extensive on-line literature search was carried out using Dialog Information Systems, Inc. The initial search strategy was to identify articles pertinent to published work relating to deicing of pavement and/or roadway. Further search work related to specific aspects of the program included information on freezing point depressant salts, modification of asphalt with rubber, and the work done with Verglimit. The database files search included:

File 5: Biosis Previews (69-89)
 File 6: National Technical Information Service (NTIS, 64-89)
 File 40: Enviroline (71-89)
 File 41: Pollution Abstracts (70-89)
 File 399: Chemical Abstracts (CA, 67-89)
 File 63: TRIS (70-89)
 File 357: Biotechnology Abstracts (82-89)
 File 293: Engineered Materials Abstract (86-89)
 File 265: Federal Research in Progress, Coverage - Current
 File 433: SCISEARCH (80-86)

The following outlines the search approach:

DIALOG FILES: NTIS (64-89)/CA (67-89)/TRIS (70-89)

Concrete/Asphalt/Icing/Deicing/Rubber Modified Pavements Search Headings

Narrow With Key Words

Additive/Chemical/Ingredient/Formulation/Preparation

Obtain Abstracts and Then Most Pertinent Articles

A brief summary of the individual searches conducted follows.

BRIEF OUTLINE OF SEARCH STRATEGIES

Search 1

DIALOG FILES: NTIS, CA, TRIS

1. Concrete or Asphalt or PCC or AC and Ice or Deice
2. Ingredient or Formulation and 1.
3. Additive or Chemical and 1.

DIALOG FILE: Current Federal Research In Progress

1. Concrete or Asphalt or PCC or AC and Ice or Deice

Search 2

DIALOG FILES: TRIS, NTIS, Engineered Materials Abs., SCISEARCH

1. Rubber or Buffings and Cement or Concrete or Bitumins? or Asphalt
2. Rubber and Buffings
3. Rubber and Concrete

Search 3

DIALOG FILES: TRIS, NTIS, SCISEARCH

1. Buffings and Concrete or Cement or Bitumin?
2. Rubberized and Concrete and Pavement
3. Rubberized and Cement and Pavement
4. Rubberized and Asphalt
5. Rubberized and Bitumin? and Pavement

Search 4

DIALOG FILES: NTIS, TRIS, Engineered Materials Abs.

1. Portland Cement or PCC or Cast Concrete and Plusride or Rubit or Rubber
2. Asphalt or Concrete or Pavement or AC or PC
3. Washington and 1. and 2.
4. Esch and 2.

Search 5

DIALOG FILES: TRIS, NTIS

1. Flexible Pavement and Salt

BRIEF OUTLINE OF SEARCH STRATEGIES
-continued-

Search 6

DIALOG FILES: TRIS, NTIS, Engineered Materials Abs., SCISEARCH

1. Salt and Eutectic
2. Alaska and Esch and Asphalt or Concrete or Pavement or PCC

Search 7

DIALOG FILES: Biosis Previews, Enviroline, Pollution Abs., Biotechnology Abs., CA

1. Sodium Formate or Acetate or Calcium or Magnesium Acetate or Formic or Acetic Acid

After reviewing the short titles of promising hits, longer abstracts of the more useful articles were printed. In addition, pertinent articles were selected and procured for review.

Literature was also procured from the Connecticut Department of Transportation Library on topics of interest to the program.

The literature has been helpful in several areas:

1. Understanding the phenomenon of ice formation
2. What has been done in the past and the problems encountered
3. Material selection
4. Test methods
5. Specific accomplishments and problems of Verglimit.

In addition, telephone inquiries were made to various commercial suppliers with regard to pavement additives, i.e. freezing point depressants (salts), encapsulants, rubber particles, surface treatments, and dispersing agents. Literature, samples and general information were requested.

A more recent (March 1990) literature search was carried out using as additional keywords - hydrophobic, hydrophilic and Portland Cement Concrete. A literature search previously carried out for the Electric Power Research Institute was also available. This was primarily oriented toward hydrophobic coatings and additives.

The literature shown in the Appendix is summarized below.

REVIEW OF THE LITERATURE

A number of selected articles are briefly discussed. They are divided into the following categories:

- I. Calcium Magnesium Acetate (CMA)
- II. Deicing Chemicals
- III. Deicing Coatings
- IV. Environmental Effects
- V. Portland Cement Concrete (PCC)
- VI. Rubber in Asphalt Concrete
- VII. Solubility Parameters
- VIII. State of Connecticut
- IX. Testing
- X. Theory
- XI. Thermal Heat Gain
- XII. Verglimit

The complete abstract is shown in Appendix A - Literature Search, arranged alphabetically in each section by author or subject. Not all of the abstracts are discussed here.

I. Calcium Magnesium Acetate (CMA)

Calcium magnesium acetate (CMA) deices roadways as effectively as salt (Dunn & Schenk^{1.4}), but at a slower rate (Chollar^{1.2}). It has been called the most promising non-salt chemical deicing agent, which is both effective and environmentally acceptable (Better Roads^{1.6}). It has been shown to be non-corrosive (Chollar and Virmani^{1.3}) to steel, and non-toxic. With compositions containing Mg levels equal to or greater than Ca, the damage to Portland cement concrete was significantly reduced (Schenk^{1.7}).

CMA has been produced from natural raw materials, which may offer the possibility of reduced cost. In Maine (Hsu^{1.5}), e.g., CMA was made from a source of high magnesium limestone and acetic acid (cider vinegar). However, in the production of any chemical from "natural" raw materials, there is often a problem of consistency of raw material sources.

A Canadian study (Bacchus^{I.1}) indicates that the additional cost of using CMA rather than salt is significantly greater than the estimated reduction in the overall environmental damage. The most substantial benefit was reduced vehicle corrosion costs. The calculated break-even cost for CMA, i.e. the price at which CMA would have to be purchased in order to balance the environmental benefits, was in the range of \$343 to \$481/ton (1985 dollars).

II. Deicing Chemicals

Kasinskas^{II.2} discussed a method of destroying snow pack and ice accumulation on roadway surfaces by using a high-speed (up to 300 psi) sodium chloride jet stream to penetrate the pavement cover and initiate an immediate melt.

Harris, et al.^{II.1}, developed two effective deicing mixtures: 75% tripotassium phosphate/25% formamide and calcium chloride/1% Emulsifier STH. This latter composition had significantly reduced corrosion.

Itagaki^{II.3} indicated that polyethylene glycol is an effective, low toxicity, high flash point deicing agent.

Palmer^{II.4} reports that CMA (calcium magnesium acetate) is effective but it is more costly than sodium or calcium formate. The freezing point curve of sodium formate is similar to that of sodium chloride, down to about -14°C . It has also been demonstrated experimentally that sodium formate does not spall cured Portland cement concrete, while spalling has been reported with uncured concrete (Stratfull, ^{II.7}).

Sandvig^{II.6} reports that alkaline earth metal (e.g., calcium) salts of carboxylic acid derivatives of polysaccharides are effective deicers.

Stratfull, et al.^{II.7}, evaluated a number of materials as potential non-corrosive deicers for PCC. Tetrapotassium pyrophosphate and sodium formate were effective.

Williams and Dotson^{II.8} melt compounded additives into several polymers and measured ice adhesion. Ethylene glycol, sodium chloride and a commercial detergent were effective in decreasing ice adhesion in cellulose acetate butyrate. Ethylene glycol was also effective as a deicer in polyvinyl butyral.

In a search (Dunn and Schenk^{I.4}) for non-corrosive deicers, two chemicals were found to be as effective as sodium chloride. One, methanol, reacts almost instantly with snow and ice but is less persistent than NaCl. The other candidate, (CMA), is as effective and as persistent as NaCl.

III. Deicing Coatings

Baum, Kendrew and Thoma^{III.1} have developed low ice adhesion polyethylene coatings for aluminum overhead conductors. These were prepared by compounding silicone or fluorocarbon oils along with other exuding additives into low density polyethylene which is then melt extruded over the conductor wire.

Calabrese, et al.^{III.2}, showed that non-solvent, unfilled polyurethane and modified polyphenylene oxide coated on ice breakers withstood ice impact, resisted abrasion, and reduced coefficient of friction against ice.

Hanamoto^{III.3} of CRREL, in a joint development with Dr. Jellinek of Clarkson College, developed a block copolymer, a poly (dimethyl-siloxane)-bisphenol -A- polycarbonate, which greatly reduces the adhesion of ice. The copolymer, applied as a coating, does not prevent the formation of ice but rather makes ice easier to remove. However, it does not resist abrasion.

A number of hydrophobic coatings were examined by Landy^{III.5} to provide low ice adhesion to the Navy's grey deck paint 20 Type A and the alkyd-type zinc chromate primer Formula 84/47. The lowest ice adhesion was achieved with crosslinked poly (dimethyl siloxane) resins. However, these coatings had a short service life (2-3 weeks) and were too slippery.

Twenty-three hydrophobic coatings were examined by Millar^{III.6} as anti-icing coatings on airplane wings. None were found effective for this purpose, but silicone resins were useful in promoting easier ice removal.

A number of coatings were evaluated by the Electric Power Research Institute^{III.4} for ice release. None were found that would prevent ice build up. However, a teflon filled hydrophobic polyurethane coating considerably reduces the force needed to open outdoor disconnect switches under icing conditions.

Screening tests to select icephobic coatings displaying low ice release forces, both before and after exposure to rain erosion in a whirling arm simulator, were performed by Minsk on approximately 60 commercial materials (Minsk, L.D., "Ice Adhesion Tests on Coatings Subjected To Rain Erosion", Special Report 80-28, CRREL, July 1980, 13 p.). A unique linear ball-slide shear test apparatus was designed to provide pure shear forces. No coating survived the erosion test to give an interfacial shear strength as low as 15 psi (103 kPa), an arbitrarily established goal. Several coatings showed shear strengths between 30 and 45 psi (207 and 310 kPa) after rain erosion.

An extensive literature search was conducted by Porte and Nappier^{III.7}. The authors' conclusion was that it is almost impossible to develop a coating to which ice will not bond. However, silicones and fluorocarbons do facilitate ice removal.

Sayward^{III.8}, John M., "Seeking Low Ice Adhesion", CRREL Special Report 79-11, April 1979. The author first broadly explores surface physics and the mechanism of ice formation and release. He then discusses a survey of over 300 manufacturers of coatings, release agents, etc., that may be useful for reducing ice adhesion. Emphasis is on hydrophobics, such as silicones and fluorocarbons, flexible (elastomer) surfaces, inhibition of ice nucleation and air entrapment. He also delineates the conditions for attaining low ice adhesion.

IV. Environmental Effects

Studies by Button and Peaslee^{IV.2} have shown that rock salt harms Sugar Maple trees. A method is offered whereby the ratio of harmful to nutritious ions,

the Metabolic Index, may be applied to monitor the health of salt sensitive trees before injury is visible.

Dupuis, et al.^{IV.5}, review literature which present the environmental effects of water runoff from highways.

Bories and Bortz^{IV.1} found that a polyphosphate-based material or a long-chain amine reduced the corrosion rate of steel exposed to salt solution. They also showed that various materials added to chloride deicer solutions reduced the rate of freeze-thaw deterioration. Typical additives were sequestering agents, such as the sodium salt of ethylenediaminetetraacetic acid and polyhydroxy sugar-type compounds, such as dextrose. However, the cost of deicing is significantly increased.

Using freeze-thaw cycling, Minsk^{IV.6} examined the effect of a variety of non-chloride deicing chemicals on both asphalt concrete and Portland cement concrete (PCC). The effect on asphalt concrete was negligible. However, the chemicals caused scaling of the PCC.

Craik and Yuill^{IV.4} agree that deicing chemicals damage concrete but not asphalt pavements, causing surface scaling. Protective methods are an entrainment in poured concrete and surface coating.

V. Portland Cement Concrete

Ashworth and Weyland^{V.1} carried out adhesion tests on Portland cement concrete and asphalt concrete over a temperature range from -0.5°C to -20°C , using as surface treatments, sodium and calcium chlorides, a silicone, a fluorocarbon and a mineral oil (#2 diesel fuel). The salts reduced adhesion above -8°C ; the other materials were more effective, especially at lower temperatures.

A study was carried out to find effective deicing agents for PCC which would not corrode steel and not affect the freeze-thaw stability of PCC. The increase in corrosion caused by chlorides may be eliminated by the addition of a polyphosphate-based material or a long-chain amine to the chloride solution. Typical additives which reduced freeze-thaw deterioration were sequestering agents, such as the sodium salt of ethylenediaminetetracetic acid and polyhydroxy sugar-type materials, such as dextrose. Longer curing of the PCC reduced freeze-thaw deterioration and reduced the amount of additive needed in the chloride solution. The cost of deicing is materially increased.

Dahl, et al.^{V.3}, indicate that polymer impregnated concrete has improved resistance to salt penetration.

Mehta, et al.^{V.6}, have also shown that corrosion of reinforcing steel can be decreased by impregnating the PCC with a liquid monomer followed by polymerization to seal the capillaries against salt intrusion. Also effective are sulfur, tar and mixtures of the two.

Seventeen candidates were investigated (Stratfull, et al.^{V.7}) in a search for a non-corrosive deicing chemical for PCC bridge decks. Tetrapotassium pyrophosphate exhibited good frost preventive properties over a two year study. Sodium formate was also effective, but it attacked the concrete. The same is true of sodium chloride, but at a lesser rate of deterioration.

However, Palmer^{II.4} discusses that experiments indicate sodium formate does not spall cured (as opposed to uncured) concrete.

VI. Rubber In Asphalt Concrete

In the late 1960s, Sweden experimented with rubber particles in asphaltic pavements. A system incorporating 3 to 4% by weight of relatively large (1/16" to 1/4") rubber particles into an asphalt pavement was developed to increase skid resistance and durability, and was found to provide a new form of wintertime ice control, as well as a reduced noise level. The ice control mechanism is the flexing of the protruding rubber particles under traffic action, which causes surface ice deposits to break down.

"PlusRide" asphalt is now used to designate this material in the U.S.A.

Field trials in Alaska in 1979-1980 (Esch^{VI.4}) were encouraging. However, the early pavements were not very durable due to their high voids content. Nevertheless, there were significant reductions in stopping distance. The void content can be reduced by modifying the formulation and by greater compaction.

Laboratory evaluation (Gannon, et al.^{VI.6}; Takallou, et al.^{VI.8}; and Carey^{VI.2}) indicate that an acceptable pavement can be obtained providing the quality of the rubber and other variables are closely controlled.

Huff and Vellerga^{VI.7} developed a membrane by blending asphalt cement, rubber extruder oil, and a mixture of ground reclaim and crumb rubber which can be hot-spray applied. It was useful for surface treatments for existing pavements, waterproofing membranes for bridge decks, etc.

VII. Solubility Parameters

Solubility parameters can be used as a guide in the formulation of optimum systems for coating solutions, in the selection of plastics for resistance to specific chemicals, and as we have used it, in determining the compatibility of asphalt concrete with deicing additives.

As a physical constant, the solubility parameter measures the force by which solvent molecules attract one another. If a liquid and a resin have the same or nearly the same solubility parameter values, this will indicate that the liquid is a solvent for the resin. The solubility parameter of polymers and resins is best expressed by a range of values, but solvents are given as a single value. When matching parameter values, the effect of hydrogen bonding must be considered. The effect of hydrogen bonding has been divided into three classes:

- A. Poor hydrogen bonds (aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, nitriles and nitroparaffins).
- B. Moderate hydrogen bonds (esters and ketones).
- C. Strong hydrogen bonds (alcohols, organic acids and amines).

The concept of solubility parameter has also been applied to compatibility. Two resins will be compatible if the midpoints of their solubility parameter ranges do not differ by more than one unit. Their hydrogen bonding capacities should also be very similar. Generally speaking, as the molecular weight of a film-forming polymer increases, it tends to become more incompatible. Polymers with very high molecular weights will not tolerate a difference of even one unit of solubility parameter.

Plasticizers behave like high molecular weight solvents and should be treated as a component of the solvent mixture.

For low molecular weight liquids, the solubility parameter, δ , is conveniently calculated using the expression $\delta = (\Delta E_v / V)^{1/2}$, where ΔE_v is the energy of vaporization at a given temperature and V is the corresponding molar volume which is calculated from the known values of molecular weight and density.

For high molecular weight polymers, the volatility is much too low for ΔE_v to be obtained directly, and hence recourse must be made to indirect methods^v for estimating δ for these materials. One such widely used method is based on additive group "molar-attraction constants" which when summed allow the estimation of δ from a knowledge of the structural formula of the material.

The methods used in this work to estimate solubility parameter are described in Appendix D.

VIII. State of Connecticut

See Appendix A

IX. Testing

The ASTM Annual Book of ASTM Standards, Section 4 - Construction, Volume 04.03 Road and Paving Materials; Travelled Surface Characteristics presents, in over 800 pages, a broad variety of test methods.

The three methods we have used the most are ice adhesion, surface friction by the British Pendulum Test and mechanical properties and flow as measured by the Marshall Test. The British Pendulum is ASTM E 303-83. The Marshall Test, ASTM D1559-82, is a Test Method for Resistance To Plastic Flow of Bituminous Mixtures.

X. Theory

Discussions on mechanism of ice adhesion and breaking of the ice bond to a surface are scattered throughout many of the papers previously discussed. This group of articles is under the heading "Theory" because understanding the mechanism involved is the primary purpose of these papers.

Ashworth and Weyland^{X.1} carried out tensile and shear interfacial strength tests over the temperature range -0.5°C to -20°C . Surface treatments included NaCl, CaCl_2 , a silicone compound, a fluorocarbon and mineral oil (#2 diesel fuel). The salts reduced adhesion above -8°C ; the others were more effective, especially at lower temperatures. Results indicate that both mechanical and chemical bonding are important at the ice/PCC interface.

Bascom, et al.^{X.2}, found no clear correlation between the contact angle of water and the adhesive strength of ice, despite the generally accepted notion that adhesion of ice is weaker on a hydrophobic surface. Previous work by Baum and Thoma⁽¹⁾ on ice adhesion to aluminum conductors, and by Baum and Cross⁽²⁾ on minimizing dust adhesion to heliostat mirrors, also indicated little or no relationship to the contact angle of water.

Forest^{X.3} examined the shear strength of ice on low energy polymers and showed that a decrease in the surface energy of the substrate results in a decrease in shear strength. However, other factors, such as surface roughness, are important.

Itagaki^{X.4} suggests that the main factor controlling bond strength is the area of "real" contact. When a substrate is hydrophobic, the actual contact between a drop of water and its surface is limited to the edge of the drop. "Real" contact between ice and substrate when the drop is frozen, therefore, is also limited to the small area around the edge of the drop. Thus, the bond strength of ice to a substrate decreases as surface energy decreases, i.e. as the surface becomes more hydrophobic.

Raraty and Tabor^{X.5} studied the adhesion of ice to various solids. If water is frozen on a clean metal surface, the interface is stronger than the ice, and fracture occurs within the ice itself. The detailed behaviour depends on the stresses developed near the interface. If the tensile stresses are below a critical limit, the failure is ductile, and the breaking stress increases linearly as the temperature is reduced below 0°C. Ductile failure appears to be determined by the onset of a critical creep rate, and the variation of breaking stress with temperature may be explained in this way. This view is supported by the observation that small quantities of dissolved salts which increase the creep rate of ice produce a parallel reduction in the adhesive strength.

Surface contaminants on metal reduce the adhesion by a very large factor, and it is suggested that this is due primarily to a reduction in the area over which strong metal/ice adhesion occurs. The adhesion of ice to polymeric materials differs from the adhesion to metals. The interfacial strength appears to be less than the strength of ice, and failure occurs truly at the interface. Friction experiments carried out with clean and lubricated metals and polymers sliding on ice provide a measure of shear strength of the solid/ice interface. The results show a marked parallelism with those obtained in the adhesion experiments. This again emphasizes the close connection between the friction and adhesion of solids. The results suggest that ice layers may be removed most readily if brittle fracture can be achieved, e.g., by adding small quantities of suitable salts, since these reduce the resistance to ductile flow if the system is above the eutectic temperature.

- (1) Baum, B. and Thoma, L., "Development of Conductor Deicing Systems", EPRI Contract #2367-1.
- (2) Baum, B. and Cross, S., "Protective Treatments To Decrease Dust Adhesion On Membrane Heliostat Mirrors", SERI Subcontract No. XX-9-19028-1.

XI. Thermal Heat Gain

Heat absorption is one of the deicing approaches we proposed originally. In his article, Esch^{XI.1} discusses several approaches to accelerate thawing of permafrost to increase the solar heat gain. These include surface cleaning and stripping, thin gravel pad construction, gravel pad surface darkening with asphalt, and the use of polyethylene film to create a "greenhouse" effect.

XII. Verglimit

A deicing compound known as Verglimit, derived from the French expression "limite' le verglas", (end slippery ice) was developed in Switzerland in 1973 and has been in use for fifteen years for ice control in Europe, eleven in Canada, and ten in the United States. This deicing material is essentially calcium chloride flakes, to which about 5% sodium hydroxide is added. The flakes are coated with linseed oil, which is polymerized to protect the flakes from water vapor. This material (flakes) is introduced into the asphalt concrete mix as part of the aggregates during the mix cycle. The treated mix is laid and compacted using conventional paving equipment. Thus Verglimit flakes are exposed as traffic wears away the pavement surface. Cameron Kamula of the distributor, P.K. Innovations in North America, also states that Verglimit is slowly extracted and brought to the surface by rain.

Morian and Arellano^{XII.5} state that Verglimit modified asphalt was three times the cost of standard asphalt concrete. Other authors and P.K. Innovations recommend that Verglimit be used only on bridge decks or an accident prone section of the road.

According to Fromm^{XII.4}, since the material increased the flow value of asphalt concrete surface mix, it should not be used where vehicles are stopping, as at an intersection. Fromm, Dohaney^{XII.3}, Morian and others report no, or at most, only slight reduction in skid resistance.

The additive was tested at two sites in New York State^{XII.9}. The first, in Albany in 1978, continued to perform as an ice-retardant after seven years. The second, on Rte. 17 near Binghamton - site of numerous winter accidents - was resurfaced in 1983. Two years of data show an 86 percent reduction in the rate of snow and ice related accidents, while two control sites, one resurfaced with a high-friction aggregate overlay in 1988, on the same roadway had increases in such accidents for the same time period.

Other reports of field trial effectiveness came from Ontario (Fromm^{XII.4}), Quebec (Dohaney^{XII.3}), and on an 0.8 of a mile section of Rte. 73 in Clinton, NJ, etc. (Rainiero^{XII.7}).

Michigan Roads and Construction^{XII.8} reports that a mixture of asphalt and a chemical compound called Verglimit, that was used on two county roads in New Jersey, is being removed. The roads became super-slippery, resulting in accidents, including one in which eight people were hurt and one person killed. However, the compound has been used successfully in New York State for a decade.

Engineers are now studying the cause of the New Jersey failure. Some experts believe contractors failed to adequately compress the mixture, leaving gaps in the AC. If the pavement was not sufficiently compacted, it is likely that the Verglimit came to the surface too quickly and in too high a concentration and was not sufficiently removed by the required washing (per standard procedure).

2. Test Methods for Asphalt Concrete

Every potential additive is screened by a series of tests with the simplest screening test first. As additives are disqualified, subsequent, more complicated, tests are run on fewer materials. The following is the test sequence:

- a. "Slush" Test (on water soluble additives)
- b. Freezing Point
- c. Percent Moisture Pick Up
- d. Effect of Organic Liquids On Asphalt Concrete
- e. Ice Adhesion
- f. Friction - British Pendulum Test (BPT)
- Bicycle Wheel Test (BWT) (Preliminary tests only)
- g. Asphalt Concrete Mix Design and Briquette Preparation
- h. Marshall Stability of the AC Briquette
- i. Effect of Continued Washing of the AC Briquette on Ice Adhesion
- j. Flake Formulation Procedure

Test details are described below:

a. Slush Test - Characteristics of Frozen Salt Solutions

A screening test was devised to enable early differentiation of potentially suitable and unsuitable salts and water soluble organics. Test tubes (16 x 125 mm) containing two and one half mL of the salt solutions were placed in a -20°C freezer for 16 hours overnight. The consistency of each mixture was first judged visually and then by probing with a pointed metal spatula. The preparation and concentration of the salt and water soluble organic solutions is discussed later in the report (Section 4).

Based upon this semiquantitative test method, the following rating scale was devised to judge the consistency of the "frozen" salt solution and to equate this rating with the relative ease with which a snowplow might remove the frozen mixture from the pavement. A rating of 8-10 implies easy removal (slush). Even at a rating of "7", a snowplow should have no problem with removal. The "4" rating would indicate, tentatively, some difficulty with plowing the road clear to the pavement. The "2" rating would indicate the ice is frozen solid.

The gaps between the ratings 2 through 5 and 5 through 7 allow more flexibility when rating frozen plugs that represent mixtures with consistencies in between the main categories.

TABLE 1

RATING SCALE FOR PHYSICAL CHARACTERISTICS
OF FROZEN SALT SOLUTIONS AT -20°C

Rating

10	Slush, 1/2 Liquid, Fine Crystals, Aggregates Break Up Easily
9	Slush, Fine Crystals, Stirrable, Aggregates Break Up
8	Mostly Solid With Liquid Phase, Crumbles Easily With Force
7	Solid Cake, Crumbles With Force
5	Solid Cake, Crumbles With Considerable Force
2	Solid Cake
1	Solid Cake, Broke Glass Test Tube

b. Freezing Point Determination

A series of salt (general term for all water soluble additives) solutions ranging in concentration from 5 to 20 percent by weight were prepared using deionized water at ambient temperature. Seven milliliters (ml) of each solution were placed in a test tube, then put into a freezer chest at -20°C. A thermocouple was centered in the solution approximately one centimeter below the meniscus. Utilizing a digital output device and chart recorder, the freezing point curves and depression temperature were recorded. The apparatus is shown in Figure 1.

Typical freezing point curves are shown in Figures 2 through 3.

c. Moisture Pick Up

It is quite critical to know the moisture pick up of the various salts. For example, Verglimit is essentially calcium chloride, made slightly alkaline with sodium hydroxide and coated with polymerized linseed oil to prevent moisture absorption and caking in the bag.

A high moisture absorption by a deliquescent salt could lead to problems -- caking in the shipping bag if there were pinholes, expansion and cracking of the pavement, and too high a rate of humidity causing exudation of the additive, leading to slippery road conditions.

One to five gram samples are weighed into preweighed dishes (2" diameter x 0.5" depth) in ambient conditions. The materials were weighed as received. Salt compounds and flake formulations were vacuum dried overnight at 80°C to remove atmospheric moisture. The samples were reweighed after vacuum drying and placed in humidity chambers.

The humidity chambers were glass dessicators with saturated salt solutions contained in the lower portion, below the perforated shelf, of the glass jar. The lid was sealed with silicone grease. The solutions were allowed to equilibrate in the jars for approximately one week before samples were placed in them.

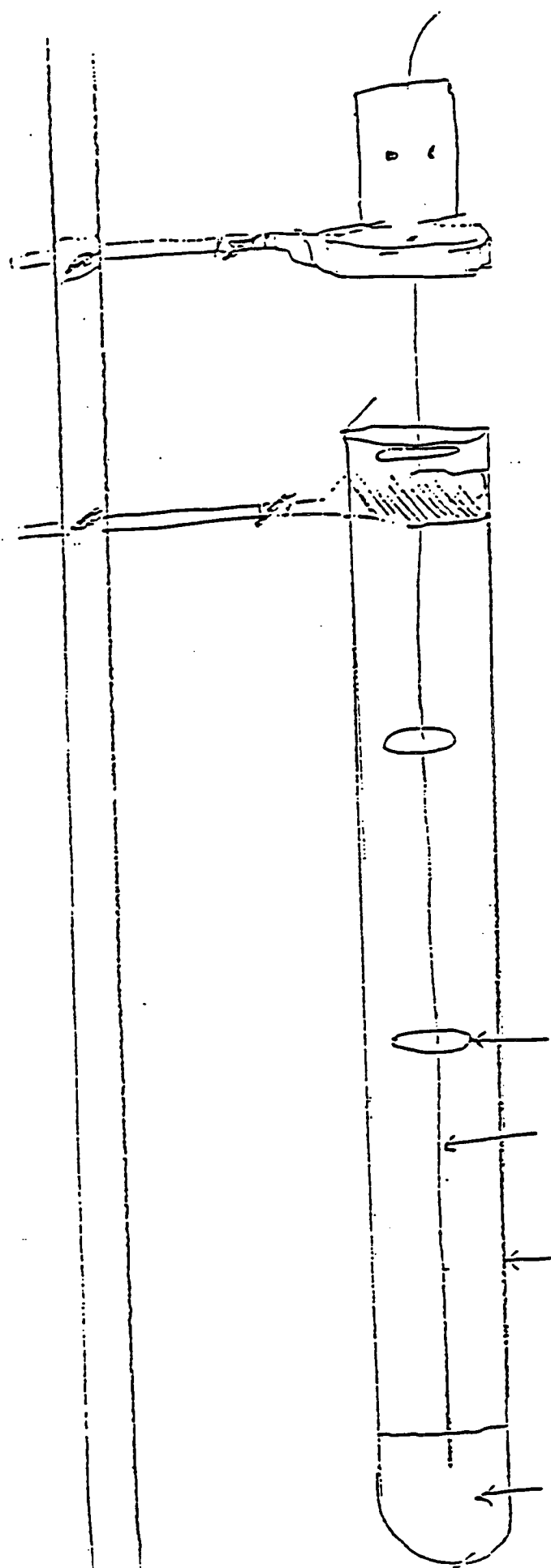
TO DIGITAL TEMPERATURE READOUT
AND CALIBRATED STRIP CHART
RECORDER

FIGURE 1

Apparatus For Freezing Point Depress
Curves and Temperature Determination.

APPARATUS PLACED IN STANDARD
CHEST FREEZER

Max. Temp. Depression = -20°C

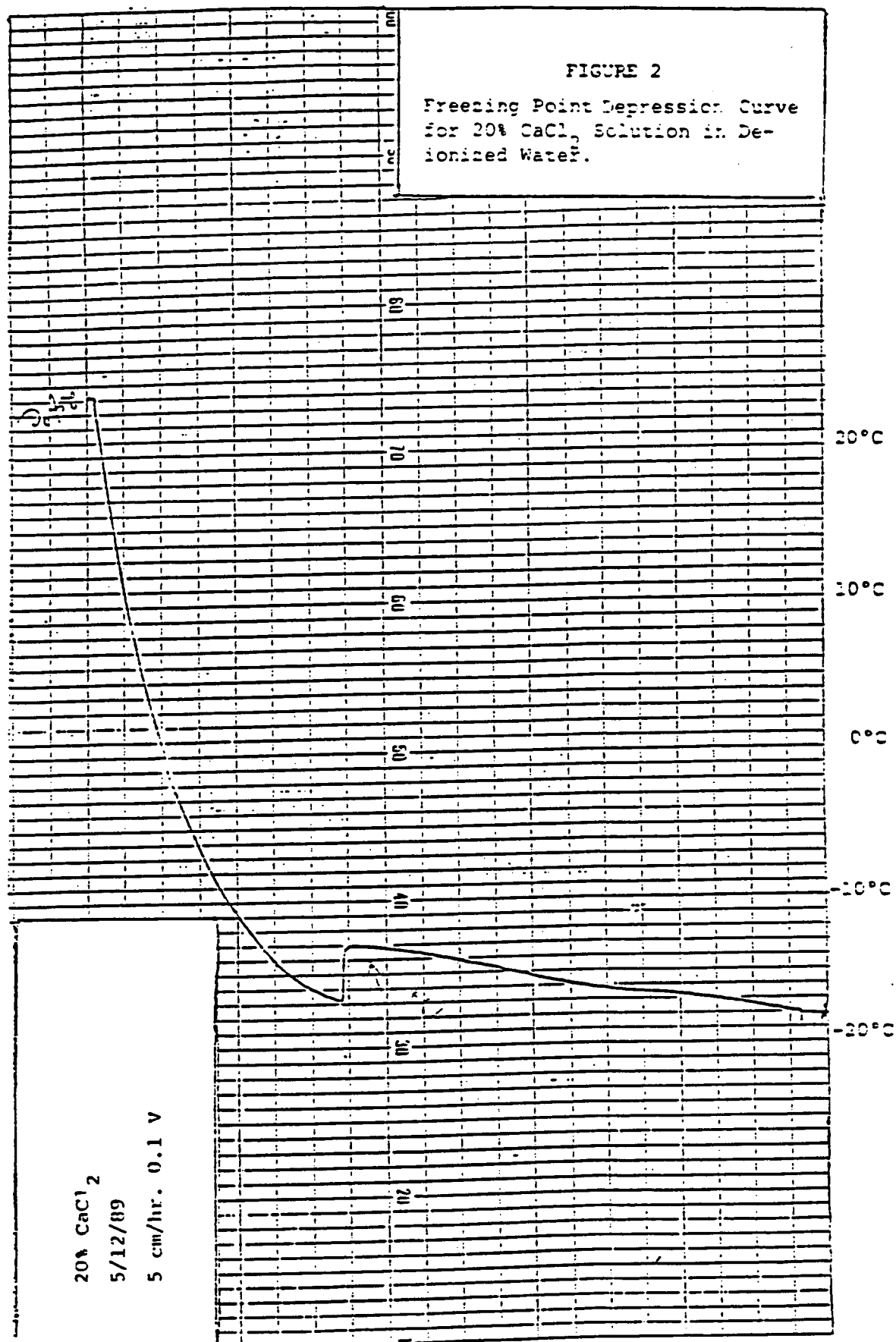


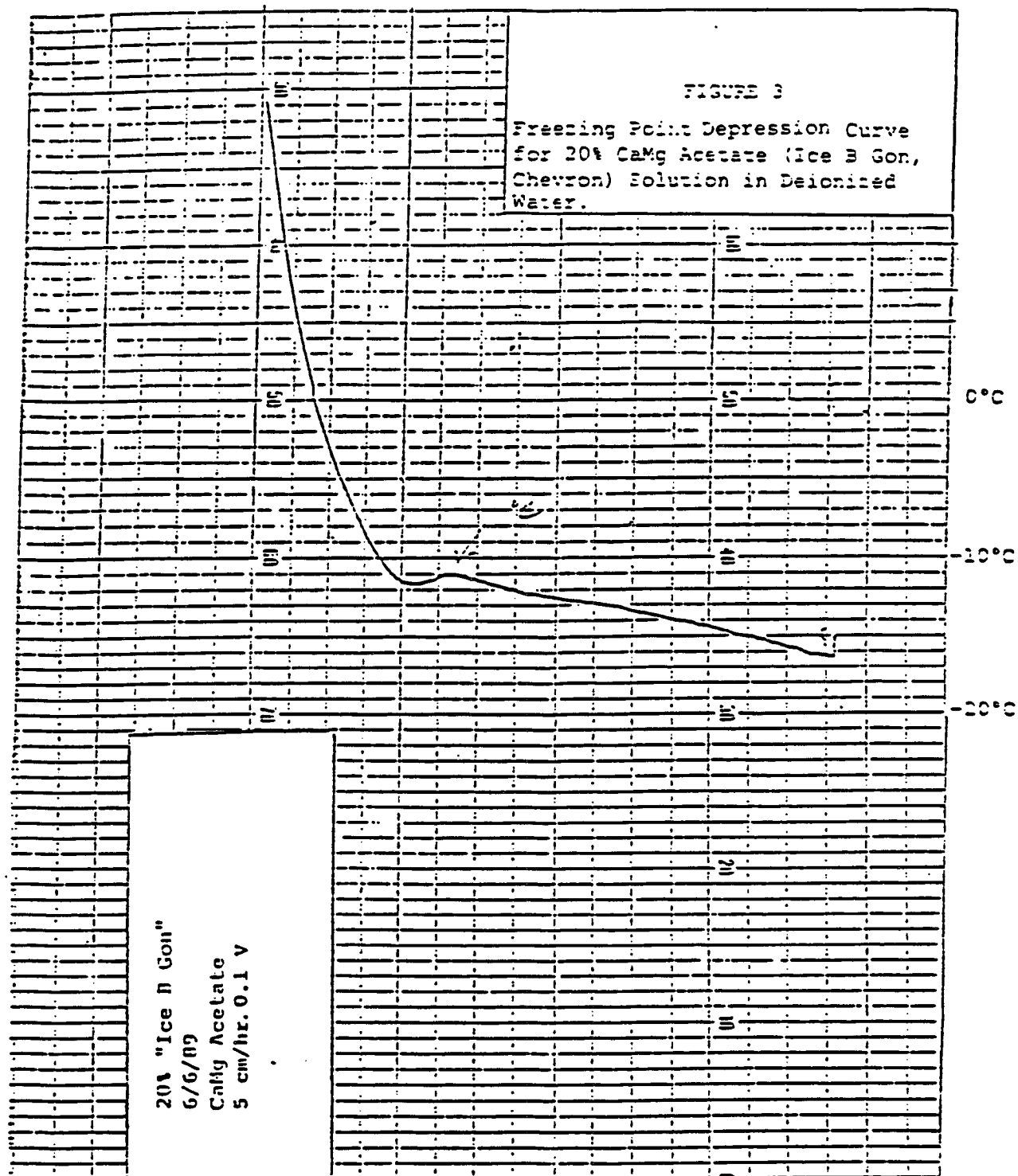
SILICONE RUBBER SPACERS

IRON CONSTANTAN THERMOCOUPLE

22 x 175 MM TEST TUBE

7 M³ SOLUTION





The *Handbook of Physics and Chemistry* was referred to for selection of the saturated solutions to use for obtaining desired relative humidity values. According to the handbook, sodium chloride (NaCl) in a saturated solution provides 75% relative humidity. NaCl was stirred into approximately one inch of water (~8 in. diameter) until crystalline NaCl no longer dissolved, and some solid NaCl was left on the bottom of the liquid portion. The upper chamber of the dessicator was ten inches in diameter and had a height of approximately 11 inches.

Samples were weighed on a weekly basis and the weights were recorded. Calculation for the percent weight gain was as follows:

$$\frac{\text{hydrated weight of sample} - \text{initial dried weight of sample}}{\text{initial dried weight of sample}} \times 100 = \% \text{ weight gain}$$

d. Effect of Organic Liquids on Asphalt Concrete

As a first step in this program, 1/2" square pieces of asphalt concrete were immersed in various organic liquids in a test tube for two weeks and signs of attack noted. By organic liquids, we mean any monomeric or polymeric liquid. As an abbreviation, we will henceforth call them oils.

Only oils that did not attack, or only slightly attack the AC, were used as additives in making briquettes.

e. Ice Adhesion Test

Ice adhesion test development work was initiated to establish a quantitative method for evaluating the shear strength of ice to the pavement surface. For this purpose, sample asphalt concrete (AC) cores, made in a standard 4-inch diameter Marshall compactor, were procured for preliminary test method development from the University of Connecticut Department of Civil Engineering. The AC cores were placed in a freezer and brought to a temperature of -10°C . Deionized water, as well as several salt solutions, were cooled to 5°C .

In the initial ice adhesion test development work, ice discs having a one inch diameter and one quarter inch thickness were molded in silicone rubber molds. A continuous indentation around the circumference of the disc was also molded into the disc around which a wire could be wrapped during testing. In addition, one surface of the ice disc had a crosshatched pattern. The purpose of the crosshatched pattern was to insure that a strong bond was formed between the salt solution and the ice, i.e. mechanical interlocking. The object of this test is to measure the shear strength of the salt solution to the asphalt surface, not of the salt solution to the pre-formed ice surface.

Ice adhesion data obtained by this preliminary method had wide scatter.

Difficulties in molding ice pieces that were identical in shape and would not themselves shear or crack during ice adhesion testing resulted in a modification of the disc formation. To improve the ice disc, one-inch inside diameter rings of aluminum having a wall thickness of 1/8 inch and a circumferential indentation in the 1/4 inch wide wall were machined. The purpose of the outer ring was to reinforce the ice discs. The rings were inserted into one inch diameter rubber molds. The molds were filled with deionized water and frozen. Again, one surface of the final one-inch diameter ice disc had a crosshatched pattern.

The asphalt/ice bond was constructed by syringing 1 ml of deionized water or salt solution onto the AC surface and quickly placing the patterned side of an ice disc upon the liquid. The samples were left overnight at -20°C .

For ice adhesion tests with oils (henceforth an abbreviated term for any organic liquid), 1.5 g of the liquid is spread over the four inch diameter AC plug, which is put in the freezer immediately for six hours and ice is frozen on the surface thereafter, as previously described. The plug is kept in the freezer overnight, and ice adhesion is run in quintuplicate the next morning.

Asphalt surface/ice shear measurements were made using an apparatus which is mounted inside the freezer. The apparatus, Figure 4, consists of a test stand on which a Chatillon digital force gauge (Model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure) is mounted and which moves horizontally in one dimension with the aid of a belt driven motor and speed controller system. On the same stand, the sample to be tested is clamped in a stationary position. A wire attached to the force gauge is wrapped around the circumferential indentation of the aluminum ring of the frozen ice disc assembly. The force gauge is then set into motion away from the sample at a preset speed of 4.5 in/min. The maximum force to remove the ice disc is recorded by the load cell.

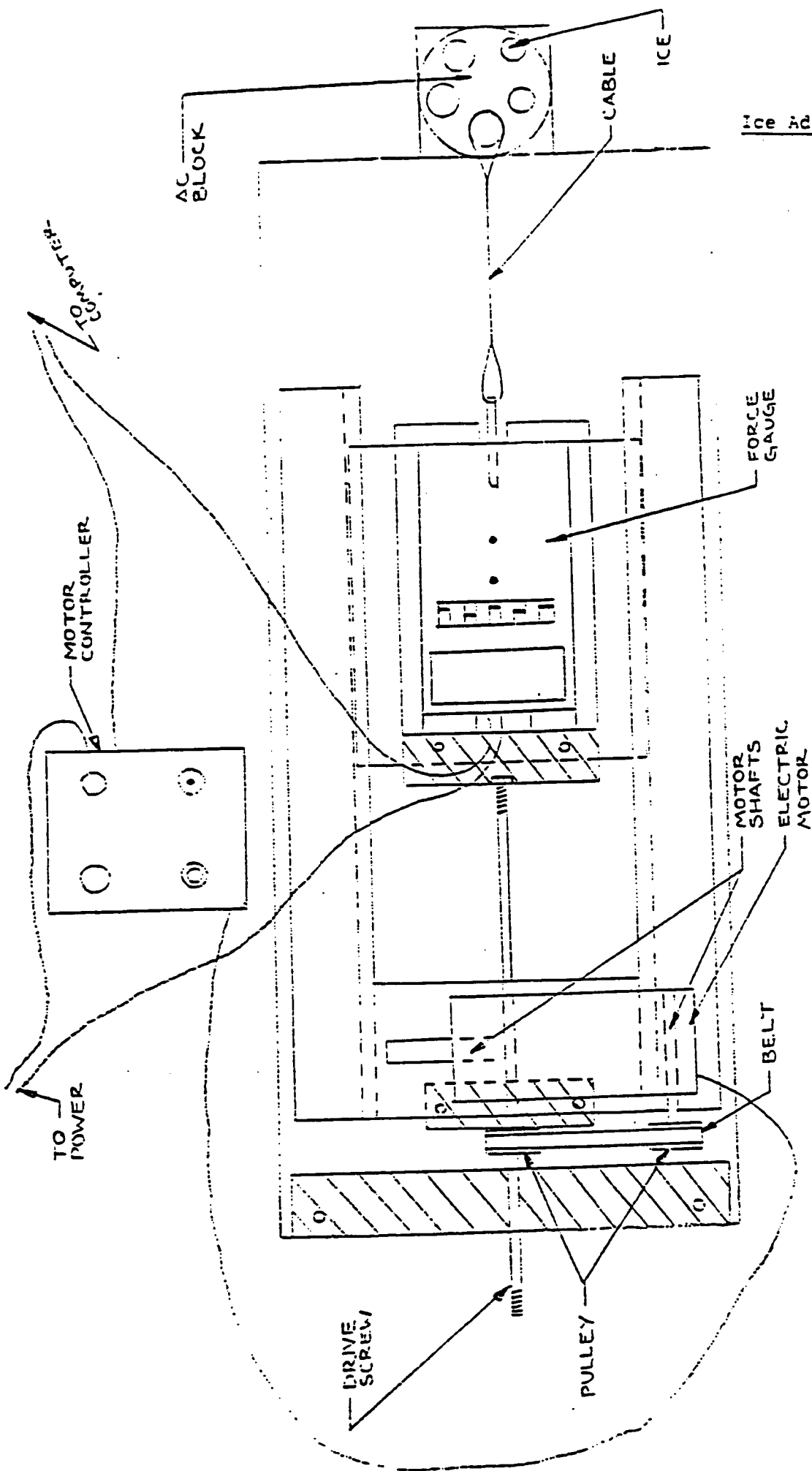
During testing, the sample is taken from a -20°C freezer temperature to the -10°C environment at the site of the test apparatus. Since the temperature of the interface affects the strength of the asphalt/ice bond, it is desirable to maintain the same interfacial temperature for all samples tested. To determine the heating rate of the interface, a thermocouple was frozen at the interface of an ice disc of deionized water and the asphalt and left overnight. To simulate conditions during actual testing, the freezer door was left open for 5 minutes followed by transferring the asphalt sample with the ice frozen onto it in the test position. The temperature versus time for the interface was measured to determine how fast the surface would warm. The test data is presented in Table 2. In the few minutes it takes to do a test, there is only approximately 2°C of warming at the interface, as shown in Table 2.

TABLE 2

TEMPERATURE OF ASPHALT CONCRETE/ICE INTERFACE
VERSUS TIME DURING ADHESION TESTING

<u>Time</u> <u>(min.)</u>	<u>Temperature</u> <u>($^{\circ}\text{C}$)</u>
0	-18
1	-18
2	-17
3	-17
4	-16
5	-16
6	-16
7	-16
8	-15
9	-15
10	-15

FIGURE 4
Ice Adhesion Test Apparatus



As discussed later in the report, ice adhesion testing conducted on formulated AC briquettes into which promising organic additives had been compounded, resulted in shear values greater than 64 lbs./in² at the -20°C test temperature, the upper limit of the measuring device. Therefore, the ice shear strength of all compounded briquettes were tested at a higher temperature, i.e. -5°C.

f. Friction Testing

Preliminary work with sliding friction utilized a 1016 gram weight bonded to a 1.5 inch diameter smooth tire stock which was pulled across a four inch asphalt concrete disc. This work was not encouraging, i.e. wet friction was about the same as dry friction. Apparently, speed is a critical factor to differentiate between wet and dry friction.

Bicycle Wheel

It was decided that a higher rate of speed might be necessary to evaluate differences in asphalt formulations. A rotating bicycle wheel friction tester, which could be operated at higher speeds and could be used on four inch diameter asphalt/concrete surfaces, was then constructed for the laboratory skid testing. A racing tire was selected for the test wheel. A drawing of the apparatus is shown in Figure 5. The bicycle tire was operated at 30 mi/hr as measured with a strobe light apparatus. The spinning tire load includes the weight of the tire plus the guides which hold the tire in place and was measured to be 10.5 lbs. when free floating. The tire pressure was 4 psi. Treadmarks from the tire left in the asphalt are included in Figure 6.

The four inch diameter concrete samples from the University of Connecticut Dept. of Civil Engineering, in addition to road cores obtained from the Connecticut Dept. of Transportation, were employed in this initial friction testing. The exact composition of these latter samples is unknown. The test consists of increasing the rotation of the wheel until a set constant speed is achieved and then lowering the wheel down onto the asphalt sample. Surfaces were as received (dry) and wet with water (pooled until saturated). The maximum amount of force produced in stopping the tire was recorded with a Chatillon digital force gauge (Model DFGRS-50). For significant data, five determinations were made at different spots. The tire burns the AC at the contact point to a new surface, even when water wet; hence, the sample disk was rotated and moved slightly between readings.

British Pendulum Test

A British Pendulum tester was loaned to us by the Connecticut Dept. of Transportation after the bicycle wheel tester had been constructed. This allowed comparison of skidding data using two different test methods. The BPT was set up as instructed in ASTM E303 and testing carried out as outlined.

The only problem encountered was that the four inch diameter AC cylinder is too narrow for the rubber faced slider assembly. The method states (6.2.1) that laboratory test panels should have a test surface of at least 3.5 by 6 inches. The contact path used for our measurements was 2.375 inches, whereas the method states that the contact path be 4.875 to 5 inches. The numbers generated are empirical dimensionless numbers in either case.

FIGURE 5
Bicycle Wheel Friction Test Apparatus

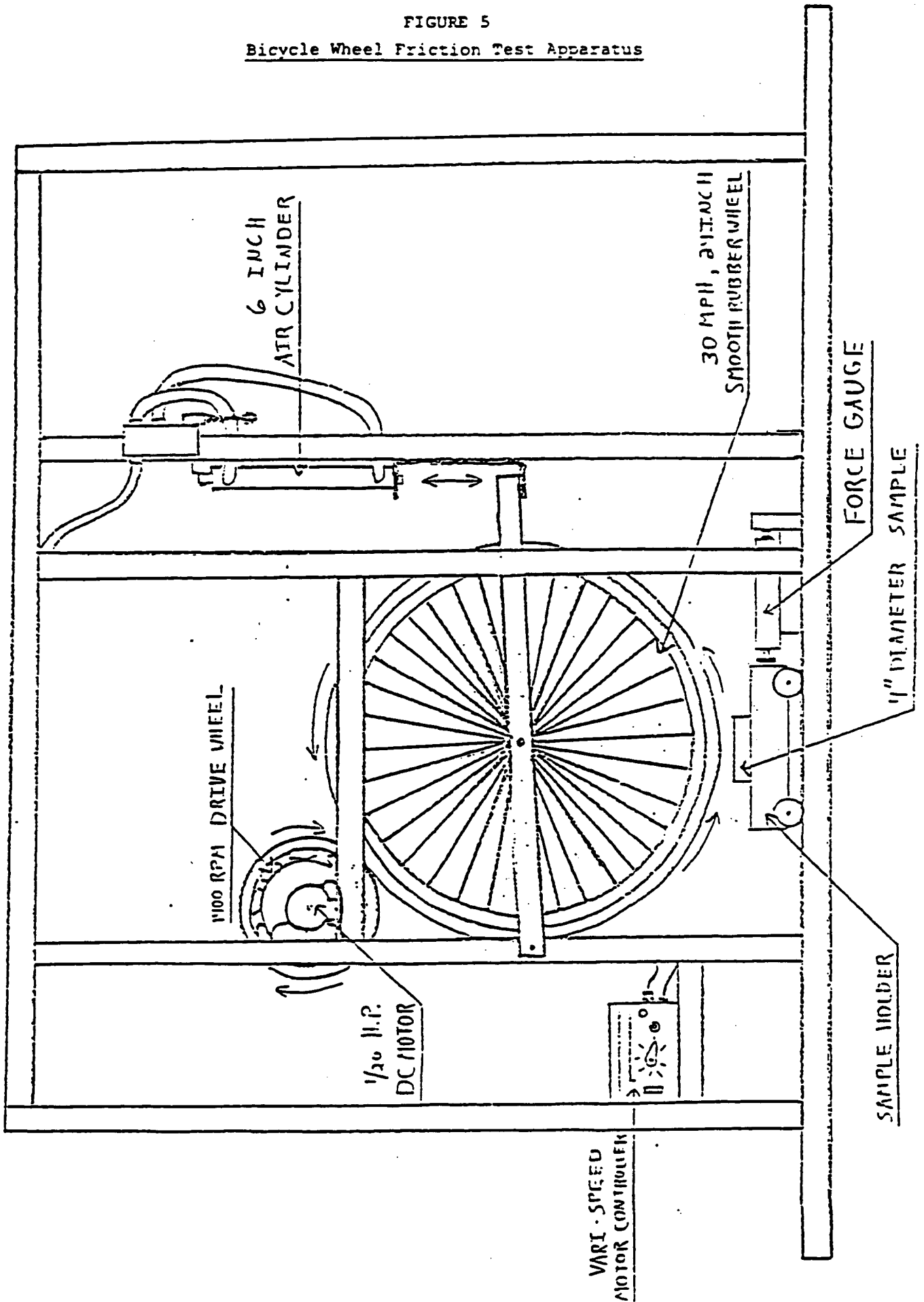
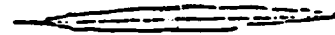
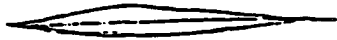


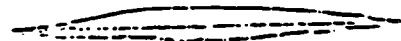
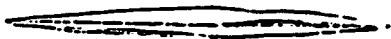
FIGURE 6
TIRE TREAD MARKS



Tire Pressure 30 psi



Tire Pressure 10 psi



Tire Pressure 4 psi

Tables 3 to 5 present the data obtained for the bicycle wheel and British Pendulum friction tests. There is a consistent difference between dry and wet friction. Thus, it appears that both the bicycle wheel and the BP tests give valid friction data. Both tests readily differentiate between wet versus dry surfaces, with the water lowering friction on the asphalt concrete surface.

There was concern at that time that the 30 miles/hour speed of the wheel may be "wiping off" the oil on the briquette surface. This does not happen with the British Pendulum Test. Therefore, the Bicycle Wheel test was also run at 15 and at 7.5 miles/hour (Table 6). However, at lower speeds there was no differentiation between dry and wet friction. Consequently, the Bicycle Wheel test cannot be run at the lower speeds.

Table 7 was set up to compare the Bicycle Wheel test with the British Pendulum test in more detail.

The Pendulum reading was divided by the bicycle friction to get a ratio. There is an approximate ratio of $10 \pm 30\%$ between the two test methods.

Henceforth, all subsequent friction data was determined by the British Pendulum test.

g. Asphalt Concrete Mix Design And Briquette Preparation

Useful salts for further testing were chosen based on:

- (a) Slush Test rating, i.e. effect on characteristics of freezing water
- (b) Freezing point lowering
- (c) Ice adhesion

Useful oils were chosen based on:

- (a) Effect on asphalt concrete properties
- (b) Ice adhesion

To examine the practical utility of the "best" additives, it is essential that they be examined blended into asphalt concrete. To this end, a compactor was purchased and a procedure developed for asphalt concrete (AC) briquette preparation. The mix design used was that of Carl Monismith, Professor at the University of California at Berkeley. The information and aggregate was provided to us by Bill Elmore of the University of Texas.

The mix design is graphed in Figure 7, and is delineated in Table 8. The bottom solid curve in Figure 7 represents the coarsest mix. There is 5% aggregate greater than 3/4 inch size, 15% between 1/2-3/4 inches (Table 8, left column), and only 12% smaller than 50 sieve size. The top dashed line in Figure 7 (second column of Table 8) contains the relatively finest aggregate. There is no aggregate greater than 3/4 inches, only 10% in the 1/2-3/4 inch range and 18% below 50 sieve size.

TABLE 3

FRICTION BY THE BICYCLE WHEEL TESTMaximum Force to Stop Wheel Rotation⁽¹⁾ (kg)

Sample:	(2)		(2)	
	AC-8A		AC-1A	
Run #	Dry	Wet ⁽³⁾	Dry	Wet ⁽³⁾
1	4.49	3.50	3.35	3.01
2	4.54	3.80	3.03	2.90
3	4.31	3.73	3.29	3.06
4	4.39	3.65	3.69	2.89
5	4.80	3.99	3.81	2.87
x ⁽⁴⁾	4.52	3.74	3.44	2.95
s	±0.19	±0.18	±0.32	±0.08
90%	4.52 ±0.18	3.74 ±0.17	3.44 ±0.31	2.95 ±0.08
95%	4.52 ±0.23	3.74 ±0.23	3.44 ±0.39	2.95 ±0.10

-
- (1) Wheel runs at 30 mph; tire pressure is 4 psi; Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure, i.e. 4.49 ± 0.01
- (2) Dense graded AC core sample from the Univ. of Connecticut
- (3) Water
- (4) x - mean value
s - standard deviation from mean
90% - 90% confidence limit for the mean value
95% - 95% confidence limit for the mean value

TABLE 4

FRICTION BY THE BRITISH PENDULUM TEST (BPT)⁽¹⁾

Sample:	AC-13A ⁽²⁾	
	Dry	Wet ⁽³⁾
Run#		
1	45 ⁽⁴⁾	30
2	44	31
3	45	31
4	44	30
x ⁽⁵⁾	45	31
s	±0.6	±0.6
90%	45 ±0.7	31 ±0.7
95%	45 ±0.9	31 ±0.9

- (1) Contact path 2.375 inches
 (2) Dense graded AC core sample from the Univ. of Connecticut
 (3) Water
 (4) British Pendulum Number (BPN): Dimensionless units
 (5) x - mean value
 s - standard deviation from mean
 90% - 90% confidence limit for the mean value
 95% - 95% confidence limit for the mean value

TABLE 5

COMPARISON OF BRITISH PENDULUM AND BICYCLE WHEEL FRICTION TEST

Test:	BPN ⁽¹⁾ (Contact path 2.375 inches)	Bicycle Wheel Test ⁽²⁾ (Tire pressure 4 psi, 30 mi/hr)
Sample:	AC-4A ⁽³⁾	AC-4A ⁽³⁾
Run#	Dry	Dry
1	40	4.11
2	40	4.18
3	40	4.29
4	42	4.39
5	42	4.28
6	42	4.45
7	44	4.23
8	44	4.14
9	45	4.31
10	45	4.12
x ⁽⁴⁾	42	4.25
s	±2	±0.12
90%	42 ±1	4.25 ±0.07
95%	42 ±1	4.25 ±0.08

-
- (1) British Pendulum Number (BPN): Dimensionless units
 (2) Wheel runs at 30 mph; tire pressure is 4 psi; Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure, i.e. 4.11 ±0.01
 (3) Dense graded AC core sample from the Univ. of Connecticut
 (4) x - mean value
 s - standard deviation from mean
 90% - 90% confidence limit for the mean value
 95% - 95% confidence limit for the mean value

TABLE 6

BICYCLE WHEEL FRICTION⁽¹⁾ OF ASPHALT CONCRETE
BRIQUETTE SURFACE IMPREGNATED WITH OIL⁽²⁾

Bicycle Wheel Speed (mph)	Maximum Force To Stop Wheel Rotation (kg)			
	Pluracol 824 ⁽³⁾		Paraplex G54 ⁽³⁾	
	Dry	Wet ⁽⁴⁾	Dry	Wet ⁽⁴⁾
30	4.4	3.4	3.7	2.7
15	3.5	3.3	3.3	3.1
7.5	1.7	1.6	1.6	1.6

- (1) Bicycle Wheel Test: Maximum force in kg to stop the wheel rotation; 4psi tire pressure, and at room temperature.
 Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure, i.e. 4.4 ± 0.01
- (2) Dense graded AC core sample from the Univ. of Connecticut.
 Liquid additive coated on surface at 1.5 g/4 inch diameter AC core sample
- (3) All additives are described in Appendix B
- (4) Water

TABLE 7

FRICITION ON ASPHALT CONCRETE ⁽¹⁾ SURFACE IMPREGNATED WITH VARIOUS OILS ⁽²⁾ :
 COMPARING THE BICYCLE WHEEL TEST ⁽³⁾ WITH THE BRITISH PENDULUM ⁽⁴⁾ TEST ⁽⁵⁾

Additive	Dry Friction			Wet ⁽⁶⁾ Friction		
	Bicycle	Pendulum	Ratio	Bicycle	Pendulum	Ratio
None [Controls]	[4.54]	[44.6]	9.8	[3.12]	[34.8]	11.2
Santicizer 160 (butyl benzyl phthalate)	3.70	25.8	7.0	2.85	25.2	8.8
Gantrez M-154 (polyvinyl methyl ether)	3.88	52.8	13.6	2.79	21.6	7.7
Acryloid 710 (polyacrylate)	3.67	46.8	12.8	2.72	31.6	14.2
Eastman SA18 (sucrose acetate butyrate)	3.60	50.4	14	2.71	29.8	11.0
Admex 760 (polyester)	3.86	39.0	10	2.69	19.8	7.3
Paraplex G-54 (polyester)	3.74	40.2	10.8	2.67	20.8	7.8
D.E.R. 331 (bisphenol diepoxide)	3.80	40.0	10.5	2.61	28.8	11.0
Indopol H-1500 (polyisobutylene)	4.22	53.6	12.7	2.43	26.4	10.9
Paraplex G-25 (polyester)	4.11	43.0	10.5	2.33	20.2	8.7
Plastolein 9789 (polyester)	4.09	38.0	9.3	1.81	19.8	10.9

- (1) Dense graded AC core sample from the Univ. of Connecticut
- (2) Liquid additive coated on surface at 1.5 g/4 inch diameter sample; All additives are listed in Appendix B
- (3) Bicycle Wheel Test: Maximum force in kg to stop rotation, run at 30 mph, 4 psi tire pressure, run at room temperature; Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure, i.e. 4.54 ± 0.01
- (4) The British Pendulum Number (BPN) is a dimensionless number, run at room temperature, wheel contact path is 2.375 inches.
- (5) The British Pendulum and Bicycle Wheel Tests were run on different portions of the same briquette surface in quintuplicate. The British Pendulum Test was run first.
- (6) Water

Asphalt Block Preparation

Method A

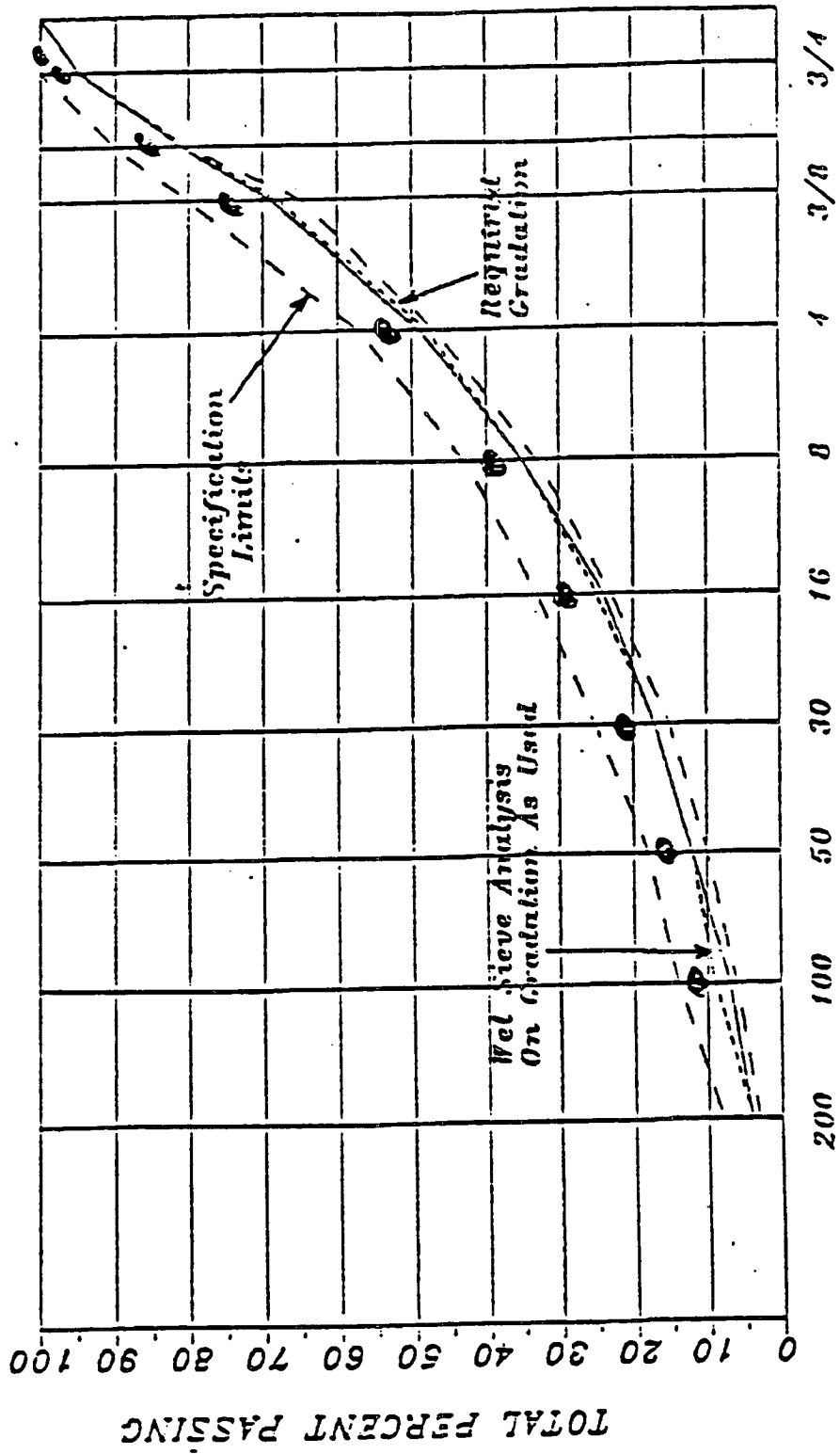
The initial procedure for asphalt block preparation using the mix design outlined in Table 8 is as follows:

1. Weigh aggregate fractions into foil pan - heat to 160°C (minimum of 4 hours).
2. Place mold in 160°C oven.
3. Place prepoured can of asphalt into 160°C oven after aggregate has been heated for correct time. Asphalt should stay in oven a minimum of 1 hour to maximum of 2 hours.
4. Remove aggregate and asphalt from oven; add correct amount of asphalt to aggregate in foil pan.
5. Transfer pan to 150°C hot plate.
6. Mix well for four minutes.
7. The very coarse aggregate is pushed away from the edge and approximately 200 g of the finer portions of the mix is set aside in a small foil pan.
8. Remove mold from oven and place in compactor. Place silicone coated release paper in bottom of mold.
9. Add 100 g of the finer mix to bottom of mold, pour in rest of mix. This is done to get a smoother surface for measuring ice adhesion.
10. Add the other 100 g of the finer mix to the top; smooth out release pan paper.
11. Secure mold, assemble rest of compactor, compact 75 cycles, flip block over and compact 75 cycles.
12. Allow to cool minimum of 30 minutes; remove from mold.

The AC block made with the coarse aggregate system (bottom solid curve of Figure 7) gave a coarse block with a poor surface, unsuited for our experimentation. The aggregate represented by the dashed line (top curve Figure 7) was so fine that it resulted in a dry, crumbly mix. Thus, we settled on an aggregate design that was halfway between the bottom and top curves (see the large dots in Figure 7).

FIGURE 7

AGGREGATE GRADATION CHART (3/4 in. Medium)



U.S. STANDARD SIEVES

TABLE 8

AGGREGATE GRADATION CHART FOR METHOD A

Sieve Size	PERCENT AT EACH AGGREGATE SIEVE SIZE ⁽¹⁾			
	Bottom (Coarse) Solid Line Curve	Upper Specification Limit-Broken Line (Fine) Curve	Middle Curve ⁽²⁾	
			%	gms
3/4	5	0	2	24
1/2-3/4	15	10	11	132
3/8-1/2	13	10	11	132
4-3/8	20	22	21	252
8-4	13	15	14	168
16-8	11	10	11	132
30-16	6	7	7	84
50-30	5	8	7	84
100-50	5	4	6	72
200-100	3	6	5	60
-200	4	8	5	60
Total	100	100	100	1200
Density	2.43	2.41	2.42	
% Voids	4.8	5.6	5.2	

 (1) Asphalt mix design, Carl Monismith, Univ. of California at Berkely
 (2) Formulation 25965-3; See the dots in between the two curves

The procedure for blending salts into the mix was as follows: Salts (at 6.4% on the aggregate) preheated five minutes at 160°C, are placed on top of the aggregate and in place of equivalent size aggregate, five minutes before removal of the aggregate from the 160°C oven. Continue with Step "4".

With oils at 3% on the aggregate, the procedure is the same through Step 5. In Step 6, there is only a two minute mixing of asphalt and aggregate, and then the oil is added and mixing continued for two minutes more on the 150°C hot plate. Continue with Step 7.

The procedure for briquette preparation was later changed at the request of SHRP to Method B. Method B consists of the sample preparation steps of Method A with the exception that the segregation of the finer fraction for the surface as described in Method A, steps 7 through 10, was abandoned (See page 33).

To have as smooth a surface as possible, an aggregate design based on the upper dashed line curve of the Monosmith aggregate gradation chart was used. This is the smallest aggregate gradation within specs.

Assuming that a finer aggregate would need a larger amount of asphalt, briquettes were prepared at 5.7% asphalt instead of 5.47%. The formulation used in samples made by Method B is presented in Table 9.

h. Marshall Stability

The intent of the procedure is to mold specimens that match actual pavement. The samples are brought to the highest temperature expected in service and loaded at a steady rate along a diameter. The load is applied through curved plates that fit the outer curved surfaces of the sample. The flat faces are unloaded and unrestrained.

The tests carried out at the University of Connecticut on samples after ice retarding treatments followed the procedure described in ASTM Method D 1559. The samples were placed in a 25 degree centigrade water bath for one half hour. They were then quickly placed in the standard breaking head and loaded by an autorecording Marshall press made by the Pine Instrument Company and distributed by Rainhart Equipment Company. This press closes at a constant rate of two inches per minute. The deformation is mechanically transmitted to the X axis of the recorder and the load is measured by a load cell and electrically plotted on the Y axis. The maximum load read from the plot in pounds is reported as the Marshall Stability. The deformation corresponding to this load is reported in hundredths of an inch as the flow.

Typical specifications in New England require a minimum stability of 1200 pounds and a flow in the range of 8 to 15.

1. Durability: Ice Adhesion After Continued Washing

The continued washing test shows the durability of the additive in lowering ice adhesion. The briquette is washed in running water from a faucet six inches above the briquette and hitting the center of the briquette, flowing at a rate of one gallon per minute for a test duration of five minutes. The briquette is allowed to air dry at room temperature overnight. Ice adhesion is rerun after each washing.

TABLE 9

FORMULATION BASED ON UPPER CURVE
OF THE AGGREGATE GRADATION CHART FOR METHOD B

<u>Sieve Size</u>	<u>Percent Aggregate</u>	<u>Weight (Grams)</u>	<u>Running Total</u>
+ 3/4	0	0	0
- 3/4 to + 1/2	10	120	120
- 1/2 to + 3/8	10	120	240
- 3/8 to + 4	22	264	504
- 4 to + 8	15	180	684
- 8 to + 16	10	120	804
- 16 to + 30	7	84	888
- 30 to + 50	8	96	984
- 50 to + 100	4	48	1032
- 100 to + 200	6	72	1104
-200	<u>8</u>	<u>96</u>	1200 g
Totals	100%	1200 g	

j. Flake Formulation For Asphalt Additives

Various salt mixtures were formulated for future addition to asphalt pavements. Solutions of various water soluble binders were made up in water and poured over salts spread out in a teflon coated pan. The mixture was then stirred gently to partly dissolve and coat the salt. The pan containing the mixture was placed in a forced air oven at 105°C to evaporate the water. The mixtures were stirred at random intervals to aid the evaporation. The drying time and stirring frequency varied with the consistency of the mixture, some of the mixtures separated, forming a hard salt layer on top and liquid layer underneath. The hard layer on top prevented evaporation, thus a longer drying time was required for some formulations. Flakes or pellets with a gravel-like texture were formed upon drying. The formulations made are listed in Table 10.

After the formulations were dry, they were broken up into pieces about 1/4 inch in diameter. The pieces were then put through standard sieves to obtain uniform sizing. The flakes that were -4 to +12 were retained for further use. Approximately ten grams of each formulation was tumbled in a pint-size jar on a standard jar roll for 2.5 hours. The portions were then resieved and reweighed to calculate the percent weight loss due to the relative break-up of the flake upon tumbling. This data is also presented in Table 10 with Verglimit included as a control.

The sodium formate/CMC mixture and the sodium formate/EMA formed the hardest flake materials with the least break-up during tumbling.

3. Additive Selection Criteria

The ideal criteria for a successful additive system would be minimum or no ice adhesion, no loss of friction, no effect on the structural integrity of the pavement, low cost, long life, no toxicity or effect on the environment, and no corrosivity to steel.

At the start of the program, it was theorized that two classes of additives would be explored: (1) water soluble salts and water soluble organic liquids, and (2) water insoluble hydrophobic organic liquids.

Salts and water soluble organics were selected on the basis of water solubility, freezing point lowering, non-toxicity, commercial availability, and price. Their primary function was to effect melting by lowering the freezing point of the ice. The salt or oil would be brought to the surface of the pavement by rainwater, extraction and/or by road wear. It was discovered early in the program that water soluble additives varied in their ability to form a soft slush with the ice, and they were initially screened in this way. This softening of the ice to a slush became a critical factor.

It has long been known that a hydrophobic surface forms a high contact angle with water, and thus is not wet by water. It was theorized that oils that would be incompatible with asphalt would diffuse to the surface of the pavement and weaken the bond of asphalt concrete to ice. This principle was followed in our work with the Electric Power Research Institute, where we developed polyethylene coatings containing exudable hydrophobic additives for coating overhead conductor wire.

TABLE 10

FLAKE FORMULATIONS

Experiment	Formulation	Drying Temp., Time	Physical Appearance	Weight Loss During Tumbling
25953-1	10 g Carboxymethyl cellulose (CMC) in 30 g H ₂ O 90 g Sodium Formate	105° C 4.5-5 hours	flaked well	0.85%
25953-2	10 g Maldene in 25 g H ₂ O pH adjusted to 7.04 w/ NaOH 90 g Sodium Formate	105° C 4 hours	pebbles and powder	13.66%
25953-3	10 g Sodium Lignin Sulfonate (CBOS-4) in 60 ml H ₂ O 90 g Sodium Formate	105° C 7 hours ⁽¹⁾	gravel texture	12.43%
25953-4	10 g EMA 1103 (Monsanto ethylene/maleic anhydride copolymer) in 60 g H ₂ O 90 g Sodium Formate	105° C 6 hours	flaked okay	0.85%
25953-5	5 g Duponol C (Dupont Sodium lauryl sulfonate) in 40 g H ₂ O 90 g Sodium Formate	105° C 3.5 hours	some flakes mostly fine powder	6.23%
25955-1	10 g CMC in 60 g H ₂ O 90 g Magnesium Acetate.4 H ₂ O (59.05 g MgOAc)	105° C 7 hours	separated into two layers flake non-homogeneous	35.31%
25955-2	10 g CMC in 60 g H ₂ O 149.2 g Sodium Acetate.3 H ₂ O (90 g NaOAc)	105° C 8+ hours	separated into two layers flake non-homogeneous	17.70%
25955-3	10 g Sodium Lignin Sulfonate (CBOS-4) in 30 ml H ₂ O 135 g Magnesium Acetate.4 H ₂ O (90 g MgOAc)	105° C 7 hours ⁽¹⁾	separated into two layers flake non-homogeneous	38.13%
25955-4	10 g Sodium Lignin Sulfonate (CBOS-4) in 30 ml H ₂ O 149.2 g Sodium Acetate.3 H ₂ O (90 g NaOAc)	105° C 7 hours ⁽¹⁾	separated into two layers flake non-homogeneous	3.97%
25957 1	Vergilmit as received			0.05%

(1) Some of the lignin volatilized into oven during drying

Thus, oils were selected by classes on the basis of polarity (quantified by solubility parameter) and molecular weight. It was originally anticipated that the oils would be incompatible with the asphalt, exude to the surface, and prevent or reduce ice adhesion. One essential criteria is that the additive not attack the asphalt. Thus, the solubility parameter of the additive must not be too close to that of the asphalt.

- a. Polarity of additive must be close enough to permit incorporation into the matrix (asphalt), but far enough from the asphalt to prevent excessive attack on the asphalt at 300°F mixing temperature, and also to expel the additive gradually over a long lifetime. Typical commercial candidates include major families of monomeric plasticizers, such as phthalates, phosphates, adipates, and fatty esters; more polar and hydrophilic oils, such as polymers and copolymers of ethylene and propylene oxides, and polyols; and less polar oils, such as polyaromatic, naphthenic, and aliphatic hydrocarbons. Since any one of these might exude too rapidly or too slowly to provide long-term performance, it might be best in future work to use a mixture of more and less compatible oils to produce continued exudation over the desired full lifetime of the asphalt concrete.
- b. Molecular weight of the oil is a critical factor, both in thermodynamic compatibility with the matrix (usually inverse), and in kinetics of exudation from the polymer to the surface (usually direct). Here again, it might be best to choose a mixture of high and low molecular weights, or use a broad molecular weight distribution of oligomers, to produce continued exudation and icephobic performance over the long desired life-span of the asphalt concrete.

To determine the relationship of the solubility parameter of potential additives versus that of asphalt, we must first know the solubility parameter of asphalt. The methods of estimating the solubility parameter of the additives and asphalt is discussed in Appendix D.

The solubility parameter of the asphalt was estimated by testing the solubility of asphalt in solvents of known solubility parameter and of known hydrogen bonding capacity. The solubility parameter "envelope" of asphalt is shown in Figure 8, where hydrogen bonding is plotted versus solubility parameter. The solubility parameter of asphalt (AC-20) ranges from 7-10.

Later in the program, it will be shown that only water soluble, or highly hydrophilic oils compounded into the AC are effective in reducing the adhesion of ice to asphalt concrete. The effective additives (Table 11) have solubility parameters greater than 11.

Furthermore, for all additives, additional criterion for selection included: 1) cost under \$1.00/lb. in bulk quantity, 2) the additive could not contain chlorine or any halogen, or other possible toxic (e.g., cyano) or potentially explosive (e.g., nitro) group and 3) it should not volatilize at the 300°F mixing temperature.

TABLE 11

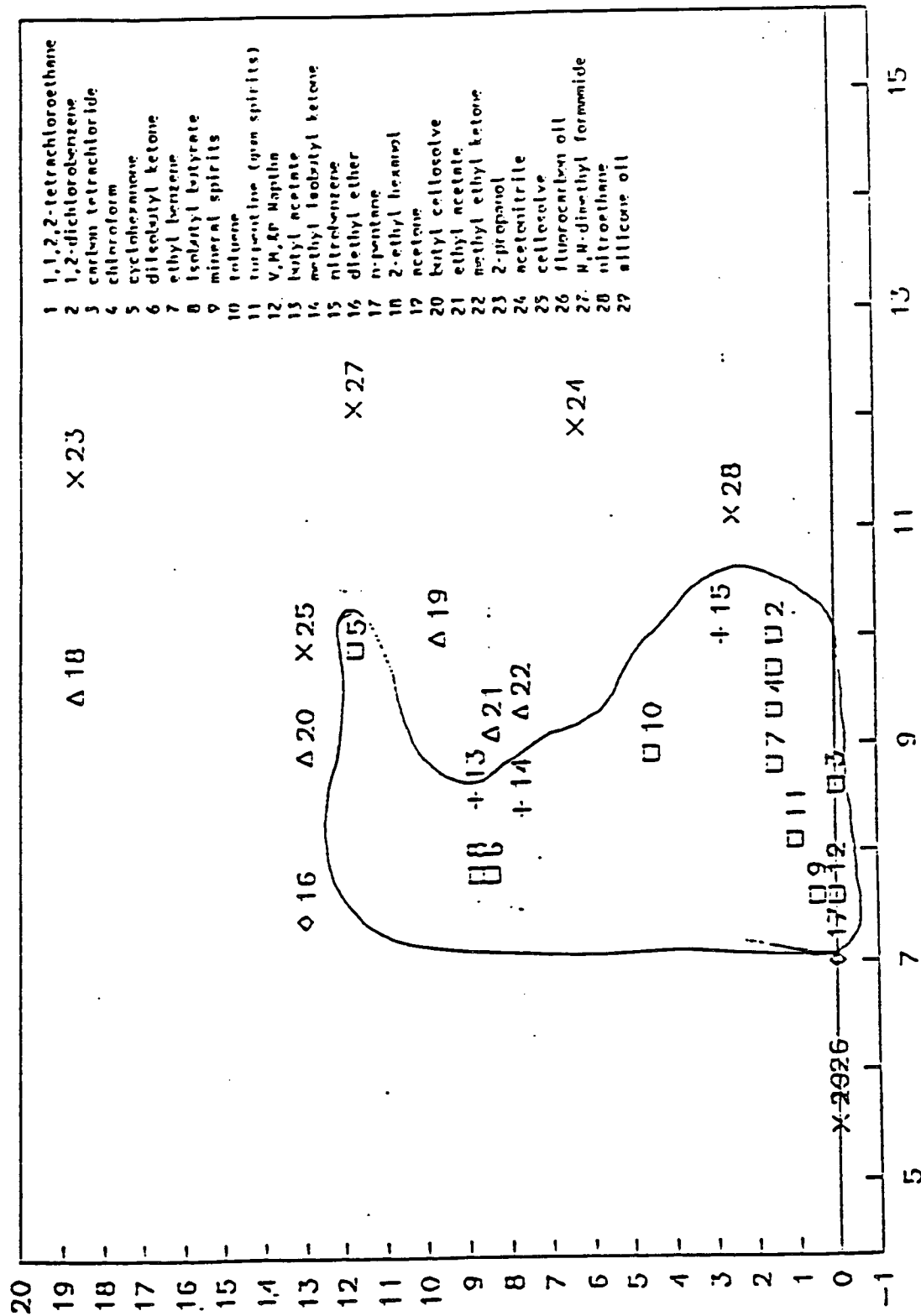
EFFECTIVE ADDITIVES AND THEIR SOLUBILITY PARAMETERS

<u>Additives</u>	<u>Ice Adhesion^(1,2) Shear Strength (psi)</u>	<u>Calculated⁽³⁾ Solubility Parameter</u>
<u>Effective Additives</u>		
Triethylene Glycol	0.5	13.7
Ethylene Glycol	0.6	14.8
Propylene Glycol	14	13.5
Tetraethylene Glycol	9	12.7
Dipropylene Glycol	22	11.7
Carbowax 300 (Polyethylene Glycol)	0.1	11.5
<u>Ineffective Additives</u>		
Pluracol 824 (Aromatic Polypropylene Glycol)	>64	9.7
Poly PPG 425 (Polypropylene Glycol 300 Molecular Weight)	51	9.3
Paraplex G54 (Adipate Polyester)	>64	7.4
Indopol L50 (Polyisobutylene)	53	7.7
BASF 380 (Polypropylene Glycol 6000 Molecular Weight)	>64	8.2

-
- (1) The briquettes were made by the early procedure (Method A, Table 8) whereby 100 g of the finer mix was positioned at both top and bottom of the briquette. The additive was incorporated into the mix as discussed previously in the report (Section C.2.g).
 - (2) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -5°C. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure
 - (3) See Appendix D for methods of estimating solubility parameters

FIGURE 11

Asphalt Solubility in Various Solvents



Solubility Parameter

□ 100% Sol + 80-90% Sol ◇ 50% Sol Δ VS Sol X Insol

4. Tasks 2 and 3: Chemical & Physical Modification

a. Slush Test and Freezing Point

The first screening tool used for salts and water soluble oils is the so-called Slush Test. The Slush Test describes qualitatively the characteristics of water soluble additive solutions at -20°C . All samples were run at 20% concentration, and some were also run at 10°C and 5°C . See Table 1 for rating scale.

Table 12 is an alphabetized listing of the various salt solutions tested by the Slush Test along with the frozen solution rating, concentration, freezing point determination if taken, and any pertinent comments. Table 13 presents the same data as Table 12, but is organized according to decreasing efficiency.

The materials shown in Tables 12 and 13 are at concentrations ranging from 5 to 20%. Originally, we started at 20% and then dropped to 10%, and finally, all later additives were screened at 5%. More promising materials were screened at all three concentrations. There are two reasons for this range of concentrations. First, the ultimate concentration to be encountered in the field is not known. Second, if a material is effective at 5%, it will certainly function even better at 10 and 20%. The reverse is also true, i.e., if the solution does not work at 20% concentration, why try a lower concentration. Where obtained, measured freezing points are indicated in the fifth column.

Table 12 allows us to see the effect of concentration and of replication. Replication by this semi-quantitative screening test is generally good. For example, most all of the samples which have been designated as repeat in the comment column have ratings consistent with the original sample evaluated, even when a new solution was made.

In some mixtures, a second additive is also present. The second additive is used primarily as a protective colloid to boost efficiency of slush or soft ice formation.

The most promising salts are those rated from 8 to 10 (Table 14). However, "7" ("solid cake crumbles with force") is also considered promising in ease of removal by a snowplow.

TABLE 12

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING
(Arranged Alphabetically)

EXPERIMENT	SALT	SLUSH TEST ⁽¹⁾ RATING	CONC., WT. %	MEASURED FREEZING POINT, °C	COMMENTS
25408-3	Deionized water (CONTROL)	2	100	0	
25412-8	Aluminum ammonium sulfate	Not evaluated	20		insoluble
25414-2	Aluminum ammonium sulfate	2	5		
25402-4	Ammonium dihydrogen phosphate	1	20	-5	
25434-3	Ammonium lignosulfonate (Lignosol TSD)	2.5	20		Daishowa
25407-3	Ammonium sulfate	8	20	-6	
25412-5	Ammonium sulfate	2	5		
25414-3	(NH ₄) ₂ SO ₄ / MgSO ₄ ·6H ₂ O	2	10		limited solubility
25415-3	(NH ₄) ₃ PO ₄ / KH ₂ PO ₄ (50/50 molar ratio)	4	20		
25420-4	NH ₄ H ₂ PO ₄ -(NH ₄) ₃ PO ₄ /Na formate	2	2.5/2.5		
25420-1	NH ₄ H ₂ PO ₄ -(NH ₄) ₃ PO ₄ /MgAc	Not evaluated	2.5/2.5		precipitate observed cools upon dissolution
25414-1	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	7	20		
25415-7	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	4	10		
25415-6	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	4	5		
25433-6	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	2-4	5		
25408-1	Calcium acetate	2	20	-6	
25411-1	Calcium chloride	10	20	-13	
25418-1	Calcium chloride	9	10	-5	
25418-2	Calcium chloride	4-7	5	-2.5	
25433-5	Calcium chloride	4	5		repeat 25418-2
25433-8	Calcium chloride	4	5		new solution, repeat 25418-2
25411-6	Calcium formate	1	10	-4	limited solubility
25411-2	Calcium propionate	2	20		
25411-4A	Calcium sulfonate (Witco)	Not evaluated	5		insoluble
25411-4	Calcium sulfonate (Witco)	Not evaluated	20		insoluble
25406	Calcium-Magnesium acetate (3/7 mol. ratio)	9	20	-6	
25412-3	Calcium-Magnesium acetate (3/7 mol. ratio)	4	5	-1	
25415-8	Calcium-Magnesium acetate (3/7 mol. ratio)	4	10	-3	
25428-1	"Ice B Gon" Ca-Mg Acetate	9	20	-11	Chevron; solubility incomplete
25428-2	"Ice B Gon" Ca-Mg Acetate	7	10		Chevron; solubility incomplete
25428-3	"Ice B Gon" Ca-Mg Acetate	7	5		solubility incomplete
25433-4	"Ice B Gon" Ca-Mg Acetate	4	5		repeat 25428-3
25433-9	"Ice B Gon" Ca-Mg Acetate	4-7	5		repeat 25433-4
25434-4	"Ice B Gon" Ca-Mg Acetate	7	5	-2	new soln.: separates into layers
25412-10	Carbowax 300 (Union Carbide)	7	20	-3	Polyethylene oxide
25415-5	Carbowax 300	7	10		
25440-4	Carbowax 300	6	10		
25415-4	Carbowax 300	4	5		
25416-1	Ca-Na lignosulfonate (D-330-9)	4	20		Daishowa
25407-2	CMC Type 7L2P	2	5	0	Carboxymethyl cellulose (Hercules)
25408-5	Dipotassium hydrogen phosphate	8	20	-5	
25440-3	Dipotassium hydrogen phosphate	7	20		
25415-10	Dipotassium hydrogen phosphate	4	10		
25412-6	Dipotassium hydrogen phosphate	3	5		
25434-1	Ethylene glycol	6	5		Mobay
25411-5	Ferric sulfate	1	20	-5	solubility exothermic

.....
(1) Run at -20 °C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 12

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING

(Arranged Alphabetically)

-continued-

EXPERIMENT	SALT	SLUSH TEST ⁽¹⁾	CONC., WT. %	MEASURED FREEZING	COMMENTS
		RATING		POINT, °C	
25411-8	Igepal CD-630 (GAF detergent)	2	5		nonyl phenol + ethylene oxide
25425-1	Magnesium acetate	9	20		
25408-2	Magnesium acetate	9	20	-12	
25415-9	Magnesium acetate	7	10	-5	
25412-4	Magnesium acetate	4	5	-2	
25421-1	Magnesium acetate (MgAc)	4-7	5		
25419-3	MgAc/Carbowax 300	4-7	4.5/0.5		
25419-1	MgAc/Ca-Na lignosulfonate (D-330-9)	5.5	4.5/0.5		
25419-2	MgAc/CMC	4	4.5/0.5		
25420-7	MgAc/EMA 1103 (Monsanto)	7	4.5/0.5		ethylene maleic anhydride; ppt.
25425-3	MgAc/EMA 1103 (Monsanto)	5-7	4.5/0.5		ppt.-hazy
25420-3	MgAc/Gafac RE-610/MgO	7.5	4.5/0.5/0.1		solubility incomplete
25425-2	MgAc/Gafac RE-610/MgO	4-7	4.5/0.5/0.1		precipitate observed
25420-5	MgAc/Hyamine 1622 (Rohm & Haas)	4	4.5/0.5		
25426-1	MgAc/n-propyl H ₂ PO ₄ /NaOH	4-7	4.5/0.5/0.05		slight ppt.
25423-8	MgAc/polyvinyl methyl ether	Not evaluated	18/2		dissolves cold w/ great difficulty
25423-7	MgAc/polyvinyl methyl ether	7	9/1		dissolves cold
25420-6	MgAc/polyvinyl methyl ether	7	4.5/0.5		
25422-1	MgAc/polyvinyl methyl ether	7	4.5/0.5		five day freeze
25422-1A	MgAc/polyvinyl methyl ether	5	4.5/0.5		
25425-4	MgAc/polyvinyl methyl ether	4-7	4.5/0.5		hazy
25420-2	MgAc/Sipon ES-12	7	4.5/0.5		foamy (sodium laureth sulfate)
25424-3	MgAc/Urea	4	4.5/0.5		
25418-9	Magnesium formate	Not evaluated	20; 15		insoluble
25418-10	Magnesium formate	7	10	-3.5	limited solubility
25418-11	Magnesium formate	3	5		
25434-2	Mg lignosulfonate (Norlig Mg)	5	20		Daishowa
25440-7	Mg lignosulfonate (Norlig Mg)	2	20		repeat 25434-2; five day freeze
25440-6	Mg lignosulfonate (Norlig Mg)	2	10		five day freeze
25411-7	Magnesium sulfate	2	20	-5	solubility exothermic
25415-1	Sodium acetate	9	20	-10	
25418-5	Na acetate	8	10	-3	
25433-3	Na acetate	8	10		repeat 25418-5
25418-6	Na acetate	4-7	5	-2	
25434-6	Na acetate	3	5	-1	repeat--new solution
25402-3	Na carbonate	2	20	-2	
25401-1	NaCl	10	20	-16	
25433-1	NaCl	10	20		repeat 25401-1
25418-3	NaCl	10	10	-7	
25418-4	NaCl	8	5	-4	
25423-5	Na formate	10	20		
25407-4	Na formate	9	20	-13	
25433-2	Na formate	9	20		repeat--new solution
25418-7	Na formate	9.5	10	-5	
25422-2A	Na formate	5-7	5		
25422-2	Na formate	4-7	5		five day freeze
25418-8	Na formate	4-7	5	-3	

 (1) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 12

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING

(Arranged Alphabetically)

-continued-

EXPERIMENT	SALT	SLUSH TEST RATING	CONC., WT. %	MEASURED FREEZING POINT, °C	COMMENTS
25421-3	Na formate/Carbowax 300	4	4.5/0.5		
25421-2	Na formate/Daishowa D-330-9	2	4.5/0.5		
25423-2	Na formate/Dupenol C (Dupont)	7	4.5/0.5		Na lauryl sulfonate; foamy, ppt.
25425-5	Na formate/Dupenol C	2	4.5/0.5		ppt. formed
25434-7	Na formate/Dupenol C	7	4.5/0.5		new soln.: separates into layers
25422-3	Na formate/EMA 1103/NaOH	4-6	4.5/0.5/0.05		
25422-5	Na formate/Gafac RE-610/NaOH	7	4.5/0.5/0.05		
25425-6	Na formate/Gafac RE-610/NaOH	6-7	4.5/0.5/0.05		foamy
25422-7	Na formate/Hyamine 1622	4-7	4.5/0.5		
25423-4	Na formate/Igepal CO-630	5-7	4.5/0.5		foamy
25423-6	Na formate/Maldene 26158/NaOH	4-7	4.5/0.5/0.05		maleic anhydride/butadiene
25434-8	Na formate/Maldene 26158/NaOH	3	4.5/0.5/0.05		repeat 25423-6: new solution
25424-2	Na formate/polyvinyl methyl ether	Not evaluated	18/2		dissolves cold w/ great difficulty
25424-1	Na formate/polyvinyl methyl ether	7.5	9/1		dissolves cold w/ great difficulty
25422-6	Na formate/polyvinyl methyl ether	4	4.5/0.5		dissolves cold
25426-3	Na formate/polyvinyl methyl ether	2-3	4.5/0.5		dissolves cold
25426-2	NaCO ₂ H/n-propyl H ₂ PO ₄ /NaOH	7	4.75/0.25/0.025		
25423-3	NaCO ₂ H/n-propyl H ₂ PO ₄ /NaOH	7	4.5/0.5/0.05		clear ice layer at surface
25421-4	Na formate/Sipon ES-12	7	4.5/0.5		
25422-4	Na formate/Sipon ES-12 (Alcolac)	7	4.5/0.5		sodium laureth sulfate
25425-7	Na formate/Sipon ES-12 (Alcolac)	7	4.5/0.5		foamy
25423-1	Na formate/Urea	4-7	4.5/0.5		
25407-1	Na lignin sulfonate (Crown)	4	20	-2	
25416-2	Na lignosulfonate (CBOS-4)	2	20		Daishowa
25416-3	Na lignosulfonate (CBX-3)	1	20		Daishowa
25412-2	Na silicate	2	20		
25408-4	Na sulfate	2	5	-1	solubility limited
25421-5	Petroleum sulfonate (Witcamide 70)	Not evaluated	20		insoluble (Witco)
25412-9	Potassium bicarbonate	2	20	-6	cools upon dissolution
25412-1	Potassium carbonate (anhydrous)	9	20	-8	
25440-1	Potassium carbonate	8.5	20		repeat--new solution
25412-7	Potassium carbonate	3	5		
25416-4	Potassium dihydrogen phosphate	2	20		
25408-7	Potassium pyrophosphate	8	20	-4	
25440-2	Potassium pyrophosphate	7	20		repeat 25408-7
25418-12	Potassium pyrophosphate	3	10		
25418-13	Potassium pyrophosphate	2	5		
25433-7	Potassium pyrophosphate	2	5		repeat 25418-13
25402-7	Potassium silicate	2	20	-1	
25402-6A	Potassium sulfate/Mg sulfate (40/55)	Not evaluated	20		saturated; insoluble
25402-6B	Potassium sulfate/Mg sulfate (40/55)	2	10	-2	solubility incomplete
25408-6	Propylene glycol (Union Carbide)	9	20	-8	
25415-11	Propylene glycol	7	10		
25440-5	Propylene glycol	8	10		
25411-3	Propylene glycol (Union Carbide)	4	5	-2	
25402-5	Urea (U.S.P. crystal)	1	20	-8	
25415-2	Zinc acetate	2	20		

 (1) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 13

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING
(Arranged by Decreasing Efficiency)

EXPERIMENT	SALT	SLUSH TEST ⁽¹⁾ RATING	CONC., WT. %	MEASURED FREEZING POINT, °C	COMMENTS
25408-3	Deionized water (CONTROL)	2	100	0	
25401-1	NaCl	10	20	-16	
25433-1	NaCl	10	20		repeat 25401-1
25418-3	NaCl	10	10	-7	
25411-1	Calcium chloride	10	20	-13	
25423-5	Na formate	10	20		
25418-7	Na formate	9.5	10	-5	
25407-4	Na formate	9	20	-13	
25433-2	Na formate	9	20		repeat 25407-4
25418-1	Calcium chloride	9	10	-5	
25428-1	"Ice B Gon" Ca-Mg Acetate	9	20	-11	Chevron; solubility incomplete
25406	Calcium-Magnesium acetate (3/7 mol. ratio)	9	20	-6	
25415-1	Sodium acetate	9	20	-10	
25408-2	Magnesium acetate	9	20	-12	
25425-1	Magnesium acetate	9	20		
25408-6	Propylene glycol (Union Carbide)	9	20	-8	
25412-1	Potassium carbonate (anhydrous)	9	20	-8	
25440-1	Potassium carbonate (repeat 25412-1)	8.5	20		
25418-4	NaCl	8	5	-4	
25418-5	Na acetate	8	10		
25433-3	Na acetate (repeat 25418-5)	8	10		
25407-3	Ammonium sulfate	8	20	-6	
25408-7	Potassium pyrophosphate	8	20	-4	
25440-2	Potassium pyrophosphate (rpt. 25408-7)	7	20		
25408-5	Dipotassium hydrogen phosphate	8	20	-5	
25440-3	Dipotassium hydrogen phosphate	7	20		repeat 25408-5
25415-11	Propylene glycol	7	10		
25440-5	Propylene glycol	8	10		repeat 25415-11
25420-3	MgAc/Gafac RE-610/MgO	7.5	4.5/0.5/0.1		
25424-1	Na formate/polyvinyl methyl ether	7.5	9/1		
25412-10	Carbowax 300 (Union Carbide)	7	20	-3	
25415-5	Carbowax 300	7	10		
25414-1	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 mol. ratio)	7	20		cools upon dissolution
25415-9	Magnesium acetate (MgAc)	7	10	-5	
25420-7	MgAc/EMA 1103 (Monsanto)	7	4.5/0.5		ethylene maleic anhydride; ppt.
25423-7	MgAc/polyvinyl methyl ether	7	9/1		dissolves cold
25422-1	MgAc/polyvinyl methyl ether	7	4.5/0.5		five day freeze
25420-6	MgAc/polyvinyl methyl ether	7	4.5/0.5		
25420-2	MgAc/Sipon ES-12	7	4.5/0.5		foamy

 (1) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 13

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING(Arranged by Decreasing Efficiency)

-continued-

EXPERIMENT	SALT	SLUSH TEST ⁽¹⁾ RATING	CONC., WT. %	MEASURED FREEZING POINT, °C	COMMENTS
25428-2	"Ice B Gon" Ca-Mg Acetate	7	10		Chevron; solubility incomplete
25428-3	"Ice B Gon" Ca-Mg Acetate	7	5		Chevron; solubility incomplete
25433-4	"Ice B Gon" Ca-MgAc (repeat 25428-3)	4	5		
25433-9	"Ice B Gon" Ca-MgAc (repeat 25428-3)	4-7	5		
25434-4	"Ice B Gon" (repeat 25433-9)	7	5	-2	new solution: separates into layers
25423-2	Na formate/Duponol C (Dupont)	7	4.5/0.5		Na lauryl sulfonate; foamy, ppt.
25434-7	Na formate/Duponol C (repeat 25423-2)	7	4.5/0.5		new solution: separates into layers
25422-5	Na formate/Gafac RE-610/NaOH	7	4.5/0.5/0.05		
25425-6	Na formate/Gafac RE-610/NaOH	6-7	4.5/0.5/0.05		foamy
25421-4	Na formate/Sipon ES-12	7	4.5/0.5		
25422-4	Na formate/Sipon ES-12 (Alcolac)	7	4.5/0.5		sodium laureth sulfate
25425-7	Na formate/Sipon ES-12 (Alcolac)	7	4.5/0.5		foamy
25423-3	Na formate/n-propyl H ₂ PO ₄ /NaOH	7	4.5/0.5/0.05		clear ice layer at surface
25426-2	Na formate/n-propyl H ₂ PO ₄ /NaOH	7	4.75/0.25/0.025		
25418-10	Magnesium formate	7	10	-3.5	limited solubility
25434-1	Ethylene glycol	6	5		Mobay
25440-4	Carbowax 300 (Union Carbide)	6	10		
25422-2A	Na formate	5-7	5		
25423-4	Na formate/Igepal CO-630	5-7	4.5/0.5		foamy
25425-3	MgAc/EMA 1103	5-7	4.5/0.5		ppt.-hazy
25419-1	MgAc/Ca-Na lignosulfonate (D-330-9)	5.5	4.5/0.5		
25422-1A	MgAc/polyvinyl methyl ether	5	4.5/0.5		
25425-4	MgAc/polyvinyl methyl ether (repeat)	4-7	4.5/0.5		hazy
25434-2	Mg lignosulfonate (Norlig Mg)	5	20		Daishowa
25440-7	Mg lignosulfonate (Norlig Mg)	2	20		repeat 25434-2; five day freeze
25418-2	Calcium chloride	4-7	5	-2.5	
25433-5	CaCl ₂ (repeat 25418-2)	4	5		
25433-8	CaCl ₂ (repeat 25418-2)	4	5		
25421-1	Magnesium acetate (MgAc)	4-7	5		
25419-3	MgAc/Carbowax 300	4-7	4.5/0.5		
25425-2	MgAc/Gafac RE-610/MgO	4-7	4.5/0.5/0.1		ppt.
25426-1	MgAc/n-propyl H ₂ PO ₄ /NaOH	4-7	4.5/0.5/0.05		slight ppt.
25418-6	Na acetate	4-7	5	-2	
25434-6	Na acetate (repeat 25418-6)	3	5	-1	new solution
25418-8	Na formate	4-7	5	-3	
25422-2	Na formate	4-7	5		five day freeze
25422-7	Na formate/Hyamine 1622	4-7	4.5/0.5		
25423-6	Na formate/Maldene 26158/NaOH	4-7	4.5/0.5/0.05		maleic anhydride/butadiene
25434-8	Na formate/Maldene 26158/NaOH	3	4.5/0.5/0.05		repeat 25423-6: new solution
25423-1	Na formate/Urea	4-7	4.5/0.5		
25422-3	Na formate/EMA 1103/NaOH	4-6	4.5/0.5/0.05		

 (1) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 13

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING

(Arranged by Decreasing Efficiency)

-continued-

EXPERIMENT	SALT	SLUSH TEST (1) RATING	CONC., WT. %	MEASURED FREEZING POINT, °C	COMMENTS
25415-6	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	4	5		
25433-6	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	3-4	5		
25415-3	(NH ₄) ₃ PO ₄ /KH ₂ PO ₄ (50/50 molar ratio)	4	20		
25415-7	NH ₄ H ₂ PO ₄ /(NH ₄) ₃ PO ₄ (50/50 molar ratio)	4	10		
25415-8	Calcium-Magnesium acetate (3/7 mol.ratio)	4	10	-3	
25412-3	Calcium-Magnesium acetate (3/7 mol.ratio)	4	5	-1	
25416-1	Ca-Na lignosulfonate (D-330-9)	4	20		Daishowa
25415-4	Carbowax 300	4	5		
25412-4	Magnesium acetate (MgAc)	4	5	-2	
25419-2	MgAc/CMC	4	4.5/0.5		
25420-5	MgAc/Hyamime 1622 (Rohm & Haas)	4	4.5/0.5		
25424-3	MgAc/Urea	4	4.5/0.5		
25407-1	Na lignin sulfonate (Crown)	4	20	-2	
25422-6	Na formate/polyvinyl methyl ether	4	4.5/0.5		dissolves cold
25421-3	Na formate/Carbowax 300	4	4.5/0.5		
25415-10	Dipotassium hydrogen phosphate	4	10		
25411-3	Propylene glycol (Union Carbide)	4	5	-2	
25412-7	Potassium carbonate	3	5		
25418-12	Potassium pyrophosphate	3	10		
25412-6	Dipotassium hydrogen phosphate	3	5		
25418-11	Magnesium formate	3	5		
25434-3	Ammonium lignosulfonate (Lignosol TSD)	2.5	20		Daishowa
25414-2	Aluminum ammonium sulfate	2	5		
25412-5	Ammonium sulfate	2	5		
25414-3	Ammonium sulfate/ MgSO ₄ .6H ₂ O (50/50)	2	10		limited solubility
25408-1	Calcium acetate	2	20	-6	
25411-2	Calcium propionate	2	20		
25407-2	CMC Type 7L2P	2	5	0	Carboxymethyl cellulose (Hercules)
25411-8	Igepal CO-630 (GAF detergent)	2	5		nonyl phenol + ethylene oxide
25411-7	Magnesium sulfate	2	20	-5	solubility exothermic
25440-6	Mg lignosulfonate (Norlig Mg)	2	10		five day freeze
25402-3	Na carbonate	2	20	-2	
25426-3	Na formate/polyvinyl methyl ether	2-3	4.5/0.5		dissolves cold
25425-5	Na formate/Dupanol C	2	4.5/0.5		ppt. formed
25421-2	Na formate/Daishowa D-330-9	2	4.5/0.5		
25420-4	Na formate/NH ₄ H ₂ PO ₄ -(NH ₄) ₃ PO ₄	2	2.5/2.5		
25416-2	Na lignosulfonate (CBOS-4)	2	20		Daishowa
25412-2	Na silicate	2	20		
25408-4	Na sulfate	2	5	-1	solubility limited
25412-9	Potassium bicarbonate	2	20	-6	cools upon dissolution
25418-13	Potassium pyrophosphate	2	5		
25433-7	K ₄ P ₂ O ₇ (repeat 25418-13)	2	5		

 (1) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

TABLE 13

EFFECT OF ADDITIVES IN PREVENTING WATER FROM FREEZING
(Arranged by Decreasing Efficiency)
 -continued-

EXPERIMENT	SALT	SLUSH TEST ⁽¹⁾	CONC., WT. %	MEASURED FREEZING	COMMENTS
		RATING		POINT, °C	
25402-68	Potassium sulfate/Mg sulfate (40/55)	2	10	-2	solubility incomplete
25416-4	Potassium dihydrogen phosphate	2	20		
25402-7	Potassium silicate	2	20	-1	
25415-2	Zinc acetate	2	20		
25402-4	Ammonium dihydrogen phosphate	1	20	-5	
25411-6	Calcium formate	1	10	-4	limited solubility
25411-5	Ferric sulfate	1	20	-5	solubility exothermic
25416-3	Na lignosulfonate (CBX-3)	1	20		Daishowa
25402-5	Urea (U.S.P. crystal)	1	20	-8	
25412-8	Aluminum ammonium sulfate	Not evaluated	20		insoluble
25411-4	Calcium sulfonate (Witco)	Not evaluated	20		insoluble
25411-4A	Calcium sulfonate (Witco)	Not evaluated	5		insoluble
25420-1	MgAc/NH ₄ H ₂ PO ₄ -(NH ₄) ₃ PO ₄	Not evaluated	2.5/2.5		precipitate observed
25423-8	MgAc/polyvinyl methyl ether	Not evaluated	18/2		solubility limited cold
25418-9	Magnesium formate	Not evaluated	20; 15		insoluble
25424-2	Na formate/polyvinyl methyl ether	Not evaluated	18/2		solubility limited cold
25421-5	Petroleum sulfonate (Witcamide 70)	Not evaluated	20		insoluble
25402-6A	Potassium sulfate/Mg sulfate (40/55)	Not evaluated	20		saturated; insoluble

(1) Run at -20°C; See Table 1 for slush rating scale. High rating (6-10) is desirable.

TABLE 14

<u>SALT</u> (1)	SLUSH TEST RATING (2)	<u>PROMISING COMPOUNDS</u>		<u>COST/LB</u>
		<u>CONCENTRATION, WTX</u>	<u>MEASURED FREEZING POINT, °C</u>	
Deionized water (CONTROL)	2	-	0	
Calcium chloride	10	20	-13	0.11
Calcium chloride	9	10	-5	
Sodium chloride	10	20	-16	0.03
NaCl	10	10	-7	
NaCl	8	5	-4	
Calcium-Magnesium acetate (reagent)	9	20	-6	0.30
" " "	4	10		
" " "	4	5	-1	
"Ice B Gon" Ca-Mg Acetate (3)	9	20	-11	0.25
"Ice B Gon" Ca-Mg Acetate	7	10		
"Ice B Gon" Ca-Mg Acetate	7	5		
"Ice B Gon" (repeat)	7	5	-2	
"Ice B Gon" (repeat)	4	5		
"Ice B Gon" (repeat)	4-7	5		
Magnesium acetate (MgAc)	9	20	-12	
" "	7	10	-5	
" "	4	5	-2	
MgAc/Gafac RE-610/MgO	7.5	4.5/0.5/0.1		
MgAc/EMA 1103 (Monsanto)	7	4.5/0.5		
MgAc/polyvinyl methyl ether	7	4.5/0.5		
MgAc/Sipon ES-12	7	4.5/0.5		
Potassium carbonate	9	20	-8	0.39
" "	8.5	20		
Sodium acetate	9	20	-10	0.58
Na acetate	8	10		
Sodium formate	10	20	-13	0.20
Na formate (repeat)	9	20		
Na formate (repeat)	7	20		
Na formate	9.5	10	-5	
Na formate	4-7	5	-3	
Na formate/polyvinyl methyl ether	7.5	9/1		
Na formate/Dupanol C (Dupont)	7	4.5/0.5		
Na formate/Gafac RE-610/NaOH	7	4.5/0.5/0.05		
Na formate/Sipon ES-12 (Alcolac)	7	4.5/0.5		
Na formate/n-propyl H ₂ PO ₄ /NaOH	7	4.5/0.5/0.05		
Na formate/n-propyl H ₂ PO ₄ /NaOH	7	4.75/0.25/0.025		
Ammonium sulfate	8	20	-6	0.03
Dipotassium hydrogen phosphate	8	20	-5	0.09
Potassium pyrophosphate	8	20	-4	0.63
Magnesium formate	7	10	-3.5	
Carbowax 300	7	20	-3	
Carbowax 300	7	10		
Propylene glycol	9	20	-8	0.51
Propylene glycol	7	10		
Propylene glycol	4	5	-2	

(1) All materials are reagent grade unless specified otherwise

(2) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.

(3) Chevron

It is pertinent to note that the various co-additives have improved the Slush Test rating of both magnesium acetate and sodium formate at the five percent concentration.

The most promising materials were investigated for ice adhesion.

b. Percent Moisture Pick Up

It is quite critical to know the moisture pick up of the various salts. For example, Verglimit is essentially calcium chloride made slightly alkaline with sodium hydroxide and coated with polymerized linseed oil to prevent moisture absorption and caking in the bag.

A high moisture absorption by a deliquescent salt could lead to problems -- caking in the shipping bag if there were pinholes, expansion and cracking of the pavement and too high a rate of humidity could cause exudation of the additive leading to slippery road conditions.

Table 15 shows moisture pick up after 14 days at 75% relative humidity. At the bottom of this table, percent weight gain is presented for the same additives throughout the 14 day period. Calcium chloride, Verglimit, sodium formate and sodium acetate have the greatest moisture pick up. Ice-B-Gon, commercial CMA (calcium magnesium acetate from Chevron), has very much less weight gain even in comparison with CMA made by us in the lab. This greater moisture pick up of Springborn CMA is undoubtedly an artifact of the methods of preparation. As expected, pellets with smaller surface area have a lower weight gain than flake (see calcium chloride and Ice-B-Gon).

Carbowax 300, a low molecular weight polyethylene glycol, has a higher moisture pick up than does its higher molecular weight analog, Carbowax 6000.

The purpose of the repeat runs (Table 16) was to observe whether the rate of moisture pick up measured over an eight week period reached an equilibrium and levelled off. The data is also presented in Figures 9-19. There is some levelling off with all but Ice-B-Gon. The sodium chloride, Carbowax 300 and Poly G71-530 have a low rate of moisture adsorption. Poly G71-530 is a sucrose amine-based polyol which lowers ice adhesion to a moderate degree.

The repeat values (Tables 15 and 16) are significantly higher for calcium chloride, Verglimit and Ice-B-Gon pellets, and calcium chloride flake, whereas the repeat values are about the same for sodium chloride and Carbowax 300. Replication and careful control of the experimental procedure variables would be necessary to pin down the cause(s) of this variability.

The last two items in Table 16 are an attempt to encapsulate sodium formate to decrease the rate of moisture pick up, using a thermoplastic polyvinyl chloride (15999-2) and a thermoset polyester (26000-1) as encapsulants. There was no decrease in the rate and amount of moisture adsorbed by the encapsulated sodium formate.

TABLE 15

PERCENT WEIGHT GAIN OF SELECTED SAMPLES
AT 75 PERCENT RELATIVE HUMIDITY FOR 14 DAYS

	<u>Salt</u>	<u>Original Data</u>	<u>Repeat Data</u>
1	Calcium chloride - pellet (Prill) ⁽¹⁾	104	257
2	Calcium chloride - flake	147	-
3	Verglimit	140	208
4	Ice-B-Gon - pellet (Prill)	3	22
5	Ice-B-Gon - flake	10	-
6	Calcium acetate/Magnesium acetate ⁽³⁾ (3/7 molar ratio reagent grade mixture)	80	-
7	Sodium chloride	0.2	0.1
8	Sodium formate - flake ⁽²⁾	12	152
9	Magnesium acetate 4 H ₂ O	55	-
10	Carbowax 300	33	35
11	Carbowax 6000	0.1	-

Percent Weight Increase Vs Time

<u>Time</u>	<u>(1) CaCl₂ prills</u>	<u>(2) CaCl₂ flake</u>	<u>(4) Ice-B-Gon prills</u>	<u>(5) Ice-B-Gon flake</u>	<u>(8) Na Formate flake</u>	<u>(3) Verglimit</u>
2 days	17	32	1.3	6	1	37
5 days	38	71	1.9	8	2	76
7 days	53	100	2.2	9	4	101
14 days	104	147	2.7	10	12	140

<u>Time</u>	<u>(6) Na acetate powder</u>	<u>(6) Ca/Mg acetate flake</u>	<u>(9) Mg acetate crystal</u>	<u>(7) NaCl crystal</u>	<u>(10) Carbowax 300</u>	<u>(11) Carbowax 6000</u>
2 days	37	7	24	0.2	13	-0.2
6 days	98	24	50	0.2	24	-0.1
9 days	127	43	56	0.2	28	-0.1
14 days	157	80	55	0.2	33	0.3

-
- (1) A rounded pellet
 (2) Sodium lignosulfonate binder
 (3) Reagents mixed at 3/7 molar ratio

TABLE 16

PERCENT MOISTURE PICK-UP OF ADDITIVE ⁽¹⁾ VERSUS TIME AT 75 PERCENT RELATIVE HUMIDITY

Time	Calcium Chloride		Ice-R-Gon		Vergalmit		Sodium Formate Powder		Sodium Acetate Powder		Sodium Formate Flake		Carbowax 300		Sodium Chloride Crystal		Poly G71-530		25999-2		26000-1	
	Prills		Prills				Powder		Powder		Flake				Crystal							
vac dried wt.	0.1		-3		-14		-1		-29		-1		0.2		-0.5		(5)		-0.4		-0.3	
2 days	130		3		85		5		64		8		16		0		5		-		-	
1 week	221		8		167		49		66		96		27		0.1		11		73		95	
2 weeks	257		22		208		126		67		152		35		0.1		14		118		142	
3 weeks	244		26		205		144		66		141		30		0.1		12		130		157	
4 weeks	257		33		215		159		67		154		35		0.0		14		138		168	
5 weeks	267		44		224		171		68		161		37		0.0		14		143		173	
6 weeks	275		60		230		177		81		170		39		0.2		16		144		177	
7 weeks	279		79		237		186		94		176		40		0.1		16					
8 weeks	286		92		240		185		93		183		42		0.2		16					

.....

- (1) See Appendix B for a description of the additives
 (2) Sodium Formate (90%)/Sodium Lignin Sulfonate (10%)
 (3) Geon 121, Santicizer 160, Pareplex G-54, Ferro 1825 (binder) + Sodium Formate (77% Sodium Formate)
 (4) Reichold polyester 32-044, Benzoyl peroxide (binder) + Sodium Formate (92% Sodium Formate)
 (5) Not vacuum dried due to volatility of compound

Verapamil

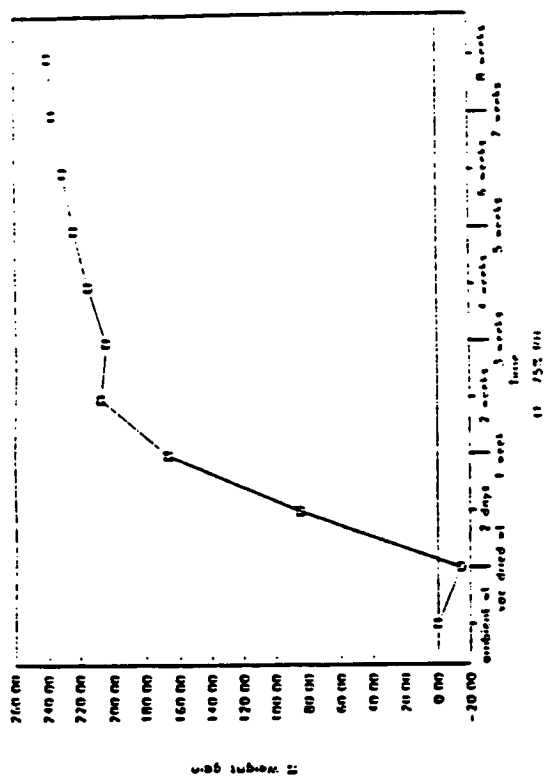


FIGURE 11

Sodium Formate (as received)

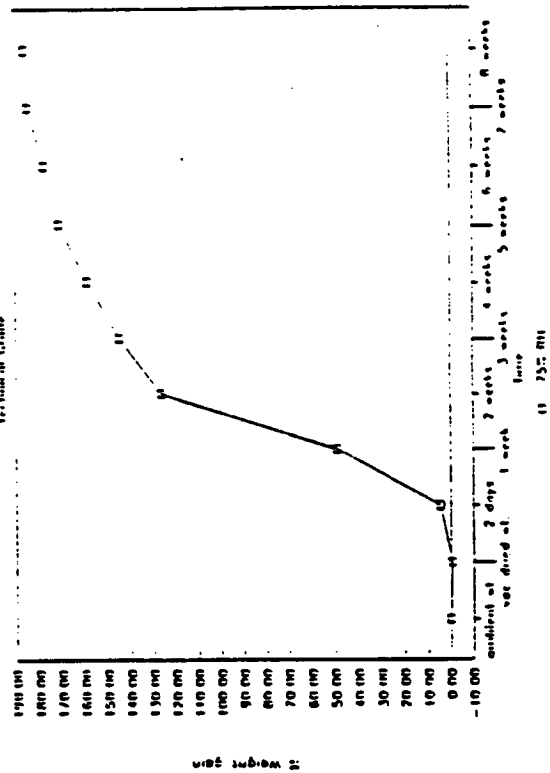


FIGURE 12

Calcium Chloride Pills

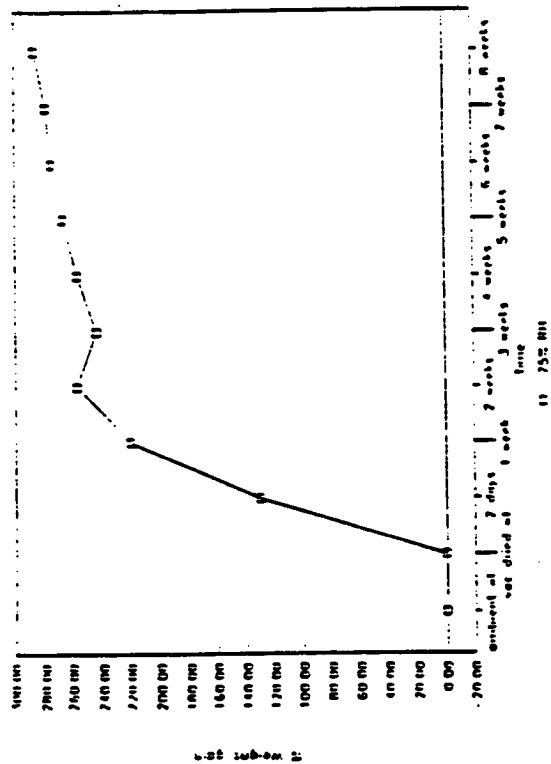


FIGURE 9

Calc B. Can Pills (Chevron)

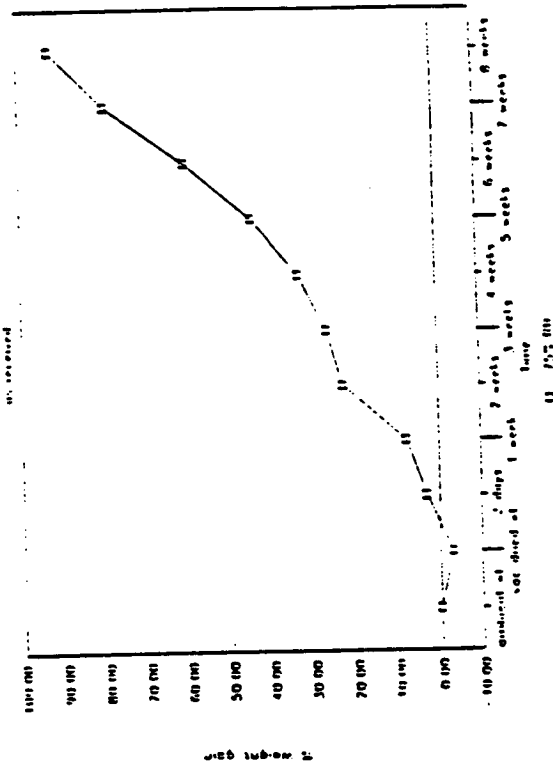


FIGURE 10

FIGURE 13

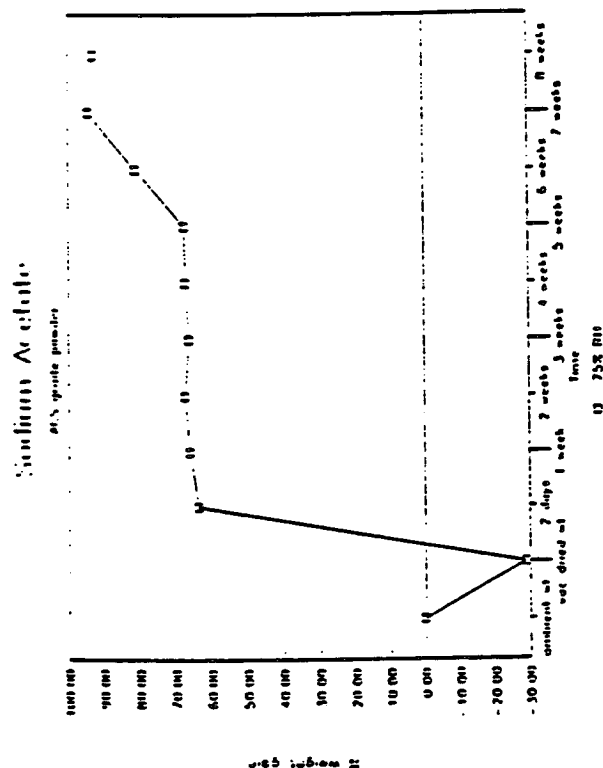


FIGURE 14

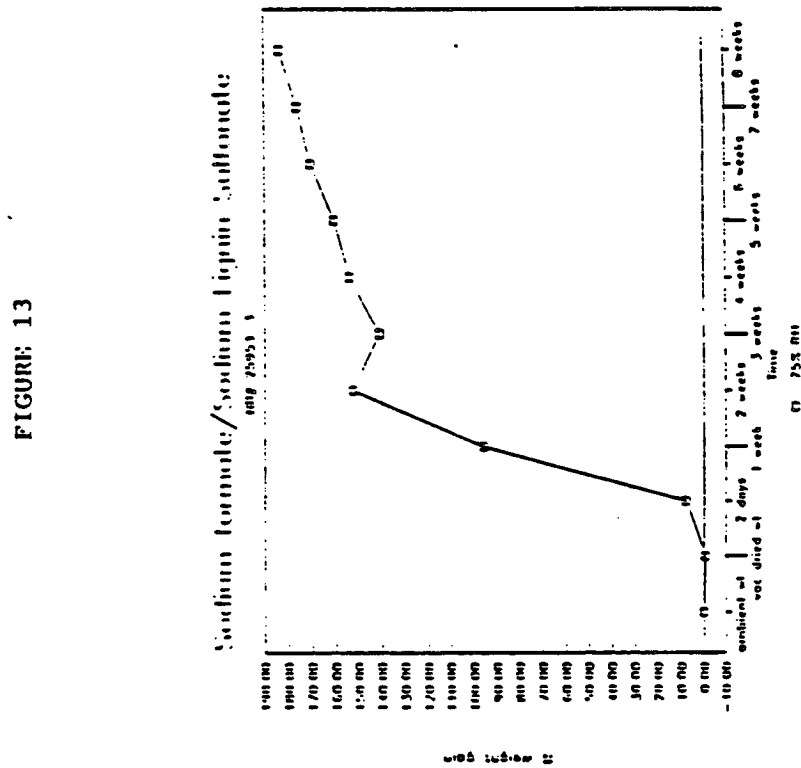


FIGURE 15

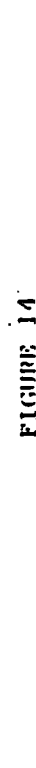


FIGURE 16

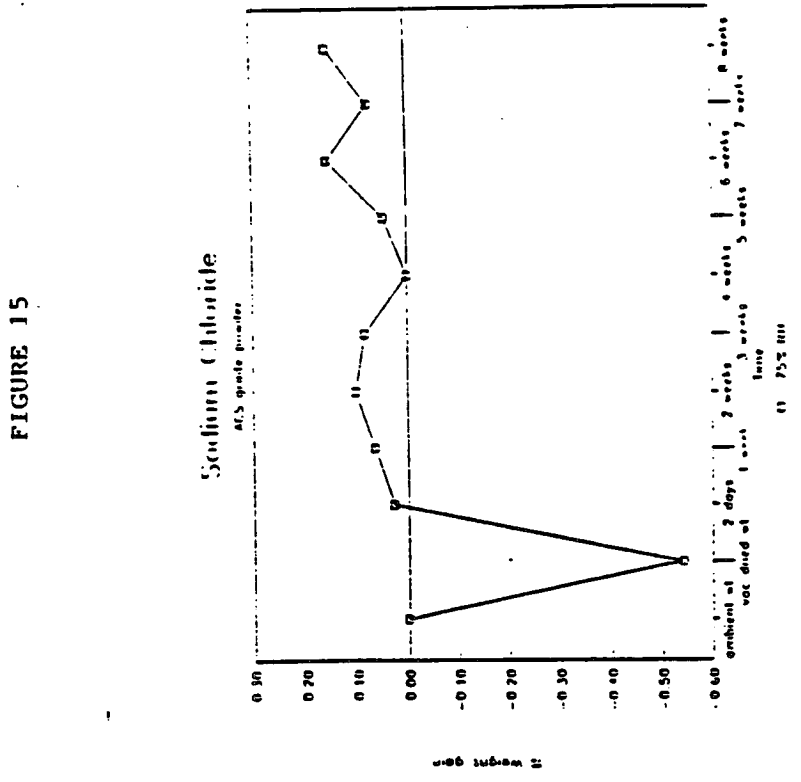


FIGURE 17



Poly G/1 5.30 (Offin Chem.)

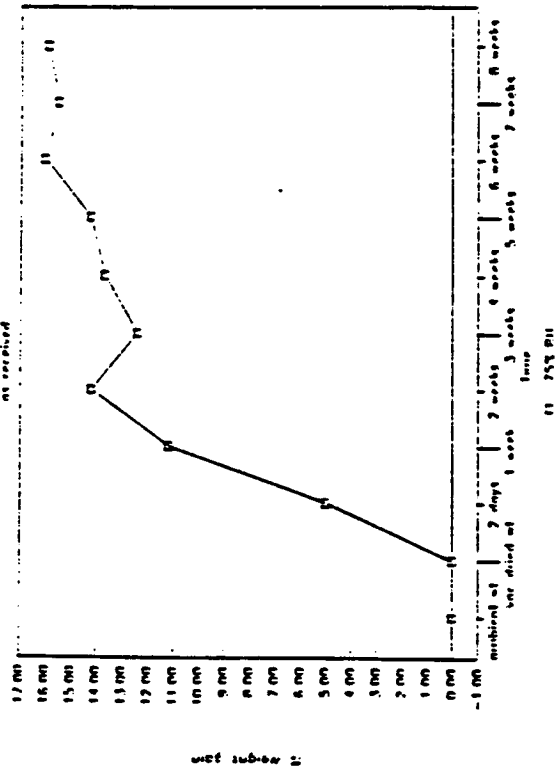


FIGURE 17

Formulation 25999-1

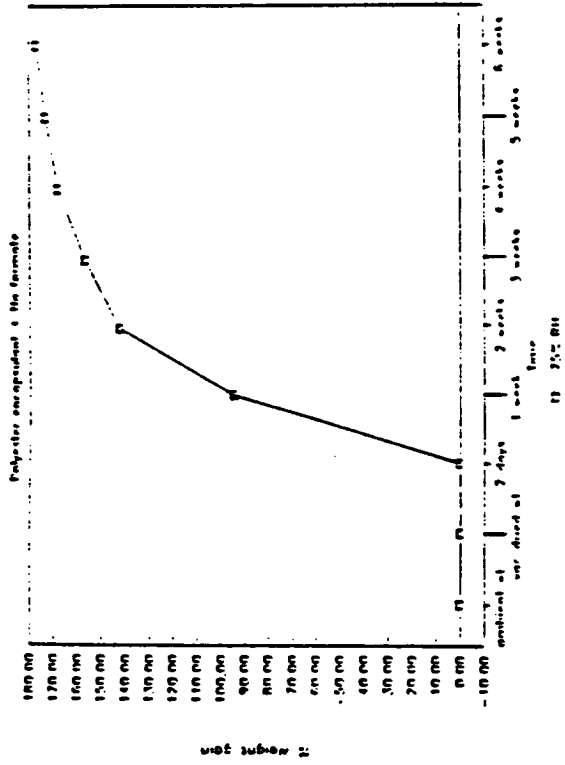


FIGURE 19

Formulation 25999-2

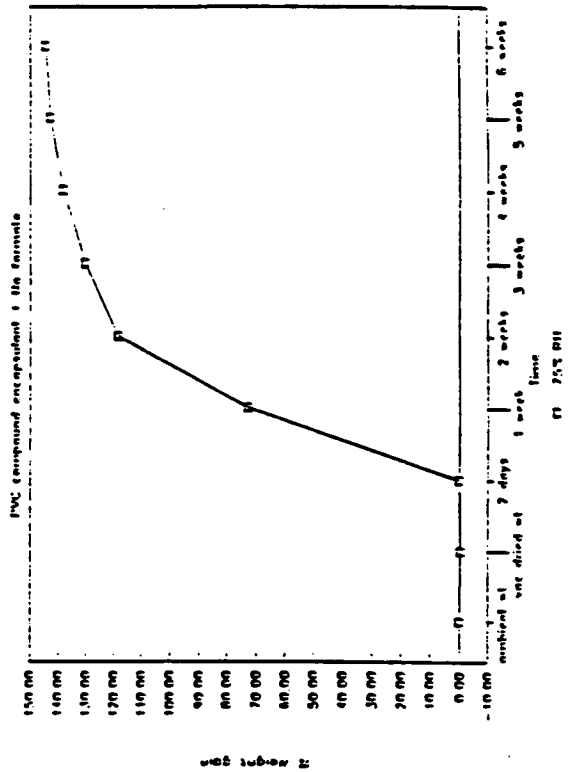


FIGURE 18

c. Effect of Organic Additives On Asphalt Concrete

It is critical that additives blended into the pavement do not attack the asphalt. Those additives whose solubility parameter is too close to that of the asphalt may very likely attack it.

As a first step in this program, 1/2" square pieces of asphalt concrete (AC) were immersed in various organic liquids in a test tube for two weeks and signs of attack noted.

Some of the organic liquids examined are shown in Tables 17 and 18. By organic liquids, we mean any monomeric or polymeric liquid.

Those oils that did not attack, or only slightly attack the AC, were used for ice adhesion and friction tests.

d. Ice Adhesion

Surface coated asphalt concrete briquettes

Water soluble additives with the best slush test rating, i.e. 7-10, were chosen for "surface coated" ice adhesion⁽¹⁾. Slush and ice adhesion tests were run at concentrations of 5, 10 and 20 percent in water. Solutions were coated on the asphalt concrete surface, an ice disk frozen on (see Section C.2. "Test Methods"), and ice adhesion measured. In Table 19, the additives are arranged in order of increasing ice adhesion at the 10% level. At 5%, most materials are poor, and at 20%, most are too good to differentiate ice adhesion characteristics. Thus, a 10% solution provides the most useful information.

The best additives for ice adhesion are sodium formate, ethylene glycol, sodium chloride and propylene glycol, followed by Ice-B-Gon and calcium chloride.

Additional salts were screened for ice adhesion, Table 20, and two, calcium nitrate and potassium thiocyanate (recommended by Prof. Stuart of the University of Missouri), were equal in efficiency to sodium acetate and sodium formate. However, calcium nitrate could be potentially explosive in the presence of organic compounds at the temperature of AC preparation, and potassium thiocyanate is too expensive (\$1.50/lb.).

Although every additive with low ice adhesion had a high slush test rating, there were two additives--ammonium sulfate and dipotassium acid phosphate--with a high slush rating but high ice adhesion.

A series of oils, primarily water insoluble, were screened for ice adhesion on the surface of the AC briquette (Table 21). Two different oil coating-ice adhesion procedures were used. The second procedure (Table 21, footnote "3") was chosen for all subsequent work because oil left on the briquette for 8 days (footnote "2") diffused at various rates into the briquette, presenting varying amounts of oil on the surface.

- (1) As an initial screening procedure, the additives were coated on the surface of the asphalt concrete briquettes.

EFFECT OF PLASTICIZERS ON ASPHALT CONCRETE

Plasticizer	Effect of Two Weeks Immersion
1. N-t-Butyl-P-Toluene Sulfonamide(2) (Monsanto)	Sl. attack hot
2. N-t-Dodecyl-P-Toluene Sulfonamide (Monsanto)	Sl. attack
3. N,N-D1-t-Butyl-P-Toluene Sulfonamide (Monsanto)	OK, sl. brown color
4. Myracet 707 Distilled Acetylated Monoglycerides D1-18 No. 71 (Eastman)	Bare stones; dissolved
5. Drapex 6.8 Epoxidized Soybean Oil (Vitco Chemical)	Some attack
6. Santolite MHP Aryl Sulfonamide-Formaldehyde Resin(2) (Monsanto)	OK, but when heated and stirred, breaks up
7. Flexol Plasticizer 3GH-Triethylene Glycol Di-2-Ethylbutyrate (Union Carbide)	Sl. attack, some color, dust
8. Flexol Plasticizer EP8-Polymeric Epoxy Plasticizer (Union Carbide)	Only stones remain or; dissolved
9. Eastman SA1B-Sucrose Acetate Isobutyrate(1)	OK, no attack
10. Admex S23 (Ashland Chemical) Polyester	No attack
11. Admex 711 (Ashland Chemical) Polyester	SL, attack - color
12. Hydricin P-10 (CAS Chemical, Inc.) Ricinoleic Acid	SL, attack - color
13. Plastolein 9785 Polymeric Plasticizer (Emery) Polyester	OK, no attack
14. Acryloid 710 (Rohm & Haas) Polyacrylate	OK, no attack
15. Paraplex G-30 (Rohm & Haas) Polyester	OK, no attack
16. Paraplex G-50 (Rohm & Haas) Polyester	No attack
17. Paraplex G-54 (Rohm & Haas) Polyester	No attack
18. Mazola 100% Pure Corn Oil	Color, excessive attack
19. Linseed Oil	Attacks surface
20. Santicizer 160 - Butyl Benzyl Phthalate (Monsanto)	Very sl. attack
21. Dow D.E.R. 331 - Bisphenol Diepoxide(1)	No attack

 (1) Very viscous
 (2) Solid

TABLE 18

EFFECT OF ORGANIC LIQUIDS ON ASPHALT CONCRETE

<u>Organic Liquid Additive</u>		<u>Effect of Two Weeks Immersion</u>
1	Indopol L-50	Dissolves
2	KeijenFlex 8	Minimal Attacking
3	Plasthall 200 DBEP	Dissolves
4	Plasthall 1 DIBA	Dissolves
5	Slipeze	Dissolves
6	Fyrol 6	No Attack
7	Fyrol DMMP	Dissolves
8	Dow 200 Silicone Oil	No Attack
9	Poly-G 74-376	No Attack
10	Poly-G 75-442	No Attack
11	Hallcomid M-8-10	Dissolves
12	KP-140 TBEP	Dissolves
13	Plasthall P-670	Minimal Attack
14	Plasthall P-550	Minimal Attack
15	Tegmer 804	Dissolves

TABLE 1c

ICE ADHESION⁽¹⁾ AND SLUSH RATING OF WATER SOLUBLE ADDITIVES
AT -20°C: OIL AND SALT SURFACE COATED⁽²⁾ ASPHALT CONCRETE

Additive	Slush Rating ⁽³⁾			Ice Adhesion Shear Strength (psi) ⁽¹⁾			Cost \$/lb.
	5%	10%	20% ⁽⁴⁾	5%	10%	20% ⁽⁴⁾	
Sodium Formate	4-7	9	9	25	3	1	0.20
Ethylene Glycol	6	8	9	15	3	0.7	0.51
Sodium Chloride	8	10	10	16	4	2	0.03
Propylene Glycol ⁽⁵⁾	4	7	9	22	5	0.7	0.51
Ice-B-Gon	7	7	9	48	9	1	0.30
Calcium Chloride	4	9	10	23	10	1	0.06
Magnesium Acetate	4-7	8	9	43	14	2	(6)
Sodium Acetate	4-7	8	9	>64	17	0.7	0.58
Dipropylene Glycol ⁽⁷⁾	-	8	-	-	28	-	0.41
Carbowax 300	4	7	7	>64	43	4	0.80

-
- (1) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -20°C. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure
- (2) Ice adhesion test for salts and oils is previously described in Section C.2.a. For ice adhesion tests with oils, 1.5 g of the liquid is spread over the four inch diameter AC plug, which is put in the freezer immediately for six hours, and ice is frozen on the surface, as previously described. The plug is kept in the freezer overnight, and ice adhesion is run in quintuplicate the next morning.
- (3) Run at -20°C; See Table 1 for slush rating scale. High rating (8-10) is desirable.
- (4) Additive concentration in water
- (5) Calcium magnesium acetate
- (6) \$1.30-1.60/lb. as solid; \$0.35/lb. as 50% solution
- (7) Polyethylene glycol, (Union Carbide)

TABLE 20

ICE ADHESION⁽¹⁾ OF INORGANIC ADDITIVES
SURFACE COATED ONTO ASPHALT CONCRETE

<u>Additive</u>	<u>Ice Adhesion Shear Strength^(1,2,3) (psi)</u>	<u>Slush Test^(3,4) Rating</u>
Sodium Chloride (Control)	2	10
Calcium Nitrate ⁽⁵⁾	1	8
Potassium Thiocyanate ⁽⁶⁾	3	9
Ammonium Sulfate	>64	8
Magnesium Lignosulfonate	>64	2
Calcium Sodium Lignosulfonate	>64	-
Sodium Lignosulfonate	>64	2
Calcium Acetate	>64	2
Dipotassium Acid Phosphate	>64	8
Urea	>64	1
Potassium Acid Carbonate	>64	2
Magnesium Sulfate	>64	2

- (1) Ice adhesion test for salts and oils is previously described in Section C.2.a. Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -20°C. Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure
- (2) Average of five tests
- (3) Additive concentration: 20% in water. Run at -20°C.
- (4) See Table 1 for slush rating scale. High rating (8-10) is desirable.
- (5) 28.8% hydrate; \$.70/lb.
- (6) \$1.50/lb.

TABLE 21

ICE ADHESION AT -20°C OF ASPHALT CONCRETE
SURFACE COATED WITH OILS

Additive by Trade Name	Ice Adhesion ⁽¹⁾ Shear Strength (psi)		Commercial Nature of Additive
	Procedure A ⁽²⁾	Procedure B ⁽³⁾	
Paraplex G-54	36	15	Polyester
Santicizer 160	48	25	Butyl Benzyl Phthalate
Acryloid 710	>64	-	Polyacrylate
Eastman SAIB	>64	>64	Sucrose Acetate Butyrate
Gantrez M154	>64	-	Polyvinyl Methyl Ether
Plastolein 9789	>64	-	Polyester Plasticizer
Paraplex G25	>64	-	Polyester Plasticizer
Admex 760	>64	-	Polyester Plasticizer
D.E.R. 331	>64	>64	Epoxy (Bisphenol Diepoxide)
Indopol H-1500	>64	-	Polyisobutylene

-
- (1) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -20°C. Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure
- (2) Procedure A: Oil left on the four inch diameter briquette for eight days at room temperature; tested at -20°C.
- (3) Procedure B: 1.5 g of oil spread on surface of four inch O.D. briquette, immediately put in freezer at -20°C for six hours, ice is frozen on, allowed to sit overnight and ice adhesion run in quintuplicate the next morning at -20°C.

Only Paraplex G54, an adipate polyester, and Santicizer 160, butyl benzyl phthalate, were promising.

Modified asphalt concrete briquettes

Surface coating of the AC briquettes allowed screening of a number of additives relatively quickly. However, it is essential that the additives be blended into the AC and that ice adhesion be examined on modified AC briquettes.

In the initial work with modified briquettes containing additives, ice adhesion was run at -20°C , the same temperature at which the surface screening test was run. However, all ice adhesions of compounded briquettes gave values greater than 64 lbs./in².

The briquettes were retested at -5°C , a more realistic winter temperature for most of the U.S. The ice adhesion of the control without additives was still greater than 64 lbs./in² (psi). However, ice adhesion values of all briquettes with additives in Table 22 now range from <1 to 39 psi shear strength.

Table 22 also reveals that salts in powder form are as effective as salts in flake or pellet form.

Two salts, sodium acetate and sodium formate, gave promising results. These are explored in more detail in Table 23. Both salts were used as powders and with various binder-encapsulants to convert the powder into flake. An earlier binder, carboxymethyl cellulose, was hydrophilic and caused eventual cracking of the briquette.

The binders in Table 23 did not cause cracking.

Table 23 also reveals that sodium acetate is equally effective as powder as it is in flake form. However, one binder--maldene (butadiene maleic copolymer)--gave the lowest ice adhesion with both sodium acetate and sodium formate.

In polyethylene film technology, solid long-chain amides are used as slip agents. These materials are partially incompatible with the polyethylene, exude to the surface and make the film slippery. This slipperiness produces a faster film extrusion rate and prevents the film from sticking to itself.

It was theorized that these same long-chain amides would be partially incompatible with asphalt, exude to the surface, and prevent ice adhesion. However, none of the amides decreased ice adhesion (Table 24).

A number of additional oils of varying structure were evaluated (Table 25). A few, Plasthall P-55 (polyester glutarate), Ketjenflex 8 (N-alkyl p-toluenesulfonamide), and Poly G 75-442 (methyl glucoside polyphenylene oxide) showed moderate lowering of ice adhesion. One, Fyrol 6, a phosphated polyol, dropped ice adhesion to one psi. This latter material is unacceptable because of high cost and harmful effect on rubber.

TABLE 22

EFFECT OF PHYSICAL FORM OF ADDITIVE AND TEST TEMPERATURE
ON ICE ADHESION OF ASPHALT CONCRETE BRIQUETTES
MODIFIED WITH SALTS AND OILS - METHOD A⁽¹⁾

Additive ⁽²⁾	Binder ⁽³⁾	Ice Adhesion Shear ⁽⁴⁾ Strength (psi)	
		-5°C	-20°C
Control	-	>64	>64
Sodium Formate (Powder)	-	17	>64
Verglimit ⁽⁵⁾ (Flake)	-	8	>64
Sodium Acetate (Powder)	-	5	>64
Sodium Acetate (Flake)	Lignin ⁽⁶⁾	7	>64
Sodium Acetate (Flake)	EMA ⁽⁷⁾	39	>64
Sodium Acetate (Flake)	Carbowax 300 ⁽⁸⁾	1	>64
Carbowax 300 (Liquid)	-	0.1	>64
Ice-B-Gon (Powder)	-	8	>64
Ice-B-Gon (Pellets)	-	31	>64

-
- (1) See Table 8 and previous discussion for Method A procedure
- (2) Salts at 6.4%; oils at 3% on the aggregate.
- (3) Binder used to put additive in flake form.
- (4) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure
- (5) Commercial flake from P.K. Innovation.
- (6) Lignin sulfonate.
- (7) Ethylene maleic anhydride copolymer.
- (8) Polyethylene glycol.

TABLE 23

ICE ADHESION OF BRIQUETTES MODIFIED
WITH SODIUM ACETATE AND SODIUM FORMATE - METHOD A ⁽¹⁾

Additive ⁽²⁾	Binder ⁽³⁾	Ice Adhesion ⁽⁴⁾ Shear Strength at -5°C (psi)
Sodium Acetate	None - Powder	5
	Maldene ⁽⁵⁾	0
	Carbowax 300 ⁽⁶⁾	1
	Lignin ⁽⁷⁾	7
	EMA ⁽⁸⁾	39
Sodium Formate	None - Powder	17
	Maldene	0.2
	Lignin	3

-
- (1) See Table 8 and previous discussion for Method A procedure
 - (2) Additives at 6.4% on the aggregate.
 - (3) Binder used to put additive in flake form.
 - (4) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure
 - (5) Butadiene Maleic Copolymer
 - (6) Polyethylene Glycol
 - (7) Lignin Sulfonate
 - (8) Ethylene Maleic Anhydride Copolymer

TABLE 24

ICE ADHESION OF BRIQUETTES MODIFIED
WITH FATTY AMIDES - METHOD A⁽¹⁾

<u>Additive</u> ⁽²⁾	<u>Ice Adhesion</u> ⁽³⁾ <u>Shear Strength</u> <u>(psi)</u>
Eramid	>64
Stearamide	>64
Oleamide	>64
Lipowax C	>64
Armid H7	>64
Kenamide P-181	>64

-
- (1) See Table 8 and previous discussion for Method A procedure
 - (2) Additives compounded into the briquette at 3% on the aggregate.
See Appendix B for description of additives.
 - (3) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -5°C. Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure

TABLE 25

ICE ADHESION OF ASPHALT CONCRETE BRIQUETTES
MODIFIED WITH ADDITIONAL OILS - METHOD A⁽¹⁾

<u>Additive</u> ⁽²⁾	<u>Ice Adhesion</u> ⁽³⁾		<u>Chemical Nature</u>
	<u>Shear Strength</u> <u>at -5°C (psi)</u>		
Paraplex G25	>64	(4)	
Indopol H-1500	>64	(4)	
Pluronic L61	>64	(4)	
Plastolein 9717	>64	(4)	
Benzoflex P200	>64		Polyethylene glycol di-benzoate
Triacetin	>64		Glycerin triacetate
Teracol 1000	>51		Glycol Mol. Wt. 1000
Citraflex A-2	>51		Triethyl citrate
Citroflex 2	>64		Acetyl triethyl citrate
Plasthall 643	>64		Polymeric glycol adipate
Ketjenflex MS-80	>64		Toluene sulfonamide condensate with formaldehyde
Plasthall P-550	34		Polyester glutarate
Plasthall P-670	48		Adipate polyester
Poly G 74-376	45		Sucrose polyphenylene oxide
Ketjenflex 8	24		N-alkyl p-toluenesulfonamide
Poly G 75-442	27		Methyl glucoside polyphenylene oxide
Fyrol 6	1		Phosphated polyol

-
- (1) See Table 8 and previous discussion for Method A procedure
- (2) Additives compounded into the AC mix design Method A at 3% on the aggregate.
- (3) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -5°C. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure
- (4) See Appendix B

All additives that showed promise by the surface screening test were compounded into briquettes. In Table 26, these additives are divided into three groups -- water soluble, hydrophilic (partially water soluble), and water insoluble. The first group contains both salts and organic liquids, referred to as oils. All ice adhesion measurements were made at -5°C .

All the water soluble additives, both salts and oils blended into the briquette, decreased ice adhesion.

For the partially water soluble group, one material -- Poly G71-530, a sucrose amine polyol -- lowered ice adhesion. Flexol 4G0 cracked the briquette, and ice adhesion was not measured. Poly PPG 425 gave a small improvement. Poly PPG 425 is merely a higher molecular weight version of propylene glycol, an effective water soluble additive.

None of the water insoluble additives were promising.

e. Friction

In our early work, friction by British Pendulum was measured on a number of oils, (Table 27), a few of which had promising ice adhesions on surface coated briquettes. Four of the oils had a dry friction at or above that of the control. Three oils gave a water wet friction close to the control, while on some of the others, there was significant loss of friction.

Friction (British Pendulum) (BPN) of a number of briquettes with blended additives is shown in Table 28. The dry friction of the control is 49 and wet friction is 35. Verglimit (commercial system composed of calcium chloride presumably coated with polymerized linseed oil), even "dry", had a friction of 34. The salts, Ice-B-Gon, sodium formate, and three of the sodium acetates, gave approximately the same friction as the control. Sodium acetate powder and sodium acetate with Carbowax 300 binder gave lower frictions. Several of the oils did not lower friction. On the other hand, Carbowax 300 did decrease friction considerably. What is interesting is that, in a compound containing both Carbowax and fly ash (Table 28), the friction is increased, indicating a possible method of increasing friction, if necessary.

These are initial friction results run on only one briquette.

In the section on replication, BP friction was run on a variety of additive modified briquettes using five briquettes per additive and five tests per briquette. This data will be analyzed statistically.

f. New Aggregate Design and Marshall Stability

A Class I Connecticut specification has a Marshall Stability of 1200 and a flow of 8-15 (Table 29). Our early work (Table 29) indicated that, in general, most briquettes containing oils at the 3% level met that specification.

TABLE 26

SUMMARY OF BEST SYSTEMS:
ICE ADHESION AT -5°C OF ASPHALT CONCRETE
BRIQUETTES CONTAINING ADDITIVES - METHOD A ⁽¹⁾

Additives ⁽³⁾	Slush ⁽⁴⁾ Rating	Ice Adhesion Shear Strength ⁽²⁾		Price \$/lb ⁽⁷⁾
		Surface Impregnated ⁽⁵⁾ Briquette (psi)	Compounded Into Briquette ⁽⁶⁾ (psi)	
<u>Water Soluble</u>				
Sodium Formate ⁽⁸⁾	9	3 ⁽⁹⁾	17	.20
Sodium Acetate ⁽⁸⁾	8	16 ⁽⁹⁾	5	.58
Ice-B-Gon ⁽¹⁰⁾	7	9 ⁽⁹⁾	8	.34
Triethylene Glycol	8	-	0.5	.54
Ethylene Glycol	8	3	0.6	.32
Propylene Glycol	7	4	14	.56
Dipropylene Glycol	8	28	22	.57
Tetraethylene Glycol	-	-	9	.88
Carbowax 300	7	43	0.1	.73
<u>Hydrophilic ⁽¹¹⁾ Polymers</u>				
Flexol 4GO	-	4	NG ⁽¹²⁾	1.45
Poly G71-530	-	9	23	0.85
Pluracol 824	-	15	>64	1.02
Poly PPG 425	-	28	51	.89
BASF 380	-	47	>64	1.05
<u>Water Insoluble Polymers</u>				
DC 200-1000 CPS				
Silicone Oil	-	6	>64	-
Paraplex G54	-	15	-	1.26
Indopol 150	-	25	53	.43
Santicizer 160	-	25	NG >64	.71

- (1) See Table 8 and previous discussion for Method A procedure
- (2) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface at -5°C. Measuring device: Chatillon digital force gauge model DFGRS-50, ±0.25% full scale, ±1 least sign. figure
- (3) See Appendix B for additive description.
- (4) See Table 1 for slush rating scale. High rating (8-10) is desirable.
- (5) Liquid additive coated on surface at 1.5 g/4 inch diameter sample
- (6) AC-20 asphalt concrete with additives blended in per procedure. Salts at 6.4%; oils at 3% on the aggregate.
- (7) Bulk quantity price.
- (8) Powder.
- (9) 10% in water.
- (10) Calcium magnesium acetate.
- (11) Partially water soluble.
- (12) NG - No good; strength degraded.

TABLE 27

BRITISH PENDULUM FRICTION ON ASPHALT CONCRETE
COATED WITH VARIOUS OILS

<u>Additive</u> (1)	BPN Dry Friction: <u>Additive</u> (2)	BPN Wet Friction: <u>Additive</u> and Water (3)
None (Controls)	45	35
Acryloid 710	47	32
Eastman SAIB	50	30
D.E.R. 331	40	29
Indopol H-1500	54	26
Santicizer 160	26	25
Gantrez M-154	53	22
Paraplex G-54	40	21
Paraplex G-25	43	20
Admex 760	39	20
Plastolein 9789-A	38	20

(1) See Appendix B

(2) Liquid additive coated on surface at 1.5 g/4 inch diameter sample

(3) Same as (1) plus surface wet with water

TABLE 28

FRICTION BY THE BRITISH PENDULUM NUMBER (BPN) OF ASPHALT CONCRETE
BRIQUETTES CONTAINING ADDITIVES - METHOD A⁽¹⁾

<u>Additives⁽²⁾</u>	<u>Dry⁽³⁾</u>	<u>Wet^(3,4)</u>
Control (None)	49	35
Verglimit	34	31
Ice-B-Gon (Powder)	48	37
Ice-B-Gon (Pellets)	49	34
Na Formate	50	35
NaAc - EMA	49	35
NaAc (Powder)	39	34
NaAc - Carbowax 300 binder	40	33
NaAc - Lignin Sulfonate	49	34
Pluracol 824	48	34
Propylene Glycol	46	33
Carbowax 300	35	35
Carbowax 300 & 4.3% Flyash ⁽⁵⁾	45	35
Paraplex G54	50	33
Dipropylene Glycol	45	32
Poly G71-530	44	36
Poly PPG 425	42	34

- (1) See Table 8 and previous discussion for Method A procedure
 (2) See Appendix B
 (3) Contact path 2.375 inches
 (4) Wet with water
 (5) Hartford flyash derived from refuse

TABLE 29

(1) (2)
MARSHALL STABILITY OF OIL MODIFIED BRIQUETTES - METHOD A

Experiment #	Type Oil	% Oil	Stability	Flow	Comments
25980-1	Paraplex G54	3	1210	12.5	G54 mixed in before asphalt
25982-1	Paraplex G54	5	462	18	G54 mixed in before asphalt
25987-1	Santicizer 160	3	1015	9	Oil mixed in after asphalt ⁽³⁾
25987-2	Pluracol 824	3	1341	11	Oil mixed in after asphalt
25988-3	Paraplex G54	3	2138	15.5	G54 and flyash ⁽⁴⁾ mixed and added after asphalt
Class I ⁽⁵⁾	CT Spec	-	>1200	8-15	

 (1) Run by Professor Jack Stephens, University of Connecticut

(2) See Table 8 and previous discussion for Method A procedure

(3) All briquettes hereafter were made with the oil added after the asphalt

(4) Hartford fly ash derived from refuse

(5) Connecticut specification

With 3% Paraplex G54, it doesn't matter whether the G54 is added before or after the asphalt. The results with 3% Pluracol 824 are also good. Physical properties have dropped somewhat with 3% Santicizer 160. Increasing percent additive to 5% G54 ruins the briquette; in fact, oil is exuding immediately after the briquette is prepared.

In all subsequent runs, the oil was added to the briquette after the asphalt. Note the fly ash run wherein the flow is good but the Marshall stability is high.

A larger list of oils and salts that lowered ice adhesion were submitted for the Marshall test (Table 30). Again, all of the briquettes containing these additives met the Marshall spec. All oils were incorporated at 3% on the aggregate, and all salts at 6.4% on the aggregate.

The procedure for briquette preparation was changed to Method E. To have as smooth a surface as possible, the Method B mix design was based on the upper (dashed line) curve of the Monosmith aggregate gradation chart. This is the smallest aggregate gradation within specs (Table 10).

Assuming that a finer aggregate would need a larger amount of asphalt, three briquettes were prepared at 5.47% asphalt (used up to now) and three at 5.7% asphalt (also within specs). The new formulation is shown in Table 10, and the Marshall results in Table 31. Thus, both 5.47% and 5.7% asphalt gave Marshall results within specification.

Briquettes containing two salts and four oils, that gave promising ice adhesion, were tested for Marshall Stability (Table 32). Three of the oils and both salts passed the minimum specification; the tetraethylene glycol did not. These were made using 5.7% asphalt.

g. Effect of Continued Washing of the AC Briquette On Ice Adhesion

Another essential criteria is that the ice releasing effect of the additives be long-lasting. As with Verlimit, water soluble or partially water soluble additives can be released to the surface of the pavement in two ways -- extraction by rain or melting ice, and abrasion by traffic exposing new surface.

Table 33 describes the former. As mentioned in the Test Methods (Section B), the briquette is repeatedly washed and retested for ice adhesion. The first data column in Table 33 provides initial ice adhesion before washing. Each of the next four columns shows ice adhesion successively after one through four washes. This is an arbitrary procedure, and obviously many more than four washes are needed to test long range persistence of the additive.

TABLE 30

MARSHALL TEST OF OIL AND SALT MODIFIED BRIQUETTES - METHOD A⁽¹⁾

	Flow	Marshall Stability ⁽²⁾
Sodium Formate	15	2500
Sodium Acetate	14.5	2576
Triethylene Glycol	12	1150
Tetraethylene Glycol	12	1170
Dipropylene Glycol	13	2277
Carbowax 300 25985-1	13	1825
Poly G 71-530	10.5	1147
Class 1 Connecticut Spec	8-15	1200 minimum

-
- (1) See Table 8 and previous discussion for Method A procedure
- (2) One briquette each test.

TABLE 31
MARSHALL TESTS OF BRIQUETTES USING THE
UPPER CURVE OF THE AGGREGATE GRADATION CHART - METHOD B⁽¹⁾

<u>Sample</u>	<u>Flow</u>	<u>Stability</u>
5.47% Asphalt		
1	12.7	3688
2	12	3846
3	11.7	3897
Avg.		3810
Std. Deviation		89
5.7% Asphalt		
1	12	3480
2	12.5	3397
6	12.5	3421
Avg.		3433
Std. Deviation		34

 (1) New Method B mix design: Upper (finer aggregate) curve used instead of a curve halfway between top and bottom curves as well as 5.7% asphalt. See Table 9 and previous discussion for Method B procedure

TABLE 32

MARSHALL STABILITY OF PROMISING ADDITIVES⁽¹⁾

	Statistical Data For Flow ⁽²⁾	Flow	Stability	Statistical Data For Stability ⁽²⁾
Poly G 71-530				
1	X = 13.3	9.5	1027	X = 1071
2	S = 2.7	15	1256	S = 124
3	90% = 2.5	16	1046	90% = ± 118
4	95% = 3.4	14.5	919	95% = ± 154
5		11.5	1106	
Triethylene Glycol				
1	X = 13.5	11.5	1341	X = 1324
2	S = 2.0	11.5	1334	S = 92
3	90% = 1.9	15	1205	90% = 88
4	95% = 2.5	16	1281	95% = 115
5		13.5	1457	
Tetraethylene Glycol				
1	X = 14.8	20	666	X = 945
2	S = 3.3	12	1053	S = 159
3	90% = 3.2	12	1031	90% = 151
4	95% = 4.2	14	997	95% = 198
5		16	980	
Propylene Glycol				
1	X = 15.4	15	1673	X = 1806
2	S = 1.8	18	2021	S = 132
3	90% = 1.7	13	1810	90% = 126
4	95% = 2.3	16	1728	95% = 164
5		15	1800	
Sodium Formate Powder				
1	X = 13.5	13	3009	X = 3195
2	S = 0.9	15	3725	S = 318
3	90% = 0.8	13	3154	90% = ± 303
4	95% = 1.1	13.5	2898	95% = ± 395
5		13	3189	
Sodium Acetate Powder				
1	X = 13.2	15	1008	X = 1251
2	S = 2.8	16	1224	S = 184
3	90% = 2.6	12	1163	90% = 175
4	95% = 3.4	9	1472	95% = 229
5		14	1387	

 (1) Method B aggregate design: Upper curve of the aggregate gradation chart; 5.7% asphalt was used. See Table 9 and previous discussion for Method B procedure

(2) X = mean value; S = standard deviation from the mean; 90% = 90% confidence limit for the mean value; 95% = 95% confidence limit for the mean value.

TABLE 33

**EFFECT OF WASHING THE ASPHALT CONCRETE BRIQUETTE
CONTAINING ADDITIVES ON ICE ADHESION AT -5°C - METHOD A** ⁽¹⁾

Additive(2)	Physical Form	Binder	Ice Adhesion ⁽³⁾ Shear Strength, psi				
			Original	Number of Washes			
				1	2	3	4
Control-no additive	-	-	>64	-	-	-	-
Verglimit	Flake	-	-(4)	16	19	15	12
	Flake	-	-(4)	8	16	14	15
Sodium Formate	Powder	-	17	13	25	27	40
	Flake	Lignin Sulfonate	3	10	28	45	>64
	Flake	Maldene	0.2	18	38	>64	-
Sodium Acetate	Powder	-	-(4)	5	15	23	26
	Flake	Lignin Sulfonate	-(4)	7	15	16	15
	Flake	Maldene	0	4	14	16	26
	Flake	EMA	-(4)	38	42	>64	>64
	Flake	Carbowax	1	6	19	29	34
Ice-B-Gon	Pellets	-	-(4)	31	>64	>64	>64
	Powder	-	8	27	25	33	36
Ethylene Glycol	Liquid	-	0.6	3	8	9	13
Propylene Glycol Duplicate	Liquid	-	14	27	36	35	29
	Liquid	-	9	11	10	11	15
Dipropylene Glycol	Liquid	-	22	26	20	19	19
Carbowax 300 Duplicate	Liquid	-	0.1	0.5	3	4	4
	-	-	18	25	19	18	22
Triethylene Glycol	Liquid	-	0.5	0.6	0.6	0.6	0.6
Tetraethylene Glycol	Liquid	-	9	9	8	10	6
Poly G71-530	Liquid	-	23	25	28	25	34
Table Salt (NaCl) ⁽⁵⁾	Powder	-	0.18	-	-	-	-
"Flour Salt" (NaCl) ⁽⁶⁾ -----	Powder	-	0.03	-	-	-	-

(1) See Table 8 and previous discussion for Method A procedure

(2) See Appendix B

(3) Shear strength to remove a one-inch diameter disc of ice from the AC sample surface. Each successive reading is taken after the briquette is washed and redried.

(4) No data available

(5) Particle size: approx. 35 mil cube

(6) Diamond Crystal Salt Co., 3-8 units particle size

When the durability series was started, ice adhesion of the briquettes modified with blended additives was run at -20°C . Immediately after initial results, it was realized that no sample was satisfactory at this temperature, and test temperature was changed to -5°C . Thus, for some additives, there is no initial value.

The unmodified control gives a value greater than 64 psi shear strength. Ice adhesion of briquettes containing sodium formate, sodium acetate, Ice-B-Gon pellets and powder, ethylene glycol, and propylene glycol increases with each successive wash. For the additives Verglimit, dipropylene glycol, Carbowax 300, tri and tetraethylene glycol and the Poly G71-530 ice adhesion remained relatively constant or very slowly increased.

In the sodium acetate series, the rate of loss depends on the binder-encapsulant, indicating that the binder -- encapsulant-type and probably concentration -- can play a significant roll in additive lifetime.

Triethylene and tetraethylene glycol still had low ice adhesion after the fourth washing.

Reproducibility, as shown by propylene glycol and Carbowax 300 is not good and requires further study.

h. Additive Toxicology, Environmental Impact and Corrosivity

Effect of the additive on ice adhesion, friction and mechanical properties of the pavement are critical. However, toxicology of the additive, its effect on the environment, and its corrosivity to metals are also important.

Table 34 presents data on LD 50, general toxicology, ecological impact, and corrosivity. LD 50 is the dosage at which half of a rat population is killed.

Salt, the most commonly used deicing agent, is ecologically damaging at high concentrations, and corrosive to metals. Verglimit, which is calcium chloride coated with polymerized linseed oil and made alkaline with sodium hydroxide, is also ecologically damaging and corrosive to metals. In general, all of the other additives have little or no ecological impact, are non-corrosive, and generally have low toxicity. One possible exception is ethylene glycol, which may present some hazards.

i. Water Insoluble Additives

The two approaches to this program involved using:

- (1) water soluble additives exuding to the surface and lowering the freezing point,
- (2) water insoluble additives that would come to the surface and prevent ice adhesion because of their hydrophobic nature.

The water soluble additives, and to a lesser extent, hydrophilic additives, have proven effective. Water insoluble additives have not.

TABLE 34

SAFETY OF SELECTED CANDIDATE MATERIALS⁽¹⁾

Compound	LD50 (lethal dose 50 percent kill)	General Toxicology	Ecological Impact	Corrosivity to construction materials	
Vergulmit	oral (rats) 2.0 mg/Kg	moderately toxic slight irritant-skin and eye	high concentrations damaging to fish, and sewage systems	corrosive to metals	
Ice-B-Gon	dermal (rabbit) >5000 mg/Kg oral (rat) 3145 mg/Kg	very low toxicity	non-toxic to fish	stable, non-corrosive	
Sodium acetate	oral (rat) 3530 mg/kg(2)	very low toxicity used in low conc. as a food additive	non-toxic biodegradable	non-corrosive	
Sodium chloride	oral (rat) 3000 mg/kg(2)	skin and eye irritant	high concentrations damaging	corrosive to metals	
Sodium formate	oral (dog) 4000 mg/kg intravenous (mice) 807 mg/Kg	skin and eye irritant effects,	low concentrations compatible with sewage systems	stable, non-corrosive	
Triethylene glycol	oral (human) 5000 mg/Kg(2) oral (rat) 17 gm/Kg(2)	no evidence of adverse effects, other than may cause nausea if swallowed	A fungicide	stable, non-corrosive	
Ethylene glycol	oral (rat) 150 mg/Kg/day no effect	suspected teratogen irritant-eye and inhalation harmful or fatal if swallowed	may present hazards	stable, non-corrosive	
Propylene glycol	None established by ACGIH or OSHA	low toxicity may cause allergic skin reaction	none established - low impact in low concentrations	stable, non-corrosive	
Dipropylene glycol	None established by ACGIH or OSHA	low toxicity	none established - low impact in low concentrations	stable, non-corrosive	
Tetraethylene glycol	oral (rat) 29 gm/Kg(2)	low toxicity skin and eye irritant	none established - low impact in low concentrations	stable, non-corrosive	
Carbowax 300 (polyethylene glycol)	oral (rat) 33750 mg/Kg(2)	very low toxicity	none established - low impact in low concentrations	stable, non-corrosive	
Polyglycol P425 (polyethylene glycol)	oral (rat) 300-500 mg/Kg(2)	very low toxicity	none established - low impact in low concentrations	stable, non-corrosive	
Silicone fluid R-200	oral (rat) 75.3 g/Kg(2)	low toxicity	none established - low impact in low concentrations	non-corrosive	
.....		may cause slight skin irritation	impact in low concentrations		

(1) Data from individual Material Safety Data Sheets unless otherwise noted.

(2) Sax, N.I., "Dangerous Properties of Industrial Materials", Sixth Ed., Van Nostrand Reinhold Co., N.Y., 1984

TABLE 34

SAFETY OF SELECTED CANDIDATE MATERIALS⁽¹⁾
(Continued)

Compound	LD50 (lethal dose 50 percent kill)	General Toxicology	Ecological Impact	Corrosivity to construction materials
Ketjenflex 8 (mixed n-butyl and n-ethyl para-toluene-sulfonamide)	oral (rat) 5600 mg/Kg	low toxicity may cause eye irritation	not a RCRA hazardous waste	no data available
Fyrol 6 (diethyl M.M.-bis(2- hydroxy ethyl) amino- methyl phosphonate)	oral (rat) >5000 mg/Kg dermal (rabbit) >2000 mg/Kg	low toxicity may cause eye irritation	none established - low impact in low concentrations	non-corrosive to glass and metals; may plasticize some polymers, particularly vinyl- based resins and natural rubbers
Poly-G 75-442 (polyether glycol) methyl- glucoside neutral polyol	oral (rat) >5000 mg/Kg	very low toxicity	none established - low impact in low concentrations	no data available
Poly-G 71-530 (polyether polyol) sucrose- aliphatic amine based polyol	oral (rat) >5000 mg/Kg	low toxicity may cause eye irritation	none established - low impact in low concentrations	no data available
Pluracol 824 (polyether polyol)	data not available	low toxicity may cause eye irritation	none established - low impact in low concentrations	no data available
Santicizer 160 (butyl benzyl phthalate)	oral (rat) 24,400 mg/Kg practically non-toxic	low toxicity may cause slight eye irritation	moderately toxic to fish in conc. 1-3 mg/l biodegradable	non-corrosive
Indopol L-50 (polybutene)	oral (rat) 34.6 g/Kg	very low toxicity	none established - low impact in low concentrations	non-corrosive
Paraplex G-54 (polyester adipate)	data not available	low toxicity, may cause slight skin or eye irritation	none established - low impact in low concentrations	no data available

(1) Data from Individual Material Safety Data Sheets unless otherwise noted.

(2) Sax, N.I., "Dangerous Properties of Industrial Materials", Sixth Ed., Van Nostrand Reinhold Co., N.Y., 1984

In an attempt to bring these oils to the surface, briquettes containing Indopol H 1500 (polybutylene), Paraplex G-25 (a polyester), and SALB (sucrose acetate butyrate) were compounded per usual into asphalt concrete. These briquettes were subjected to three temperature cycles consisting of eight hours at 40°C, overnight at room temperature, and eight hours at -5°C. Ice adhesion was measured after each cycle. The original ice adhesion for all three additives was greater than 64 psi.

There was no change in ice adhesion with the Indopol H 1500. The Paraplex G-25 gave an ice adhesion of 25 psi after the second cycle, and 48 psi after the third cycle. The SALB was 28 psi, and then 33 psi after the third cycle.

Thus, temperature cycling does cause some oils to diffuse to the surface. However, ice adhesion is still not lowered to the low levels obtained with water soluble additives.

j. Replication Study of Best Ice Adhesion Lowering Additives in Asphalt Concrete

To statistically examine the results and to verify reproducibility, five salts - Verglimit as a commercial control -- sodium chloride, sodium formate, sodium acetate and calcium magnesium acetate (Ice-B-Gon), were blended as previously described into asphalt concrete at 6.4% on the aggregate. Ten promising commercial oils were used at 3% concentration on the aggregate. Five briquettes were made for each additive. In all systems, 5.7% asphalt and the finer (upper) aggregate gradation curve were used, as previously described (See Table 9).

Verglimit was investigated at two concentrations, the same 6.4% as the other salts and also at 4.5% on the aggregate, because the 6.4% briquettes exuded and had a "pockmarked" surface.

The final set of five, marked "C", is a control without additives.

Properties tested on all samples included ice adhesion and friction by the British Pendulum. As detailed in Table 32 in this report, Marshall Stability was run on six materials.

Table 35 shows the run number, additive and manufacturer; the general chemical nature of trade name materials can be found in Appendix B.

In Table 36, the average ice adhesion in psi is presented for each of the five briquettes, which in turn is an average of five tests on each briquette. Finally, the average ice adhesion for all five briquettes and price/lb. in bulk quantity is given. This data cannot be directly compared with ice adhesion data in Table 7 of the 3rd Quarter report since a different mix design curve was used in making the briquettes.

TABLE 35

REPLICATION STUDY OF BEST ADDITIVES FOR
REDUCING ICE ADHESION TO ASPHALT CONCRETE

	Additive	Manufacturer
0	Verglimit at 6.4% ⁽¹⁾	P. K. Innovations
1	Sodium Formate (Powder)	Perstorp
2	Sodium Acetate (Powder)	Fisher Scientific
3	Ice-B-Gon (Powder)	Chevron
4	Triethylene Glycol	Matheson Coleman & Bell
5	Ethylene Glycol	Fisher Scientific
6	Propylene Glycol	Union Carbide
7	Dipropylene Glycol	Union Carbide
8	Tetraethylene Glycol	Aldrich Chemicals
9	Carbowax 300	Union Carbide
10	Poly-G 71-530	Olin Chemicals
11	Verglimit at 4.5%	
12	Ketjenflex 8	Akzo Chemicals
14 ⁽²⁾	Fyrol 6	Akzo Chemicals
15	Table Salt	Morton Thiokol
16	Poly-G 75-442	Olin Chemicals
	"C" Control - no additive	

- (1) All salts are at 6.4% (except #11) on the aggregate and all organic liquids are at 3% using Method B (See Table 9).
- (2) Run No. 13 was dropped.

TABLE 36

ICE ADHESION: REPLICATION STUDY
ON THE BEST ADDITIVES FOR ASPHALT CONCRETE

		(1) Ice Adhesion psi, for Each Of Five Briquettes	(2) Average Ice Adhesion, psi	Price \$/Lb.	(7) Statistical Data	
0	Verglimit ⁽⁴⁾	0.31, 0, 0, 0.03, 0.04	0.1 ⁽⁶⁾	0.82	X = 0.08 S = 0.13	90% = 0.13 95% = 0.16
1	Sodium Formate ⁽⁴⁾	0.05, 0.2, 0.18, 0.03, 0	0.1	0.20	X = 0.09 S = 0.09	90% = 0.09 95% = 0.11
2	Sodium Acetate ⁽⁴⁾	0.13, 0.2, 0.38, 0.15, 0.18	0.2	0.58	X = 0.21 S = 0.10	90% = 0.10 95% = 0.12
3	Ice-B-Gon ⁽³⁾⁽⁴⁾	0.84, 2.8, 0.84, 0.96, 0.84	1.3	0.34	X = 1.26 S = 0.86	90% = 0.22 95% = 1.08
4	Triethylene Glycol ⁽⁸⁾	1.3, 0.6, 0.6, 0.5, 0.6	0.8	0.54	X = 0.72 S = 0.33	90% = 0.31 95% = 0.41
5	Ethylene Glycol ⁽⁸⁾	0.76, 0.64, 0.64, 0.51, 0.76	0.6	0.31	X = 0.66 S = 0.10	90% = 0.10 95% = 0.12
6	Propylene Glycol ⁽⁸⁾	18, 2.5, 7.6, 24, 7.6	12	0.56	X = 11.9 S = 8.9	90% = 8.4 95% = 10.9
7	Dipropylene Glycol ⁽⁸⁾	2.5, 7, 8.5, 5.5, 4.6	6	0.57	X = 5.6 S = 2.3	90% = 2.2 95% = 2.8
8	Tetraethylene Glycol ⁽⁸⁾	10, 5, 2, 1.3, 0.6	4	0.88	X = 3.78 S = 3.86	90% = 3.68 95% = 4.80
9	Carbowax 300 ⁽⁸⁾	11.2, 4.2, 7.8, 5.9, 11	8	0.73	X = 8.02 S = 3.09	90% = 2.94 95% = 3.84
10	Poly G 71-530 ⁽⁸⁾	8.9, 10.2, 11.5, 7.6, 17.8	12	0.85	X = 11.2 S = 4.0	90% = 3.8 95% = 4.9

 (1) Method B. Each value is an average of five ice adhesion tests per briquette.

(2) Bulk quantity.

(3) Calcium magnesium acetate.

(4) At 6.4% on the aggregate.

(5) At 4.5% on the aggregate.

(6) All figures are rounded off.

(7) X = mean value; S = standard deviation from the mean; 90% = 90% confidence limit for the mean value; 95% = 95% confidence limit for the mean value.

(8) All oils (organic liquids) are at 3% on the aggregate.

TABLE 36

ICE ADHESION; REPLICATION STUDY
ON THE BEST ADDITIVES FOR ASPHALT CONCRETE

-continued-

		Ice Adhesion ⁽¹⁾ psi, For Each Of Five Briquettes	Average Ice Adhesion, psi	Price ⁽²⁾ \$/Lb.	Statistical Data ⁽⁷⁾	
11	Verglimit ⁽⁵⁾	0.6, 0.03, 0.03, 0.1, 0.01	0.15		X = 0.15 S = 0.25	90% = 0.24 95% = 0.31
12	Ketjenflex 8 ⁽⁸⁾	11, 5.7, 2.5, 20, 14	10	2.45	X = 10.6 S = 6.9	90% = 6.6 95% = 8.6
13	Eliminated					
14	Fyrol 6	0.4, 0.6, 0.3, 0.25, 0.4	0.4	1.93	X = 0.39 S = 0.13	90% = 0.13 95% = 0.17
15	Table Salt ⁽⁴⁾	0.14, 0.06, 0.2, 0.03, 0	0.1	0.03 ⁽⁹⁾	X = 0.09 S = 0.08	90% = 0.08 95% = 0.10
16	Poly G 75-442	25.6, 26, 13.5 20.6, 20.9	19	0.94	X = 21.3 S = 5.1	90% = 4.8 95% = 6.3
C	Control	>64, >64, >64, >64, >64	>64	-	X = >64 S = 0	90% = 0 95% = 0

(1) Method B. Each value is an average of five ice adhesion tests per briquette.

(2) Bulk quantity.

(3) Calcium magnesium acetate.

(4) At 6.4% on the aggregate.

(5) At 4.5% on the aggregate.

(6) All figures are rounded off.

(7) X = mean value; S = standard deviation from the mean; 90% = 90% confidence limit for the mean value; 95% = 95% confidence limit for the mean value.

(8) All oils (organic liquids) are at 3% on the aggregate.

(9) Highway bulk treated (anti-caking) grade price is \$0.02.

Two materials are immediately rejected due to price -- Ketjenflex 8 and Fyrol 6. The latter also attacks rubber. Of those remaining, Poly G 71-530 and Poly G 75-442 are at the higher price end. However, they would not be eliminated until their lifetime, as shown by water extraction, is carried out. Obviously, other factors, such as friction, effect on mechanical properties, environmental effect, water resistance, etc., being equal, the lower the price the better, e.g., ethylene glycol may have toxicity problems.

Several of the briquettes containing additives had dry/wet friction which is close to that of the control (Table 37). However, an initial low friction does not necessarily eliminate a material. Verglimit, which is used commercially, is slippery because of exudation, and "dry" friction is the same as wet friction. However, the distributor (P.K. Innovations) recommends that a road containing Verglimit be washed daily over a two week period to remove the exudation. In addition, sand is put on the road immediately after the road is resurfaced.

k. Preliminary Portland Cement Concrete Studies

Very preliminary work was carried out to see the effect of deicing additives on Portland cement concrete, followed by ice adhesion testing.

Disposable polypropylene molds, eight inches high and four inches in diameter, were used. The commercial cement mixture "Watta Crete"⁽¹⁾, 1200 g, was stirred in a one gallon bucket with approximately 110-130 grams of deionized water. The amount of water used was regulated to give the same consistency of the cement mixture.

The Watta Crete water mixture was poured into the polypropylene mold and 60 grams of additive stirred in by hand. The mold was loosely covered and allowed to stand at room temperature for 24 hours at which time the excess water was poured off (Table 38).

Next, a 50 ml polypropylene beaker filled with water was taped to the inside to provide 100% humidity. The mold was closed tightly and stored for one week at room temperature. In the second part of the cure cycle, the cover was removed, and the mold remained at room temperature for one week.

Condition of the PCC with various additives is shown in Table 39. All of the water soluble oils gave poor PCC briquettes. Those additives which gave well-formed PCC briquettes were tested for ice adhesion (Table 40).

Sodium formate gave low adhesion but caused scaling. None of the other additives except Polyol PPG 425 had any effect on ice adhesion.

(1) Watta-Crete Co., Canaan, CT, "Cement Mix"

TABLE 37

FRICTION BY BRITISH PENDULUM: REPLICATION
STUDY ON THE BEST ADDITIVES FOR ASPHALT CONCRETE

		Dry/Wet Friction On Each of five briquettes	Dry/Wet Average	Statistics ⁽¹⁾ Dry/Wet	
0	Verglimit at 6.7%	37/36, 31/35, 31/33, 31/35, 30/28	32/33	X = 32/33 S = 2.8/3.2	90% = 2.7/3.1 95% = 3.5/4.0
1	Sodium Formate	45/35, 49/35, 46/31, 46/36, 46/34	46/34	X = 46/34 S = 1.5/1.9	90% = 1.4/1.8 95% = 1.9/2.4
2	Sodium Acetate	40/35, 35/30, 39/35, 34/31, 41/38	38/32	X = 38/34 S = 3.1/3.3	90% = 3.0/3.1 95% = 3.9/4.1
3	Ice-8-Gon	43/31, 44/32, 48/36, 46/35, 45/36	45/34	X = 45/34 S = 1.9/2.3	90% = 1.8/2.2 95% = 2.4/2.9
4	Triethylene Glycol	35/36, 35/33, 35/35, 37/37, 37/37	36/35	X = 36/36 S = 1.1/1.7	90% = 1.0/1.6 95% = 1.4/2.1
5	Ethylene Glycol	44/34, 45/37, 44/35, 48/35, 46/34	45/35	X = 45/35 S = 1.9/1.2	90% = 1.8/1.2 95% = 2.4/1.5
6	Propylene Glycol	47/33, 49/34, 48/33, 44/32, 46/30	47/32	X = 47/32 S = 1.9/1.5	90% = 1.8/1.4 95% = 2.4/1.9
7	Dipropylene Glycol	45/30, 45/31, 49/35, 46/30, 45/32	46/32	X = 46/32 S = 1.7/2.1	90% = 1.6/2.0 95% = 2.2/2.6
8	Tetraethylene Glycol	32/36, 36/36, 33/35, 36/35, 34/35	34/35	X = 34/35 S = 1.8/0.5	90% = 1.7/0.5 95% = 2.2/0.7
9	Carbowax 300	32/31, 35/33, 35/34, 31/31, 31/31	33/32	X = 33/32 S = 2.0/1.4	90% = 2.0/1.3 95% = 2.5/1.8
10	Poly G 71-530	45/35, 44/33, 45/35, 41/31, 44/32	45/33	X = 44/33 S = 2.1/1.6	90% = 2.0/1.5 95% = 2.6/2.0

 (1) X = mean value.

S = standard deviation from the mean.

90% = 90% confidence limit for the mean value.

95% = 95% confidence limit for the mean value.

TABLE 37

FRICTION BY BRITISH PENDULUM: REPLICATION
STUDY ON THE BEST ADDITIVES FOR ASPHALT CONCRETE

-continued-

		Dry/Wet Friction On Each of Five Briquette.	Dry/Wet Average	Statistics ⁽¹⁾ Dry/Wet	
11	Verglimit at 4.5%	33/34, 34/36, 33/36 34/39, 35/37	34/35	X = 34/36 S = 0.8/1.8	90% = 0.8/1.7 95% = 1.0/2.3
12	Ketjenflex 8	42/32, 34/17, 42/33, 44/34, 39/33	40/32	X = 40/30 S = 3.9/7.2	90% = 3.7/6.8 95% = 4.8/8.9
13	Eliminated				
14	Fyrol 6	40/33, 42/34, 40/35, 42/36, 41/34	41/34	X = 41/34 S = 1.0/1.1	90% = 0.95/1.1 95% = 1.2/1.4
15	Table Salt	39/30, 48/35, 45/35, 47/35, 47/35	45/34	X = 45/34 S = 3.6/2.2	90% = 3.5/2.1 95% = 4.5/2.8
16	Poly G 75-442	46/33, 47/31, 48/35, 48/30, 50/35	48/33	X = 48/33 S = 1.5/2.3	90% = 1.4/2.2 95% = 1.8/2.8
C	Control: Previous	49/36, 47/34, 49/36,	48/35	X = 48/35 S = 1.2/1.2	90% = 1.9/1.9 95% = 2.9/2.9
C	Control: Repeat	50/35, 48/33, 48/35 50/35, 51/52	50/35	X = 49/35 S = 1.3/0.9	90% = 1.3/0.9 95% = 1.7/1.1

(1) X = mean value.

S = standard deviation from the mean.

90% = 90% confidence limit for the mean value.

95% = 95% confidence limit for the mean value.

TABLE 38

POSSIBLE DEICING ADDITIVES IN PORTLAND CEMENT CONCRETE

<u>Additive</u>	<u>Grams Of H₂O Used</u>	<u>Grams of Liquid Poured Off After One Day</u>	<u>Comments</u>
<u>Water Soluble</u>			
Sodium Formate (Powder)	131	38	
Sodium Acetate (Powder)	118	28	
Ice-B-Gon (Pellet)	144	61	Floated to top/ dissolved
Triethylene Glycol	132	44	
Ethylene Glycol	111	6	
Propylene Glycol	127	26	
Dipropylene Glycol	111	18	
Tetraethylene Glycol	119	18	
Carbowax 300	122	17	
<u>Partially Water Soluble</u>			
Flexol 4G0	211	39	
BASF 380	253	0	Top has cured skin
Poly-G 71-530	170	39	
Pluracol 824	149	27	
Polyol PPG 425	165	37	
<u>Water Insoluble</u>			
DC - 200	169	42	
Paraplex G-54	187	54	Surface very rocky
Indopol L-50	171	26	
Santicizer 160	115	29	

TABLE 39

CONDITION OF PCC AFTER TWO WEEKS CURE

<u>Additive</u>	<u>Results</u> ⁽¹⁾
<u>Water Soluble</u>	
Sodium Formate (Powder)	Good to fair (skin on surface)
Sodium Acetate (Powder)	Good to fair (skin on surface)
Ice-B-Gon (Pellets)	Briquette falls apart
Triethylene Glycol	Fair to poor
Ethylene Glycol	Briquette falls apart
Propylene Glycol	Fair to poor
Dipropylene Glycol	Fair to poor
Tetraethylene Glycol	Fair to poor
Carbowax 300	Fair to poor
<u>Partially Soluble</u>	
Flexol 4G0	Good to fair
Poly-G 71-530	Poor
Pluracol 824	Fair to poor
Polyol PPG 425	Good to fair
BASF 380	Good to fair
<u>Water Insoluble</u>	
D.C. 200 Silicone Oil	Good
Paraplex G-54	Poor
Indopol L-50	Good
Santicizer 160	Good
Control (SL) - No additive	Excellent
Control (DOT) - No additive	Excellent

 (1) Strength is categorized as Good - Fair - Poor

TABLE 40

ICE ADHESION OF PCC CONTAINING
POSSIBLE DEICING ADDITIVES

Additive	Ice Adhesion Shear Strength, psi ⁽¹⁾		Remarks
	-5°C	-20°C	
Sodium Formate	-	4	scaling
Sodium Acetate	-	>64	
Flexol 4G0	>64	>64	
Polyol PPG 425	22	>64	
BASF 380	-	40	
DC 200 Silicone Oil	36	>64	
Indopol L50	>64	>64	
Santicizer 160	>64	>64	
Control made at SL	>64	-	
Control - Highway Core	>64	-	

- (1) Shear strength to remove a one-inch diameter disc of ice from the PCC sample surface at -20°C. Measuring device: Chatillon digital force gauge model DFGRS-50, $\pm 0.25\%$ full scale, ± 1 least sign. figure

D. STATISTICAL ANALYSIS

Statistical analysis of the data was carried out by Dr. Uwe Koehn of the University of Connecticut. There are two types of data being analyzed. In the first, comprising the bulk of the work, there are single points of information obtained by the Slush (screening) test, ice adhesion and friction, although in the latter two cases, there were five replicates on each briquette. In order to obtain a measure of variability, analysis consisted of ordering the data and using normal probability plots.

The second set of data to be analyzed consists of replicate runs (five briquettes for each additive) of the best systems to date, and again five tests per briquette along with a commercial additive (Verlimit) control and a base control without additive. This data was subjected to an analysis of variance to determine whether there are significant differences among additives.

1. Normal Probability Plots

The slush ratings, ice adhesion shear strengths and friction data were analyzed for the various materials studied. In order to obtain a measure of variability, since the experiments were not replicated, analysis consisted of ordering the data and using normal and probability plots. This is a plot of data against the expected values of an ordered sample of that size from a normal standard distribution⁽¹⁾.

The readings for the ice adhesion shear forces in pounds per square inch range from 0 to 63.7. The upper value is due to the limitations of the measuring machine. Since smaller values are desirable, this upper value limitation is of little consequence. Table 41 and Figure 20 list the mean shear force for various tested compounds and give a normal probability plot. The plot shows that the seven or so lowest values follow a different pattern than the others. The first 12 on Table 41 have low ice adhesions versus the control value of 63.66 psi.

Taking the logarithms of the readings yields a Figure 21 and Table 42. (.01 was added to the readings to remove zeros.) Using logarithms is equivalent to considering percentage changes. Here the compounds divide into four groups. The group with the smallest readings consists of 11 compounds, the next group also 11 compounds, etc. These groupings may be useful to study.

The next measurements considered were ratings (physical properties) of ice crystals. These slush ratings were defined previously. Because these ratings are confined to a ten point scale, the information from a normal plot is limited. Nonetheless, the plot is a useful method of presenting the ordered data. Because many compounds were used in various concentrations, 5, 10 and 25% being the most common, the least squares means from an analysis of covariance were used to put the compounds on a comparable basis. Figure 22 and Table 43 show these results. The lowest six ratings seem to form a group as do the next four.

(1) Normal probability plots are discussed in various experimental design books, including: Box, George, E.P., Hunter, William G., Hunter, J. Stuart. "Statistics for Experiments: An Introduction to Design, Data Analysis, and Model Building", 1978, John Wiley and Sons, Inc., New York.

NORMAL PLOT OF SHEAR FORCES
 UNITS ARE LBS. PER SQUARE INCH

93

LEGEND: A = OBS, B = 2 OBS, ETC.

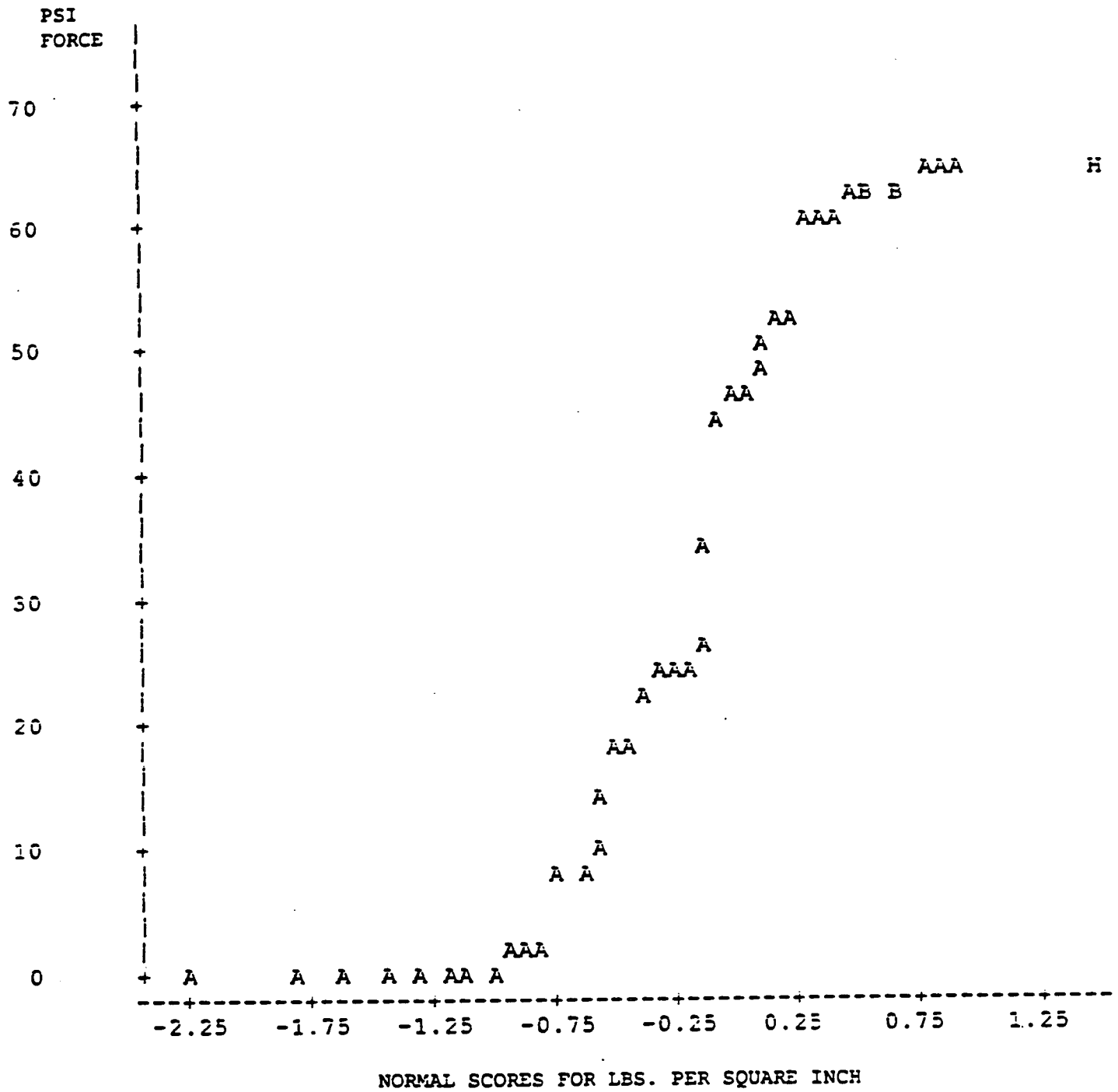


FIGURE 20

TABLE 41

ORDERED LIST OF ICE ADHESION SHEAR FORCES

(Units Are Lbs. Per Square Inch)

I.D.	Abbreviated Name	Force (psi)	Full Description
25998-03	NaFormate	0.0204	Sodium formate (powder) + Paraplex G-54
25998-02	Floursalt	0.0280	Flour salt
25986-01	Carbowax	0.1273	Carbowax 300 + fly ash (Hartford)
25991-02	NaFormate	0.1604	Sodium formate (Maldene Binder)
25998-01	Tablesalt	0.1783	Table salt
25992-03	TriEth	0.4915	Triethylene glycol
25992-02	EthylGly	0.5602	Ethylene glycol
26606-07	Fryol6	0.9065	Fryol 6
25986-02	NaAc/Carb	1.2223	Sodium acetate (Carbowax 300 binder)
25991-01	NaFormate	2.8266	Sodium formate (Lignium binder)
25980-03	IceBGon	7.4612	Ice-B-Gon (Powdered)
25992-08	PropGly	8.7090	Propylene glycol
25992-04	TetraEth	9.4220	Tetraethylene glycol
25990-01	PropGly	14.0566	Propylene glycol
25990-03	NaFormate	17.0360	Sodium formate (powder)
25992-07	Carbowax	17.9018	Carbowax 300
25992-01	Dipoly	22.4854	Dipropylene glycol
25992-17	Poly71	23.0966	Poly-G 71-530
26606-01	Ketjen	23.9369	Ketjenflex 8
25997-03	Poly-g	24.9963	Poly-G 71-357
26606-06	Poly75	26.2542	Poly-G 75-442
26606-02	Plasth550	34.1228	Plasthal P-550
26606-05	Poly74	44.6907	Poly-G 74-376
25997-05	CitroA2	46.4224	Citroflex A-2
25997-06	Teracol	46.7279	Teracol 1000
25992-18	NIAX	48.4341	NIAX polyol PPG 425
26606-03	Plasth670	49.0198	Plasthall P-670
25997-08	Benzoflex	52.2793	Benzoflex P-200
25992-12	Indopol	52.4830	Indopol L50
25994-04	Kemamide	59.7659	Kenamide P-181
25992-11	Indopol	59.7914	Indopol H 1500
25997-02	Plst643	60.8354	Plasthall 643
25987-01	Santiciz	61.3702	Santicizer 160
25997-01	Ketjenf	61.7267	Ketjenflex MH
25987-03	Pluracol	62.0068	Pluracol 873
25992-16	Pluronic	62.8217	Pluronic L61
25987-02	Pluracol	63.0254	Pluracol 824
25994-01	Plasto	63.1018	Plastolein 9717
25997-07	Triacetin	63.5602	Triacetin
25992-06	BASF380	63.6620	BASF 380
25944-01	Control	63.6620	Made by UConn
25992-15	Paraplex	63.6620	Paraplex G-25
25992-19	SAIB	63.6620	SAIB
25994-02	Lipowax	63.6620	Lipowax C Prills
25994-03	ARMID	63.6620	ARMID HT
25997-04	Citroflex	63.662	Citroflex -2

NORMAL PLOT OF LOG (SHEAR + .01) FORCES
UNITS ARE LBS. PER SQUARE INCH

LEGEND: A = 1 OBS, B = 2 OBS. ETC.

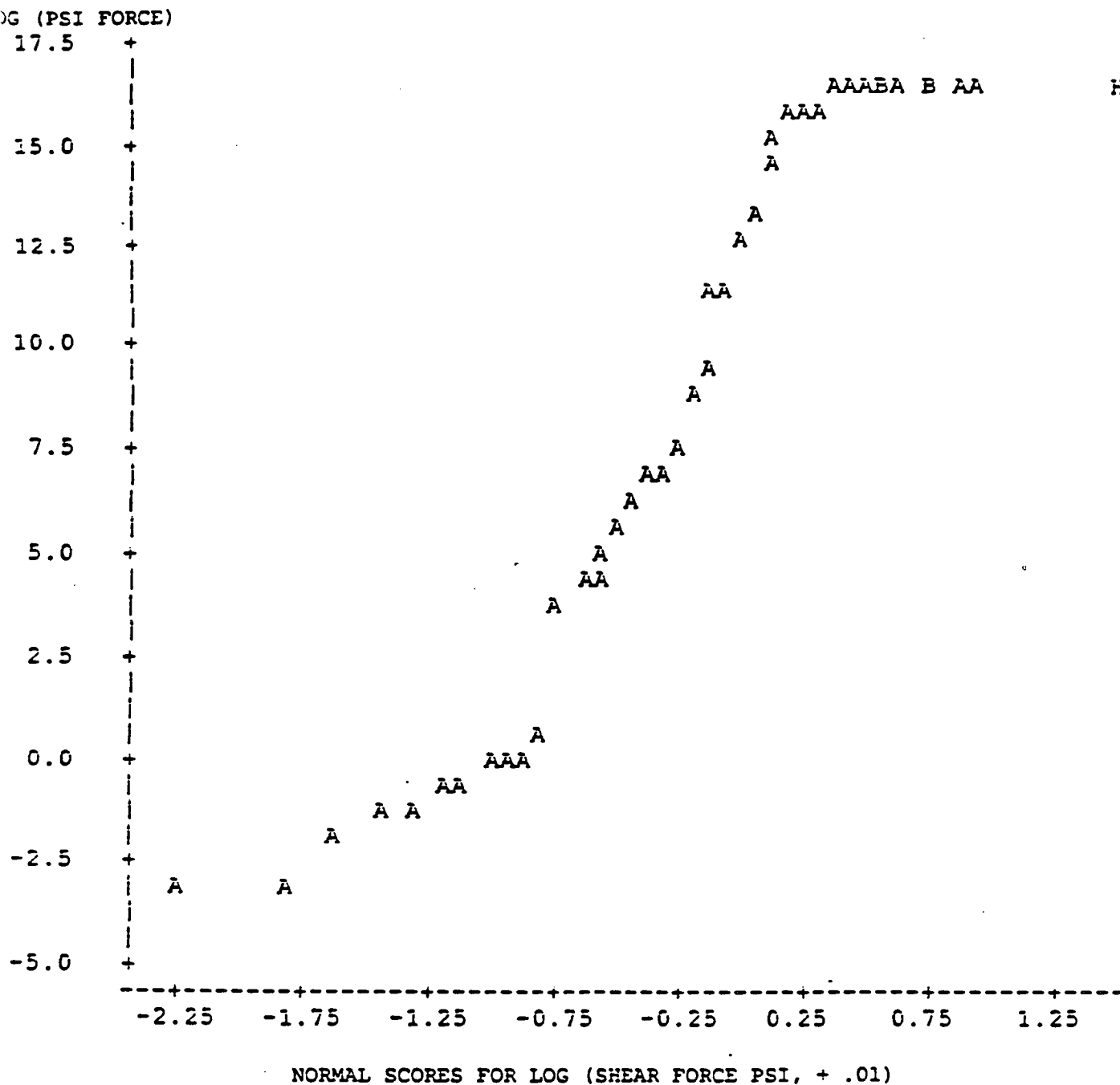


FIGURE 21

TABLE 42

ORDERED LIST OF ICE ADHESION SHEAR FORCES

(Units Are Log Lbs. Per Square Inch)

<u>I.D.</u>	<u>Name</u>	<u>Log(Force+.01)</u>
25998-03	NaFormate	-3.0644
25998-02	Floursalt	-2.9920
25986-01	Carbowax	-1.7997
25998-01	Tablesalt	-1.4706
25991-02	NaFormate	-1.4041
25992-03	TriEth	-0.5713
25992-02	EthylGly	-0.3419
25991-01	NaFormate	-0.0302
26606-07	Frytol6	0.0453
25986-02	NaAc/Carb	0.2484
25992-08	PropGly	3.9592
25980-03	IceBGon	4.3593
25992-04	TetraEth	4.4762
25990-03	NaFormate	4.9536
25990-01	PorpGly	5.6423
25992-07	Carbowax	6.2468
26606-06	Poly75	6.5750
25992-01	Dipoly	7.1329
26606-01	Ketjen	7.4316
25977-03	Poly-g	8.5687
25992-17	Poly71	9.3583
25997-05	CitroiA2	11.2040
26606-05	Poly74	11.5109
26606-02	Plasth550	12.4802
26606-03	Plasth670	12.8576
25992-12	Indopol	14.5571
25997-06	Teracol	15.1816
25987-02	Pluracol	15.4188
25992-18	NIAx	15.7461
25997-08	Benzoflex	15.8382
25992-11	Indopol	15.9829
25994-04	Kemamide	15.9883
25997-02	Plst643	16.0052
25987-01	Santiciz	16.0159
25997-01	Ketjenf	16.0224
25987-03	Plur873	16.0282
25992-16	Pluronic	16.0420
25994-01	Plasto	16.0464
25997-07	Triacetin	16.0538
25002-06	BASF380	16.0554
25944-01	Control	16.0554
25992-15	Paraplex	16.0554
25992-19	SAIB	16.0554
25994-02	Lipowax	16.0554
25994-03	ARMID	16.0554
25997-04	Citroflex	16.0554

NORMAL PLOT OF SLUSH RATINGS SCALED FOR CONCENTRATION

LEGEND: A = 1 OBS, B = 2 OBS, ETC.

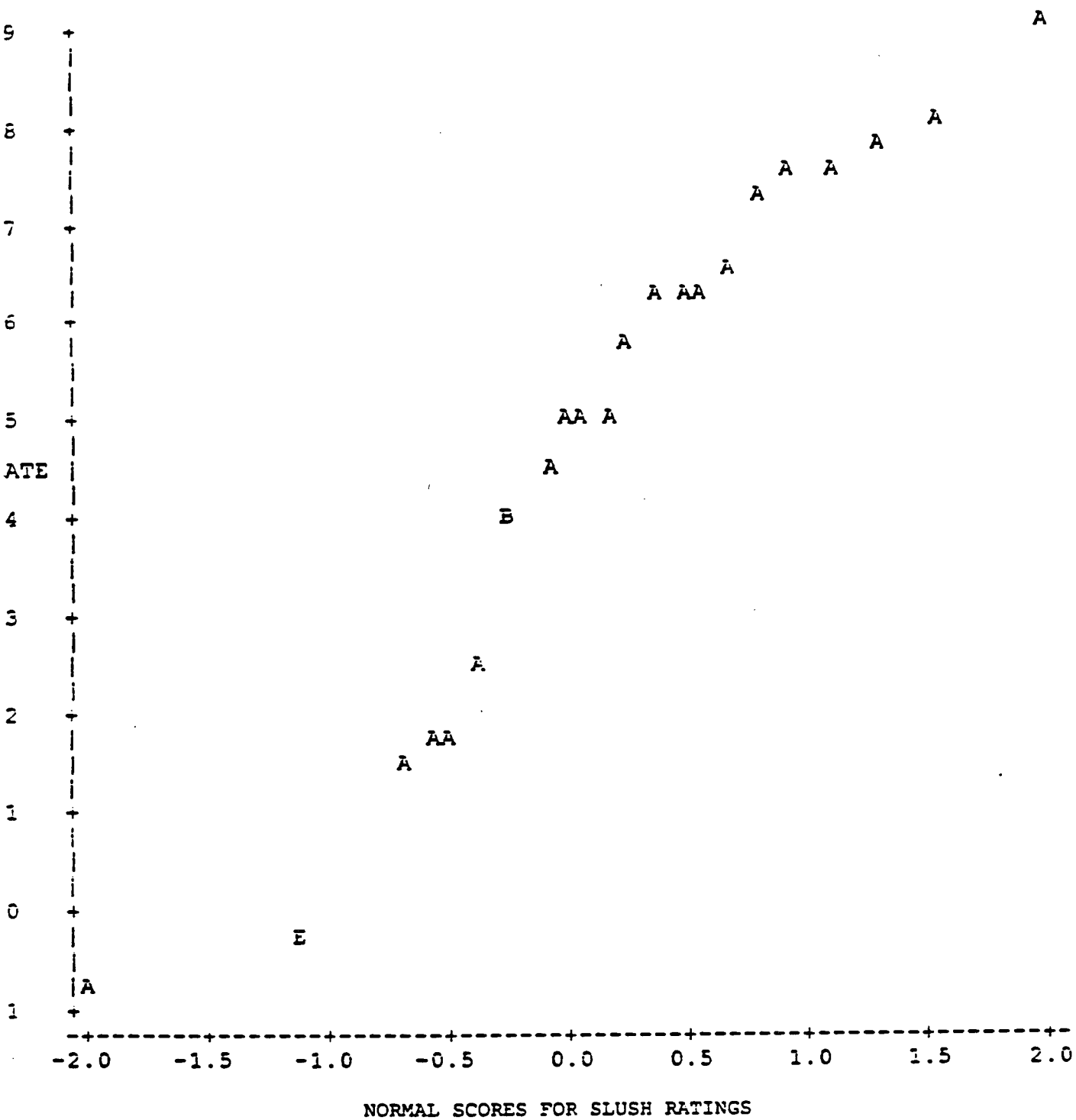


FIGURE 22

TABLE 43

PHYSICAL PROPERTY OF ICE CRYSTALS (SLUSH) RATING

Name	Slush Least Square Means	
Na Linosulfonate	-0.70926340	Sodium lignosulfonate ⁽¹⁾
Calcium Propionate	-0.20926340	
Magnesium Sulfate	-0.20926340	
Na Carbonate	-0.20926340	
Na Silicate	-0.20926340	
Potassium Bicarb	-0.20926340	Potassium bicarbonate
Calcium Formate	1.57947892	
Mg Lignosulfonate	1.72031738	
Na Lignin Sulfonate	1.79073660	
Potassium Sulfate	2.57947892	
Aluminium Ammoni	3.57947892	Al ammonium sulfate
Na Sulfate	3.97385009	
Potassium Pyroph	4.42173046	Potassium pyrophosphate
Ammonium Sulfate	4.88229334	
Dipotassium Hydr	5.03370055	Dipotassium hydrogen phosphate
NH ₄ H ₂ PO ₄	5.07947892	Ammonium diacid phosphate
Calcium-Magnesium ⁽²⁾	5.78135520	Calcium magnesium acetate (Ca-MgAc)
Potassium Carbonate	6.18510776	
Carbowax 300	6.23088613	
Magnesium Formate	6.27666450	
Magnesium Acetate	6.42173046	
Propylene Glycol	7.23088613	
Calcium Chloride	7.45835316	
Na Acetate	7.52666450	
"Ice B Gon" CA-Mg Ac	7.71093598	
Na Formate	7.91046271	
NaCl	9.03370055	

(1) Explanations are added as needed.

(2) Made at Springborn Labs.

We assumed that there could not be greater than 10% loss in dry and wet friction to provide road safety. The vertical line in Figure 23 is the 10% loss line in dry friction and the horizontal line is the 10% loss in wet friction. All data to the right of the vertical line is greater than approximately 44 in dry British Pendulum friction and above the horizontal line, is greater than approximately 33 in wet friction.

Many additives in Table 44 meet the requirement of no greater than 10% loss in both dry and wet friction. However, one must be careful in interpreting the data. Verglimit, which is used commercially blended into asphalt concrete, has a dry/wet friction of 32/23. The distributor of Verglimit recognizes this effect of exudation and recommends that roads containing Verglimit be washed repeatedly after the pavement is laid down. This washing removes the exudation and would undoubtedly increase friction.

2. Analysis of Variance

This section discusses the comparison of various additives, including a control, with respect to the force per square inch needed to break ice adhesion from pavement briquettes and the British Pendulum test for wet and dry friction. It refers to and is an analysis of the replication studies shown in Tables 36 and 37.

For all three measurements, force to break ice adhesion, wet friction value, and dry friction value, the analysis was of a one way layout with 5 replications per treatment. For ice adhesion, the readings for the control were so large as to be beyond the measurement capabilities of the measuring devices and so were not included in the statistical analysis. Because of the great differences in variability, a logarithm transformation of the data was done to stabilize the variances. Both the analysis of variance and variance stabilizing transformations are explained, for example, in Snedecor and Cochran's Statistical Methods⁽¹⁾.

There clearly was a difference among the 14 additives tested as shown by the analysis of variance since $PR > F$ was .0001 (Table 45) from the output of the Analysis of Variance procedure in SAS (Table 46). The REGWQ multiple comparisons procedure in SAS was used to compare the 14 means. The lowest 3 or 4 means seem to be smaller than the other mean values.

The first data (Table 45) shows that the differences in test results for ice adhesion are true and not due to test variability. The value of 0.0001 for $PR > F$ states that the chances of the values being the same, i.e., being due to test variability, are only 1/10,000.

The second set of data reveals where the difference lies (Table 47). Thus, there is no real difference between any two values with the same letter.

(1) Snedecor, G.W. and Cochran, W.G., Statistical Methods, 7 ed. 1980, Iowa State University Press, Ames, Iowa.

BRITISH PENDULUM FRICTION SCORESWET VERSUS DRY SCORES

PLOT OF WET*DRY SYMBOL USED IS *

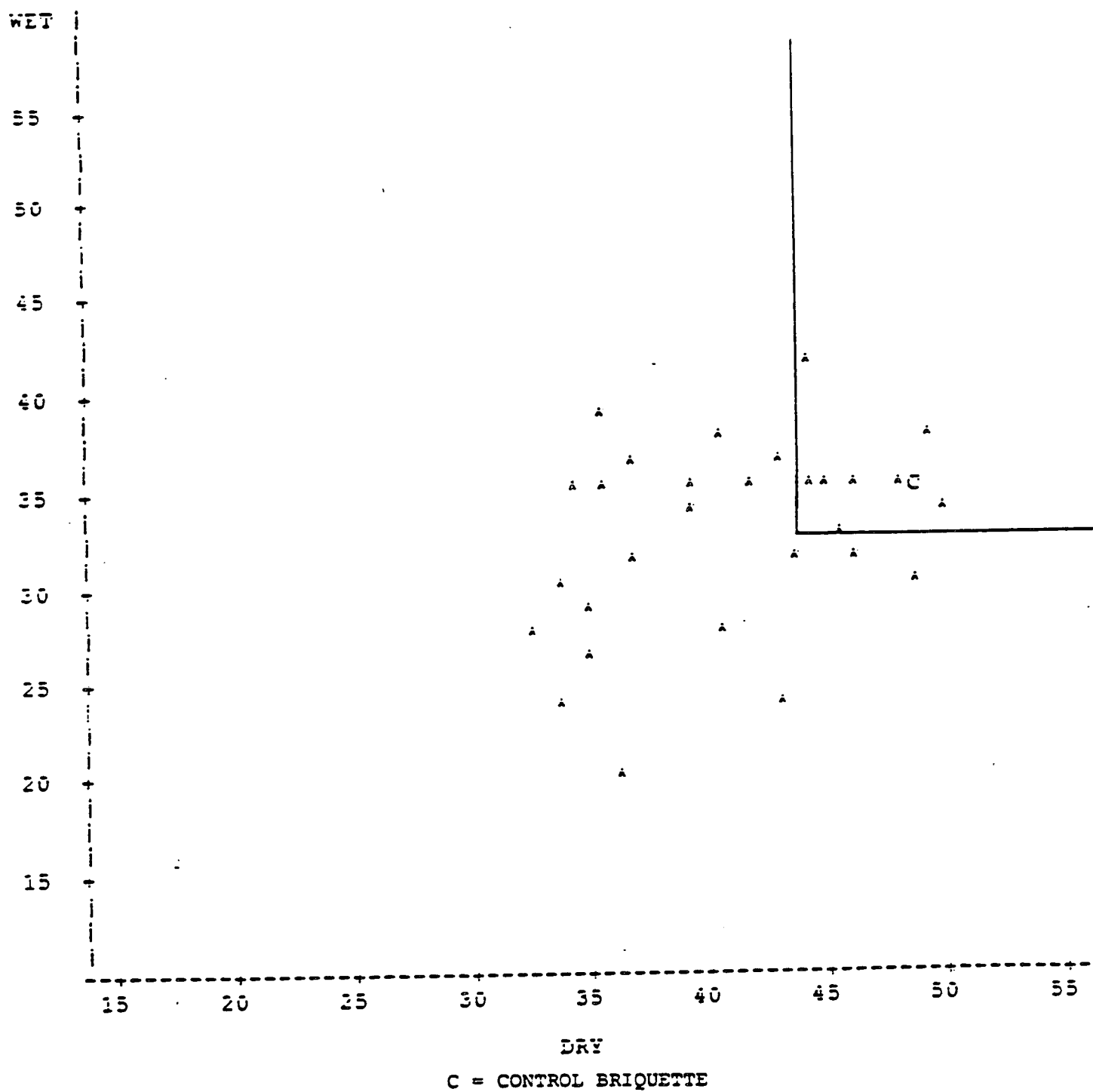


FIGURE 23

TABLE 44

BRITISH PENDULUM FRICTION SCORES
WET VERSUS DRY SCORES

OBS	Code	Dry	Wet	
1	25987-1	32.2	27.8	Santicizer 160
2	25997-5	33.8	30.4	Citroflex A-2
3	25994-2	34.0	23.6	Lipowax C
4	25985-1	34.6	34.6	Carbowax 300
5	25985-1	34.6	34.6	Repeat
6	25994-4	34.8	28.2	Kemamide P-181
7	25992-13	35.0	26.6	Eramid
8	25992-3	35.4	38.6	Triethylene Glycol
9	25992-4	35.6	35.0	Tetraethylene Glycol
10	25994-3	36.4	19.4	Armid HT
11	25992-7	37.0	36.0	Carbowax 300
12	25997-8	37.0	31.6	Benzoflex P-200
13	25987-2	39.2	34.2	Fluracol 824
14	25985-3	39.4	33.0	Sodium Acetate (Powder)
15	25992-12	39.6	34.8	Indopol L50
16	25986-2	40.0	22.2	Sodium Acetate (Carbowax Binder)
17	25992-19	40.6	27.4	SAIB
18	25992-2	40.8	37.6	Ethylene Glycol
19	25992-18	41.8	34.4	MIAX Polyol PPG 425
20	25982-1	41.8	35.0	5% Paraplex G-54 (Before Asphalt)
21	25988-2	43.0	23.8	Paraplex G-54 (After Asphalt)
22	25988-3	43.0	35.8	Paraplex G-54 (Hartford Fly Ash)
23	25992-6	44.0	31.2	BASF 380
24	25992-17	44.2	41.8	Poly-G 71-530
25	25988-1	44.6	35.6	Paraplex G-54 (Fines/After Asphalt)
26	25986-1	45.0	35.2	Carbowax 300 (Hartford Fly Ash)
27	25992-1	45.8	32.4	Dipropylene Glycol
28	25980-2	45.8	35.4	Sodium Acetate (Maldene Binder)
29	25992-15	46.0	35.0	Paraplex G-25
30	25994-1	46.0	31.4	Plastolein 9717
31	25992-16	46.2	35.6	Pluronic L61
32	25986-3	47.8	37.0	Sodium Acetate (Lignium Binder)
33	25980-3	48.0	37.4	Ice-B-Gon (Powdered)
34	25987-3	48.2	34.8	Fluracol 873
35	25992-11	48.8	29.8	Indopol H 1500
36	25997-7	49.4	37.2	Triacetin
37	25985-2	49.6	36.2	Sodium Acetate (EMA Binder)
38	25992-8	50.0	33.2	Propylene Glycol
39	25980-1	50.2	33.4	Paraplex G-54 (Before Asphalt)
40	25982-2	52.2	41.4	Ice-B-Gon (Pellets)
C	Control	49	35	No additive

TABLE 45

ANALYSIS OF ICE ADHESION FOR VARIOUS ADDITIVES
 Original Unit = Pounds/Sq. In.
 Variance Stabilizing Transformation To Logarithm Of Force
 Five Replications

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: LOGFORCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	
MODEL	15	342.18844526	22.81256302	
ERROR	64	42.97842412	0.67153788	
CORRECTED TOTAL	79	385.16686938		
MODEL F -	33.97		PR > F - 0.0001	
R-SQUARE	3.V.	ROOT MSE	LOGFORCE MEAN	
0.888416	2427.2529	0.81947415	-0.03376140	
SOURCE	DF	ANOVA SS	F VALUE	PR > F
ADDITIVE	15	342.18844526	33.97	0.0001

TABLE 46

ANALYSIS OF ICE ADHESION FOR VARIOUS ADDITIVES

Original Unit = Pounds/Sq. In.

Variance Stabilizing Transformation To Logarithm Of Force
Five Replications

ANALYSIS OF VARIANCE PROCEDURE

SAS

OBS	ADDITIVE	A1	A2	A3	A4	A5
1	Verglimit 6.7%	0.31	0.000	0.000	0.03	0.040
2	Sodium Formate	0.05	0.200	0.180	0.03	0.000
3	Sodium Acetate	0.13	0.200	0.380	0.15	0.180
4	Ice-B-Gon	0.84	2.800	0.840	0.96	0.840
5	Triethylene Glycol	1.30	0.600	0.600	0.50	0.600
6	Ethylene Glycol	0.76	0.640	0.640	0.51	0.760
7	Propylene Glycol	18.00	2.500	7.600	24.00	7.700
8	Dipropylene Glycol	2.50	7.000	8.500	5.50	4.600
9	Tetraethylene Glycol	10.00	5.000	2.000	1.30	0.600
10	Carbowax 300	11.20	4.200	7.800	5.90	11.000
11	Poly G 71-530	8.90	10.200	11.500	7.60	17.800
12	Verglimit 4.5%	0.59	0.025	0.025	0.10	0.013
13	Ketjenflex 8	11.00	5.700	2.500	20.00	14.000
14	Fryol 6	0.40	0.600	0.300	0.25	0.400
15	Table Salt	0.14	0.060	0.200	0.03	0.000
16	Poly G 75-442	25.60	16.000	13.500	20.60	20.900
17	Control

TABLE 47

ANALYSIS OF ICE ADHESION FOR VARIOUS ADDITIVES
 Original Unit - Pounds/Sq. In.
 Variance Stabilizing Transformation To Logarithm Of Force
 Five Replications

ANALYSIS OF VARIANCE PROCEDURE

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

REGWQ	GROUPING		LOG MEAN	MEAN	N	ADDITIVE
	A		2.9371	18.8611	5	Poly G 75-442
	A					
B	A		2.3726	10.7252	5	Poly G 71-530
B	A					
B	A		2.2123	9.1267	5	Propylene Glycol
B	A					
B	A		2.1395	8.4952	5	Ketjenflex 8
B	A					
B	A		2.0170	7.5157	5	Carbowax 300
B	A					
B	A	C	1.6487	5.2002	5	Dipropylene Glycol
B		C				
B	D	C	0.8778	2.4056	5	Tetraethylene Glycol
	D	C				
E	D	C	0.1030	1.1085	5	Ice-B-Gon (CMA)
E	D					
E	D	F	-0.3772	0.6858	5	Triethylene Glycol
E	D	F				
E	D	F	-0.4076	0.6652	5	Ethylene Glycol
E		F				
E		F	-0.9591	0.3832	5	Fryol 6
		F				
	G	F	-1.5923	0.2035	5	Sodium Acetate
	G					
H	G		-2.6390	0.0714	5	Verglimit 4.5%
H	G					
H	G		-2.7718	0.0625	5	Sodium Formate
H	G					
H	G		-2.7882	0.0615	5	Table Salt
H						
H			-3.3129	0.0364	5	Verglimit 6.7%

In the analysis of dry friction (Table 48), we find significant differences among the mean values, ($PR > F$ is .0001) (British Pendulum). The multiple comparisons procedure says that roughly the highest 10 means are not different from each other. This, of course, is desirable. In the ideal situation, all frictions would equal that of the control. The drop in friction must be greater than 10% to see a real difference from the control.

The analysis of wet friction does not show statistical significance, so that we cannot say that the 16 additives and the control differ in this respect. Differences in wet friction cannot be seen because of the high variability, e.g., $PR > F$ has a value of 0.0917 (Table 49). This indicates that high experimental error makes the chance of seeing real difference among the wet friction values only one in eleven (1/11) as compared to 1/10,000 for dry friction and ice adhesion.

Table 50, dry-British Pendulum friction, and Table 51, wet friction, reveal where the differences lie among additives. Thus, there is no real difference between any two values with the same letter.

TABLE 48

ANALYSIS OF FRICTION - BRITISH PENDULUM TEST
FIVE REPLICATIONS

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: DRY

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE
MODEL	16	2558.96224900	159.93514056
ERROR	66	324.26666667	4.76161616
CORRECTED TOTAL	82	2873.22891566	

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREATMENT	16	2558.96224900	33.59	0.0001

TABLE 49

ANALYSIS OF FRICTION - BRITISH PENDULUM TEST
FIVE REPLICATIONS

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: WET

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE
MODEL 16.85321285		16	269.65140562
ERROR 10.51313131		66	693.86666667
CORRECTED TOTAL	82	963.51807229	

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREATMENT	16	269.65140562	1.60	0.0927

TABLE 50

ANALYSIS OF FRICTION - BRITISH PENDULUM TEST
FIVE REPLICATIONS - DRY

ANALYSIS OF VARIANCE PROCEDURE

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

REGWQ	GROUPING		MEAN	N	TREATMENT
	A		49.400	5	Verglimit 4.5%
	A				
B	A		48.333	3	Control
B	A				
B	A		47.800	5	Poly G 75-442
B	A				
B	A		46.800	5	Propylene Glycol
B	A				
B	A		46.400	5	Sodium Formate
B	A				
B	A		46.000	5	Dipropylene Glycol
B	A				
B	A	C	45.400	5	Ethylene Glycol
B	A	C			
B	A	C	45.200	5	Ice-B-Gon (CMA)
B	A	C			
B	A	C	45.200	5	Table Salt
B	A	C			
B	D	C	43.800	5	Poly G 71-530
	D	C			
E	D	C	41.000	5	Fryol 6
E	D				
E	D		40.200	5	Ketjenflex 8
E	D				
E	F		37.800	5	Sodium Acetate
	F				
G	F		35.800	5	Triethylene Glycol
G	F				
G	F		34.200	5	Tetraethylene Glycol
G					
G			32.800	5	Carbowax 300
G					
G			32.000	5	Verglimit 6.7%

TABLE 51

ANALYSIS OF FRICTION - BRITISH PENDULUM TEST
FIVE REPLICATIONS - WET

ANALYSIS OF VARIANCE PROCEDURE

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

REGWQ	GROUPING	MEAN	N	TREATMENT
	A	38.000	5	Verglimit 4.5%
	A			
B	A	35.600	5	Triethylene Glycol
B	A			
B	A	35.400	5	Tetraethylene Glycol
B	A			
B	A	35.333	3	Control
B	A			
B	A	35.000	5	Ethylene Glycol
B	A			
B	A	34.400	5	Fryol 6
B	A			
B	A	34.200	5	Sodium Formate
B	A			
B	A	34.000	5	Ice-B-Gon (CMA)
B	A			
B	A	34.000	5	Table Salt
B	A			
B	A	33.800	5	Sodium Acetate
B	A			
B	A	33.400	5	Verglimit 6.7%
B	A			
B	A	33.200	5	Poly G 71-530
B	A			
B	A	32.800	5	Poly G 75-442
B	A			
B	A	32.600	5	Propylene Glycol
B	A			
B	A	32.000	5	Carbowax 300
B	A			
B	A	31.600	5	Dipropylene Glycol
B				
B		29.800	5	Ketjenflex 8

E. CONCLUSIONS

1. Several water soluble salts and several water soluble organic liquids gave significant reductions in ice adhesion when compounded into asphalt concrete at 6.4% concentration on the aggregate for the salt and 3% for the organic liquid.
2. This greatly lowered ice adhesion was accomplished in many cases with less than 10% reduction in both dry and wet friction.
3. Most systems met these requirements while still meeting the specifications for Marshall stability, i.e. without loss of physical properties when the additives were at the concentrations mentioned above.
4. Significant reduction in ice adhesion was also found when the same additives were surface coated onto asphalt concrete.
5. There are several criteria for water soluble additive selection:
 - o Water solubility.
 - o Calculated solubility parameter greater than 11.
 - o Lowering freezing point.
 - o Non-toxic and non-corrosive.
 - o Price.
 - o Not volatile at 300°F asphalt mixing temperature.
6. For additive screening, the testing was in the following sequence with materials ruled out at each step:
 - o Slush test to determine the effect of the additive on the freezing characteristics of the ice.
 - o Effect of organic liquid additives on the asphalt concrete (AC), i.e. is the AC attacked.
 - o Ice adhesion and friction of briquettes compounded with the additive.
 - o Marshall stability and flow.
 - o Durability of the additive to repeated washings.
7. Ice adhesion test temperature is critical and was changed from -20°C to -5°C. At -20°C there was no change in ice adhesion.
8. The surface impregnation screening test does not always predict results of additives blended into the asphalt concrete.

9. An attempt was made to understand why only some organic-liquids (oils) were effective in lowering ice adhesion to asphalt concrete. Neither the viscosity of the oil nor its freezing characteristics were related to ice adhesion. However, the polarity and hydrophilic nature of the oil and its water solubility are related. All water soluble additives and at least one partially water soluble additive decreased the bond strength between ice and the asphalt concrete.

10. Some water insoluble additives were effective in the surface screening test, e.g., Paraplex G54. To date, however, none were effective when blended into the briquette. After temperature cycling between -5°C and 40°C , there was a small reduction in ice adhesion.

11. Continued washing and retesting of modified briquettes for ice adhesion reveals that ice adhesion of briquettes containing sodium formate, sodium acetate, Ice-B-Gon pellets and powder, ethylene glycol, and propylene glycol increases with each successive wash (up to four washings). For the additives Verglimit, dipropylene glycol, Carbowax 300, tri and tetraethylene glycol and the Poly G71-530 ice adhesion remained relatively constant or very slowly increased.

12. A "Bicycle Wheel" friction test was developed. Several wheel speeds were explored in the Bicycle Wheel friction test, but only the original speed of 30 miles/hour could distinguish wet from dry friction. The British Pendulum test was selected as the more effective method for rapid screening of friction of asphalt concrete briquettes. There is an approximate relationship between friction results from the British Pendulum and the Bicycle Wheel tests. The numerical values for the British Pendulum test are tenfold $\pm 30\%$ greater than those from the Bicycle Wheel test.

13. Additives which significantly lowered ice adhesion were investigated for toxicology, ecological impact and corrosivity to steel, using information from MSDS sheets and from Sax "Dangerous Properties of Industrial Materials".

Most additives examined are non-toxic, environmentally safe, and do not cause corrosion. Verglimit, primarily calcium chloride, and sodium chloride are exceptions, since they cause corrosion. Ethylene glycol appears to be more toxic than the other additives.

14. Replication studies for ice adhesion and friction, using 5 briquettes and 5 tests/briquettes, were carried out on twelve promising additives and Verglimit. A more limited replication study was carried out using the Marshall Test.

15. Statistical analysis of the data was carried out by Dr. Uwe Koehn of the University of Connecticut. There are two types of data being analyzed. In the first, comprising the bulk of the work, there are single points of information obtained by Slush (screening) test, ice adhesion and friction, although in the latter two cases, there were five replicates on each briquette. In order to obtain a measure of variability, analysis consisted of ordering the data and using normal probability plots.

The second set of data to be analyzed consists of replicate runs (five briquettes for each additive) of the best systems to date, and again five tests per briquette along with a Verglimit control and a base control without additive. This data was subject to an analysis of variance to determine whether there are significant differences among additives. The analysis shows that there are significant differences and delineates the best systems.

16. Percent moisture pick up of the additives alone at 75% relative humidity was followed for eight weeks. There is some levelling off in most cases, i.e. the rate of moisture pick up is decreasing. An attempt to decrease the rate of moisture pick up of sodium formate by encapsulation with thermoplastic polyvinyl chloride or a thermoset polyester was unsuccessful.

17. The additives which lower ice adhesion to the greatest extent are:

- sodium formate
- sodium acetate
- sodium chloride.
- triethylene glycol
- Ice-B-Gon (CMA)

There are also significant reductions, i.e. to approximately 10-12 psi or less, in ice adhesion with all the other additives. A summary of the best additive systems is given in Table 52.

TABLE 52

SUMMARY OF BEST ADDITIVE SYSTEMS

	Ice ⁽¹⁾ Adhesion (psi)	British Pendulum Friction(2,3) Dry/Wet	Marshall ⁽³⁾ Stability/ Flow	Price \$/lb.	Slush ⁽⁴⁾ Test Rating
Control	>64	49/35	3433/12	-	
Verg'imit	0.1	32/33	-	0.82	
Sodium Formate	0.1	46/34	3195/13.5	0.20	9
Sodium Acetate	0.2	38/32	1251/13.2	0.58	8
Sodium Chloride	0.1	45/34	-	0.03	10
Ice-B-Gon (CMA)	1.3	45/34	-	0.34	9
Propylene Glycol	12	47/32	1806/15.4	0.56	9
Dipropylene Glycol	6	46/32	-	0.57	8
Tetraethylene Glycol	4	34/35	945/14.8	0.88	8
Triethylene Glycol	0.8	36/35	1344/13.5	0.54	8
Carbowax 300	8	33/32	-	0.73	7
Poly G 71-530	12	45/33	1071/13.3	0.85	-
Connecticut Class I	-	-	>1200/8-15	-	-

Specification

- (1) Data taken from Table 36
 (2) Data taken from Table 37
 (3) Average of five tests
 (4) Water alone gives a rating of "0"

F. RECOMMENDATIONS

1. Additives dissolved, dispersed or emulsified in an asphalt emulsion, or water, should be applied to the surface of asphalt concrete. The additives to be used will be those salts, water soluble organic liquids, and hydrophilic polymers which were used successfully to lower ice adhesion when blended into the asphalt concrete during the first year of the program. Penetration is expected to occur either via the porosity of the pavement and/or by diffusion through the asphalt concrete, perhaps assisted by a surface active agent (surfactant).

With Portland cement concrete, the additives could be incorporated in a cement sealer or in water, perhaps assisted by a penetrant, such as a surfactant.

2. In a second phase (second half year) of the work, the salts and organic liquids which previously lowered ice adhesion should be investigated further. They would be incorporated into the asphalt concrete, used alone, and/or adsorbed on rubber particles for placement as an overlay. Several questions need to be answered.

- a. Does adsorption on the rubber provide a long-lasting additive reservoir?
- b. Is ice removal aided not only by the additive but also by the presence of incorporated rubber, as has been demonstrated in Sweden, Alaska and elsewhere?
- c. What is the effect of continued washing and road wear on long term ice adhesion?
- d. What is the durability of treatment after extensive temperature cycling and weathering exposure?
- e. What is the effect of additive concentration on ice adhesion? Are there co-additives that would be synergistic, e.g., combinations of salts and organic liquids?
- f. Would combinations of additives of low and high water solubility provide a longer effective lifetime of low ice adhesion?
- g. What is the effect on ice adhesion of molecular weight, solubility parameter (in the range 10-14), and degree of water solubility of the organic liquids?
- h. Would the same additives used for lowering ice adhesion in asphalt concrete be effective in Portland cement concrete?
- i. Could encapsulants be used to regulate the availability of ice releasing additive?

3. The second half of the second year program should also include field testing of successful surface treatments developed during the first half of the second year.

APPENDICES

Appendix A:	Literature Search
Appendix B:	Chemical Nature of The Additives
Appendix C:	Ice Adhesion versus Viscosity and Freezing Characteristics
Appendix D:	Solubility Parameters
Appendix E:	Statistical Analysis - Definitions

APPENDIX A

LITERATURE SEARCH

<u>Section</u>	<u>Page</u>
I. CMA (Calcium Magnesium Acetate)	A-2
II. Deicing Chemicals	A-5
III. Deicing Coatings	A-8
IV. Environmental Effects	A-13
V. Portland Cement Concrete (PCC)	A-16
VI. Rubber In Asphalt Concrete	A-20
VII. Solubility Parameters	A-24
VIII. State of Connecticut	A-25
IX. Testing	A-26
X. Theory	A-27
XI. Thermal Heat Gain	A-31
XII. Verglimit	A-33

I. CMA (CALCIUM MAGNESIUM ACETATE)

1. Bacchus, A., (The Research and Development Branch, Ministry of Transportation of Ontario), "Financial Implications of Salt vs. CMA as a Deicing Agent: Costs & Benefits Estimated by an MTD Expert Group", December 1987. Note: Report ME-87-20. This report is one of a number published by the Ministry dealing with aspects of calcium magnesium acetate. Other reports published to date are M1-84-02 and ME-87-16.

A study was undertaken using a modified Delphi technique, to develop a model for evaluating the costs and benefits of switching from salt to any other deicing chemical, and to apply the model to calcium magnesium acetate (CMA). The additional cost of using CMA rather than salt was significantly greater than the estimated reduction in the five categories of environmental damage considered: vehicle corrosion, bridge deterioration, parking garage deterioration, groundwater contamination, and damage to vegetation and other private property. The most substantial benefit was reduced vehicle corrosion costs. The calculated break-even cost for CMA, i.e. the price at which CMA would have to be purchased in order to balance the environmental benefits, was in the range of \$343 to \$481/tonne (1985 dollars), depending upon the assumptions made for the discount rate and the amount of material used.

2. Chollar, B.H., (Federal Highway Administration, Office of R&D), "Field Evaluation of Calcium Magnesium Acetate During the Winter of 1986-87". Public Roads, June 1988, 52, No. 1, pp 13-18. SUBFILE: HRIS available from: Government Printing Office, Superintendent of Documents, Washington, DC 20402.

The key findings of field deicing studies of calcium magnesium acetate (CMA) conducted in Wisconsin, Massachusetts, California, and Ontario are discussed. Various features of CMA spreading, that have become apparent, are discussed, and practical problems are noted. Storage and handling characteristics of CMA are also noted. The trials tested the comparative deicing effects of both CMA and salt in snowstorms, with temperatures ranging from 24 to 32 degrees F. It was found that CMA deices roadways as effectively as salt, but requires a longer period of time to accomplish this. The amounts of CMA used and the application rates are discussed.

3. Chollar, B.H. and Virmani, Y., "Effects of Calcium Magnesium Acetate on Reinforced Steel Concrete", Public Roads, 51, pp 113-115, Mar. 1988. SUBFILE: HRIS available from: Government Printing Office, Superintendent of Documents, Washington, DC 10402.

A Federal Highway Administration-initiated project to study calcium magnesium acetate (CMA) as an alternative deicer is reported. The project

included 4 major tasks: (a) evaluation of the effects of CMA on the environment; (b) determination of the feasibility and development of its economical production; (c) determination of the physical and chemical properties and deicing ability; and (d) the evaluation of the effects on highway and transportation materials. Study results show that the potential of the black steel rebars in slabs ponded with salt solutions started increasing numerically within the first 3 months of exposure, while that of rebars in slabs ponded with CMA solution did not increase at all during that time period. The CMA solutions did not cause any significant potential shift or corrosion after 4 years on/of ponding in an outdoor environment.

4. Dunn, Stanley A.; Schenk, Roy, (Bjorksten Research Lab., Inc., Madison, WI). "Alternative Highway Deicing Chemicals", Mar. 1980. Corp. Source Codes: 057852000, Sponsor: Federal Highway Administration, Washington, DC. NTIS Prices: PC A08/MF A01 Country of Publication: United States, Contract No. DOT-FH-11-9100.

A search has been made for road deicing chemicals to replace sodium chloride (NaCl). The impetus for this search stems from the numerous drawbacks associated with the prevalent use of NaCl as a road deicer. All types of chemical compounds were reviewed. Selections were made on the basis of criteria, such as water solubility and freezing point lowering, corrosion, toxicity, relative cost or cost potential, effect on soils and plants and water supplies, flammability, concrete compatibility, traction, friction, highway performance, etc. Information was sought first in the literature, then supplemented or verified in the laboratory as needed. Two candidate deicers were found to be as effective as sodium chloride. One, methanol, reacts almost immediately upon contact with snow and ice, but is less persistent than NaCl. The other candidate, calcium magnesium acetate (CMA), acts at about the same rate as NaCl in the temperature range of common activity, and shows about the same persistence.

5. Hsu, M.T., (Maine Department of Transportation). "Production and Testing of Calcium Magnesium Acetate in Maine". Transportation Research Record, 1984, N 962, pp 77-82 2. SUBFILE: HRIS available from: Transportation Research Board Publications Office, 2101 Constitution Ave., NW, Washington, DC 20418.

The search for an effective substitute for the deicing agent, sodium chloride, has led to the development of calcium magnesium acetate (CMA). However, CMA is not commercially available. A project for the production of CMA, using resources in Maine, was carried out at the Maine Department of Transportation. After the product was made, other physical and chemical tests were also performed. The results indicated that CMA can be made in Maine from an apparent abundant source of high magnesium limestone and acetic acid (cider vinegar). A 10 percent solution of acetic acid with 10 min. of agitation with the magnesium limestone coarse aggregate provides the best production of CMA for this grade. A commercial production of CMA should consider the constant reflux method with constant monitoring of the pH. Evaporation of the solution by solar energy is not effective because of the large amount of rainfall in Maine. Bituminous concrete batch plants have waste heat, which might be able to aid in this

evaporation need. The field trial of CMA as a deicing agent demonstrated both advantages and disadvantages. A major concern is its dustiness. Outdoor uncovered storage of CMA is not practical. The corrosion effect of CMA solution toward metal or concrete needs further study. This paper appeared in Transportation Research Records 962, Bridge Maintenance Management, Corrosion Control, Heating, and Deicing Chemicals.

6. "Salt-Substitute Test Gets Underway", Better Roads, 56, p 43, Dec. 1986. Data available from: Better Roads, P.O. Box 558, Park Ridge, IL 60068. FILE: HRIS.

A new granular form of calcium magnesium acetate (CMA) is being tested by the Federal Highway Administration along a 7 mile length of U.S. Highway 14 in Wisconsin. Road salt, granular CMA, and sand coated with CMA are being applied, and a side by side comparison is being made of the effectiveness of each substance. The granular CMA looks like rock salt and handles like it. It is noted that, to date, CMA appears to be the most promising non-salt chemical deicing agent which is both effective and environmentally acceptable. CMA is less corrosive, non-toxic, and degrades in the environment slowly. The calcium and magnesium in CMA are precipitated as carbonates and can actually be beneficial additives to the soil.

7. Schenk, R.U., (Bjorksten Research Lab., Inc., Madison, WI), "Ice-Melting Characteristics of Calcium Magnesium Acetate", Jan. 86, Final Report. Corp. Source Codes: 057852000, Sponsor: Federal Highway Administration, McLean, VA., Office of Engineering and Highway Operations Research and Development. NTIS Prices: PC A04/MF A01, Country of Publication: United States, Contract No. DTFH61-83-C-00041.

Pertinent chemical and physical properties of calcium magnesium acetate (CMA) were determined. Included were comparisons of ratios of calcium to magnesium varying from 100% CaAc2 to 100% MgAc2. The objective was to determine the optimum composition of CMA for road deicing. In a 12-month study involving wetting/drying tests with 11 ratios of Ca/Mg and five pH's, it was found that CMA at pH's above 7.0 and at any Ca/Mg ratio produced no more harm to Portland cement concrete than did NaCl. In addition, with compositions containing Mg at levels equal to or greater than Ca, the damage to concrete was significantly reduced.

II. DEICING CHEMICALS

1. Harris, J.C., Gibson, J.R., Street, D., "Chemical Means for Prevention of Accumulation of Ice, Snow, and Slush on Runways", Mar. 1965. Source Codes: 000000. Available copy will not permit fully legible reproduction. Reproduction will be made if requested by users of DDC. Copy is available for public sale. NTIS Prices: PC A02, Contract No. FA WA4577; 430 006 01R.

The objective of this contract was to develop a mixture capable of melting snow, ice, and slush at temperatures as low as -10°F . Two surviving candidate mixtures were demonstrated as easily prepared in simple, standard mixing equipment, and their storage characteristics as free flowing granules determined at two temperature extremes. The application rate to produce melting at -10°F was quite nominal (2 oz/sq. ft.), and the compositions had, at most, slight spalling effect on concrete. The prime candidate for runway deicing has the following composition: tripotassium phosphate 75% - formamide 25%. A second combination proved outstanding for preventive corrosion of steel not under the potentially high stress of landing gear. Quite suitable for road or highway usage was calcium chloride to which was added 1% by weight of Emulsifier STH. This composition retained all its ice-melting qualities with marked corrosion control.

2. Kasinskas, Michael M., (State of Connecticut, Department of Transportation, Wolcott Hill Road, P.O. Drawer A, Wethersfield, CT 06109), "Evaluation of the Use of Salt Brine for Deicing Purposes", Final Report, May 1982, Research Report No. 396-F-82-6.

A new method of destroying snow pack and ice accumulation on roadway surfaces is discussed. The method utilizes high-speed sodium-chloride jet streams to penetrate the pavement cover and initiate an immediate melt. The brine is applied to the pavement from nozzels connected to a distribution bar located under the midsection of a truck. A pressure of up to 300 psi is utilized to produce the high speed streams. The results of field observations of both tests (high-speed brine streams) and control (crystalline salt) sections are presented. Comparisons are made between amount of salt used in each section over a three-year period, and problems involving equipment design and malfunction are discussed. The units have been successful for snow and ice removal and have a definite effect on salt consumption. They have also been employed in other types of maintenance operations yielding increased productivity.

3. Itagaki, K., "Polyethylene Glycol As An Ice Control Coating", (Cold Regions Research and Engineering Lab., Hanover, NH), Journal Vol. U8510, Report Date Dec. 1984, 15 p. Report No. CRREL-84-28, Contract No. MIPR-FY76-168200394, Proj. No. 4A161102AT24, Tack No. C, Mntr. Agency C.

The properties of polyethylene glycol (PEG) as a sacrificial ice control coating are discussed. PEG is effective longer than many single component coatings, and it has low toxicity and a high flash point. The results of preliminary experiments on PEG's ability to control snow accumulation on a panel and ice accumulation on a cryogenic tank are also discussed.

4. Palmer, D.A., "Formates as Alternative Deicers", Transportation Research Board, 1987, Record N1127, pp 34-36. SUBFILE: HRIS available from: Transportation Research Board Publications Office, 2102 Constitution Avenue, NW, Washington, DC 20418.

The cost of deicing the nation's road system is roughly 20 times greater than the cost of the salt that is spread. This is due to chloride corrosion, which hits the vehicle fleet hardest. Next hardest hit are the nation's bridges, whose life has been reduced from about 20 to 5 years. Because corrosion inhibitors have proven ineffective, attention has turned to alternative chemical deicers. Though most current government support is dedicated to evaluation of calcium magnesium acetate (CMA), this chemical compound has many technical and economic drawbacks. In fact, CMA might continue to be too expensive to generate much use. At less than half the cost, it may be possible to produce sodium, calcium, or dolomitic lime formates. They can probably be made directly from carbon monoxide, rather than using formic acid. Sodium formate is much less toxic than initially thought. Further, it can probably be spread as a very concentrated solution or even as a slurry. The freezing-point curve of sodium formate is similar to that of sodium chloride, down to about -14 degrees C. It has now been demonstrated experimentally that sodium formate does not spall cured concrete. This paper appeared in Transportation Research Record No. 1127, Innovation, Winter Maintenance, and Roadside Management.

5. Special Product Evaluation List (SPEL) (August 1983), American Association of State Highway and Transportation Officials, Washington, DC. Source Codes: 060869000, Sponsor: Federal Highway Administration, Washington, DC. See also PB81-158214. NTIS Prices: PC A99/MF E04 Country of Publication: United States.

This document is a listing of special products which have been evaluated in some manner by State highway or transportation departments. It is intended only to provide interested governmental employees with a guide as to who has made tests on these products. The listing contains 4,244 evaluations contributed by 38 States and the FHWA. Evaluated products in this listing include: adhesives, aggregates, barriers, fencing and roadside structures, bituminous rejuvenators and preservative treatments, bituminous materials and additives, culverts and drainage structures, deicing materials, joint sealers and fillers, mulch and erosion controls, patching materials, Portland cement concrete finishing products,

reflective crack controls, rust passivators, skid control systems, soil sterilization and weed control materials, soil treatments, structural materials and components, structural paints, testing and construction equipment, traffic marking materials, and waterproofing membranes and materials.

6. Sandrig, Robert L., Klemm, William A., Gaines, Jack R., Looyenga, Robert W, "Deicing Chemicals and Their Preparation From Polysaccharide Sources". ASSIGNEE: United States Dept. of Transportation, PATENT: US 4430240A, DATE: 2/7/84, APPLICATION: US 338848 (1/12/82), 6 pp.

Alkaline earth metal salts, e.g., calcium, of carboxylic acid derivations of polysaccharides were effective deicers.

7. Stratfull, R.F., Spellman, D.L., Halterman, J., "Further Evaluation of Deicing Chemicals", Jan. 1974. NTIS Prices: PC A03/MF A01;, Contract No. FHWA-B-4-3.

Severe corrosion of reinforcing steel and concrete deterioration in reinforced concrete bridge decks caused by salt applied to the decks to control ice and snow has prompted a search for a noncorrosive deicing chemical suitable for maintenance use. Seventeen candidate chemicals have been evaluated. Tetrapotassium pyrophosphate (TKPP) exhibited good frost preventing properties and two years of limited field testing on bridge decks is reported. A skidding car method of coefficient of friction is presented. The test results of sodium formate used as a deicer and its detrimental effect on concrete is evaluated.

8. Williams, Robert F., and Dotson, Billy E., "Plastic Anti-Icing and Tar De-Icing Surfaces", SPE 33rd ANTEC, March 5-8, 1975.

Additives were melt compounded into several polymers and ice adhesion measured. Ethylene glycol, sodium chloride and a detergent (commercial mixture of sodium phosphate, sodium sesquicarbonate and sodium tripolyphosphate) were effective in cellulose acetate butyrate and ethylene glycol was effective in polyvinyl butyral.

III. DEICING COATINGS

1. Baum, B., Kendrew, T., and Thoma, L., "Research To Develop Conductor Deicing Compounds", Fourth International Workshop on Atmospheric Icing of Structures, Paris, France, Sept. 5-7, 1988.

Extensive damage to utility overhead lines and, consequently, outages occur when ice accumulates on overhead conductors. The goal of this program was the development of ice repellant-ice shedding coatings for overhead conductor wire.

A variety of methods have been explored, involving low energy treatments, or coatings for the conductor wire to promote shedding due to low wettability and low work of adhesion. These included (a) the preparation of low molecular weight reactive compounds, (b) the synthesis of oligomeric compounds that are reactive with the surface of the bare conductor and, (c) the investigation of polymeric coatings.

The use of polymers was considered to be the most feasible approach, and a broad variety of commercial coatings were investigated. However, none of these provided the necessary combination of low ice adhesion and durability. What was needed was a material with a continually renewable surface.

Low surface energy silicone or fluorocarbon oils were compounded into low density polyethylene, as a low cost matrix polymer, in two ways:

1. Melt compounding directly into polyethylene with and without filler.
2. Vacuum impregnating porous polyethylene.

These oil-filled polyethylene compounds molded around aluminum rods evidenced significant ice repellant and ice release properties.

2. Calabrese, S. J., et al, "Low Friction Hull Coatings For Icebreakers", Rensselaer Polytechnic Institute, Report No. CG-D-107-74, Prepared for the Coast Guard, June 1974, Distributed by NTIS, AD-784 361.

Part I of the first phase of development of low friction coatings for icebreakers involved the evaluation of state-of-the-art coating available from industry. Laboratory simulation tests were conducted to determine materials' ability to withstand ice impact forces, abrasion resistance and scratch resistance, as well as quantifying various frictional properties

of the materials with varying ice properties. Several coatings were selected out of over 100 samples tested for application on icebreakers.

Part II of Phase I: The coatings selected in Part I were applied to small icebreakers for initial full scale evaluation. Tests are described and results discussed.

An investigation was conducted to isolate low friction, abrasion resistant coatings for the hulls of icebreakers. Within the limits of conditions defined, the following results were obtained:

- (1) Of the materials evaluated, the most promising coatings were the unfilled polyurethanes and the modified polyphenylene oxide. They resisted damage, wear, and spalling in the abrasion tests; they also gave (with the exception of polyethylene) the lowest coefficient of friction. Friction coefficient of these materials are less than 0.15 from 0 degrees C to -25 degrees C. Steel under similar conditions gave friction values between 0.10 and 0.40.
- (2) Frictional behavior of ice is influenced primarily by three factors: temperature, roughness and time in contact. A reduction in static friction takes place at temperatures above -7 degrees C. This is attributed, as has been suggested by others, to a reduction in the strength of ice. For steel, static friction increases from 0.4 at a surface roughness of 40 CLA to a value of 1.2 at 240 CLA. Increase in static friction is found with increasing time in contact. This effect is more pronounced at greater surface roughnesses. Thus, there is a time dependence of static friction which should be taken into account.
- (3) There is an optimum hardness value for materials used in ice abrasion. Coatings softer than ice are severely damaged. Hard coatings, such as epoxies, are chipped and pitted by ice abrasion. Soft coatings appear to be roughened by ice abrasion and give high friction near 0° C.
- (4) With the high contact angle materials used in these experiments, no correlation could be established between contact angle and friction. This was attributed to the overriding influence of surface roughness.
- (5) Without the use of plastic coatings, large reductions in friction could be obtained by using a smooth corrosion resistant surface on the icebreaker hulls.

Calabrese, S. J. and Ling, F. P., "Low Friction Hull Coatings for Ice Breakers", Phase III Technical Report, CG-D-32-76, Rensselaer Polytechnic Institute, October 1978.

Phase III is a continuation of the Low Friction Hull Coatings for Icebreakers program in which nonsolvent coatings gave the best protection for icebreaker hulls. This effort documents the reduction in resistance obtained. a laboratory study to determine the optimum

application parameters, fouling characteristics and the cost benefit obtained from coating an icebreaker hull with the nonsolvented coatings.

In addition, a model test program was run to determine the effect of a partial hull coating.

The full-scale resistance test indicates that a reduction in resistance in ice can be obtained by the application of a low friction hull coating. The percentage reduction is dependent on speed. The size and design of the hull will also influence percentage reduction. However, with the 110 ft. icebreaking tugs, the reduction was on the order of 15% at 8 knots and 8% at 3 knots.

A significant reduction in friction coefficient has been measured in laboratory tests of a hull plate coated with the nonsolvented materials.

The nonsolvented polyurethane has survived four years of icebreaking service and still is over 90% intact. The nonsolvented epoxy gave good results for one-half year of service, and after one and one-half years service, the coating appears to be over 95% still intact.

3. Hanamoto, I., "Application of a Block Copolymer Solution to Ice-Prone Structures", Proceedings of First International Workshop, Atmospheric Icing of Structures, June 1-3, 1982, Hanover, NH, L. D. Minsk, Ed., p 155-157.

A block copolymer, a poly(dimethyl siloxane)-bisphenol -A- polycarbonate was developed jointly by CRREL and H.H.G. Jellinek of Clarkson College which greatly reduces the adhesion of ice. The copolymer, applied as a coating, does not prevent the formation of ice, but it does make ice easier to remove. However, it is not resistant to abrasion and rubbing.

4. "Ice Release Coatings For Air-Break Switches", Electric Power Research Institute, Palo Alto, CA, Information Sheet No. 29.

A number of coatings were evaluated for ice release. None were found that would prevent ice buildup. However, a teflon filled hydrophobic polyurethane coating considerably reduces the force needed to open outdoor disconnect switches under icing conditions.

5. Landy, M., Naval Applied Science Lab, Lab Project 930-18, SF013-99-02, "Ice Adhesion and A Deicing Coating", 5/21/69.

A number of hydrophobic coatings were examined to provide low ice adhesion to the Navy's grey deck paint 20-type A, and the alkyd-type zinc chromate primer Formula 84/47. The lowest ice adhesion was achieved with crosslinked poly(dimethyl siloxane) resins. However, they had a short service life (2-3 weeks) and they were slippery.

6. Millar, Donald M., National Aviation Facilities Experimental Center, Atlantic City, NJ, "Investigation of Ice Accretion Characteristics of Hydrophobic Materials", Federal Aviation Administration, Aircraft Development Service, Washington, DC; , Final Report No. FAA-DS-70-11, May 1970, 12 pp.

Twenty-three hydrophobic coatings were examined as anti-icing coatings on airplane wings. None were found effective for this purpose, but silicone resins were useful in promoting easier ice removal.

7. Porte, Howard, A. and Nappier, Thomas E., U.S. Naval Civil Engineering Laboratory, Port Hueneme, CA, "Coating Material For Prevention of Ice and Snow Accumulations - A Literature Survey", Accession No. N65-11193, TK-541, 10/11/63, pp 1-8.

An extensive literature search was conducted. The author's conclusion was that it is almost impossible to develop a coating to which ice will not bond. However, silicone and fluorocarbons facilitate ice removal.

8. Sayward, John M., "Seeking Low Ice Adhesion", CRREL Special Report 79-11, April 1979.

Icing impairs operation of helicopters and other aircraft, antennae, power and communication lines, shipping and superstructures, canal locks, etc. Prevention or easier removal of icing requires reduction of its adhesion strength. Literature study shows that adhesion results from secondary (van der Waals) forces yet exceeds normal cohesive strengths. It depends on free surface energy, low contact angle, good contact and wetting, cleanliness, and texture. Modes of adhesion testing are briefly discussed. Poor adhesion occurs with low energy surfaces or contaminants, e.g., hydrocarbons, fluorocarbons, waxes, oils, etc., particularly when textured or porous. The resulting low contact angle, poor wetting and occlusion of air at the interface weaken the bond or provide stress loci which can initiate cracks and failure.

Coefficient of expansion differences may help in release of ice. Further ideas appear among the 100 abstracts presented. A survey of over 300 manufacturers produced over 100 replies. Half of them offered some 100 products deemed worth testing. These are listed with addresses and contacts. Besides simple resins and other release agents, they include composites which combine low surface energy and stronger materials as micro-mixture, interpenetrating-network, "plastic-alloy", or filler-matrix systems. About 15 to 20 products appear of special interest. Samples of liquid coating or supplier-prepared panels of many are available for the testing phase to follow.

Conditions for low ice adhesion, i.e. adhesion, release or parting, may include:

- (1) Low energy surfaces of solid substrates (for applied coatings).
- (2) Absence of contamination of the surface by high energy materials or of the water by surfactant (surface tension reducing) substances.
- (3) Presence of contamination with even lower energy material to impair bonding across the interface and create consequent non-uniform stress distribution.

- (4) Occlusion of air at the interface to impair bonding and promote stress concentrations that can initiate or propagate adhesive cracks and failure.
- (5) An optimum degree of roughness-smoothness to encourage co-planar air entrapment and stress concentration and consequent initiation of cracks and their propagation to joint failure.
- (6) Appropriate substrate construction or properties that encourage generation and/or transmission of suitable stress and production of cracks for adhesive failure (i.e. self-shedding or easy removal of ice).
- (7) Appropriate stress (shock, flex, vibration, heat or thermal gradient) to induce loosening or failure.

These factors will be, to varying degrees, applicable in the several situations where low ice adhesion, self-shedding or easy removal of ice is desired.

In connection with factor #6, "Flexible coatings have been noted to exhibit lower ice adhesion (Jellinek 1959, Stallabrass and Price 1963, Landy and Freiburger 1967 and 1968, Landy, undated and 1969). A degree of general flexibility can generate local stress and encourage crack initiation according to the Griffith-Irwin crack theory".

IV. ENVIRONMENTAL EFFECTS

1. Boies, D. B., Bortz, S., "Economical and Effective Deicing Agents For Use on Highway Structures", Highway Research Board Nchrp Reports, 1965, No. 19, pp 1-19.

SUBFILE: HR1S research results are presented of an 18-month experimental program directed to the development of economical and effective deicing agents to minimize the corrosion of structural steel elements and vehicles, and the freeze-thaw deterioration of concrete. Corrosion experiments employing sodium chloride and calcium chloride were conducted under environments approximating critical field conditions for both vehicles and structures, and corrosion rates for test experiments were observed. Subsequent studies were made to determine the potential of various materials as corrosion inhibitors. The studies of concrete deterioration by deicing chemicals was approached in a manner similar to that used for corrosion studies. A composite deicing agent of urea and calcium formate having an uetectic point of minus 3F is suggested to increase the corrosion rate. Formamide can be added, if lower temperature performance is needed. The increase in corrosion rate encountered with chloride solutions may be eliminated by the addition of a polyphosphate-based material or a long-chain amine to the sodium chloride solution. Various materials added to chloride deicer solutions reduced the rate of freeze-thaw deterioration. Typical additives were sequestering agents, such as the sodium salt of ethylenediamine tetracetic acid, and polyhydroxy sugar-type compounds, such as dextrose. Longer curing periods reduced the rate of cement mortar deterioration during freeze-thaw testing, and reduced the amount of additive needed in the chloride solution to afford protection. The cost of deicing is materially increased when the deicing methods found to be less reactive to steel and concrete are used.

2. Button, Edward F., Peaslee, Doyle E., "The Effect of Rock Salt Upon Roadside Sugar Maples in Connecticut", 1965.

In order to establish and assess the toxicity of rock salt used for highway deicing operations, to roadside trees, it was decided in 1964 to intensively study a group of roadside sugar maples (*Acor Saccharum*). The trees selected were the same age, and were planted in 1896. The site is located on Route 17 near the Durham-Middletown line, a heavily travelled highway, where rock salt applications have been made for several years. Trees on the west side of the highway, either level with or downslope from the pavement, were noticeably declining in vigor, demonstrated more leaf burn injury, and defoliation, than the trees on the east side, which is upslope from the pavement. Three trees of the same species and age were selected from a non-highway site not contaminated with rock salt as control, or reference trees.

3. Button, Edward F., Connecticut State Department of Transportation, Division of Research and Development, Unit 105, "Metabolic Index as a Diagnostic Tool in Tree Health Determination", October 1969.

An earlier Connecticut study suggested that high levels of sodium and chloride ions had a depressing effect upon the levels of calcium, magnesium, phosphorus and potassium ions. A method is offered whereby the ratio of harmful to nutritious ions, the METABOLIC INDEX, may be applied to monitor the health of salt sensitive trees before injury is visible. The calculated metabolic index, based on chemical analysis of both leaves and twigs, of 24 Sugar Maples, in four groups variously exposed to salts, observed over a three-year period, showed good correlation with state of health. The study of leave tissue only, i.e. the youngest cell tissue, could be misleading. In combination with twig tissue studies, i.e. wood tissue subject to gradual ion accumulations, a more realistic evaluation evolves. Validity is lent to the hypothesis that a metabolic index remaining near or below ten will lead to the need for tree removal. An index of 30 and below is an indicator of declining vigor, which may be accelerated by physical damage, disease, insect infestations or severe drought. The prognosis is good for trees with indices ranging from 35 upward. It is hoped that the proposed method will be tested, refined and expanded upon by other researchers.

4. Craik, D. W. and Yuill, G. K., "Deicing Chemicals Corrosion Investigation", 1965, Report No. HS-700-212 to the Metropolitan Corp. of Greater Winnipeg.

SUBFILE: HSL. The main variables determining corrosion rates of automobile steels in several Canadian cities were temperature, precipitation, amount of chemicals used, and atmospheric fallout. Deicing chemicals damaged concrete but not asphalt pavements, causing surface scaling. The mechanism is physical and accentuates frost damage. Protective methods are an encasement in poured concrete and surface coatings.

5. Dupuis, T., Kobriger, N., Kreutzberger, W., and Trippi, V., "Effects of Highway Runoff on Receiving Waters, Volume III: Resource Document For Environmental Assessments", Final Report, Mar. 1985, Federal Highway Administration, 400 7th St., SW, Washington, DC 20590, Report No. RHW/ RD-84/064, FOP 33B1 012, Contract No. DTFH-61-80-C00001. Contract SUBFILE: HRIS available from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

This resource document is intended to serve as a user tool to supplement the Procedural Guidelines Manual (Volume IV). State highway agencies can use these resources to more comprehensively address the effects of stormwater runoff in environmental documents. This document provides a critical summary and review of the technical literature on hydrological, water quality, sediment, and biological impacts of runoff from operating highways. Major pollutant categories include oxygen-consuming materials, nutrients, bacteria, road salt, petroleum hydrocarbons, and metals. Subcontract work by: University of Wisconsin-Milwaukee, Center for Great Lake Studies, Milwaukee, WI 53201.

6. Minsk, L.D., "Freeze-Thaw Tests of Liquid Deicing Chemicals On Selected Pavement Materials", CRREL Report No. 77-20, Nov. 1977, 16 p.

Portland cement concrete and asphalt concrete were exposed to a variety of non-chloride deicing chemicals during freeze-thaw cycling per ASTM C672-717.

Sodium chloride, distilled water and dry specimens were used as controls and for comparison. Pavements included new and old specimens of open-graded asphaltic concrete and old specimens of dense-graded asphaltic concrete. Portland cement concrete specimens used were new and old, with and without air-entrainment. New and old tar rubber concrete specimens were also tested. Samples were subjected to up to 60 freeze-thaw cycles with deicing chemicals flooding their upper surface. Each specimen was rated on a scale of 0-5 after every five freeze-thaw cycles. All PCC specimens showed some surface degradation, whereas the dense- and open-graded asphaltic concretes were largely unaffected.

V. PORTLAND CEMENT CONCRETE (PCC)

1. Ashworth, T., and Weyland, J., "Investigation of the Basic Forces Involved In The Adhesion Of Ice to Highway Surfaces", 7807-7907, June 1982, Federal Highway Administration Office of University Research, 400 7th St., SW, Washington, DC 20590, Report No. DOT/RSPA/DPE50/82/5, Contract No. DOT-OS-70072, Contract SUBFILE: HRS available from: South Dakota School of Mines and Technology, 500 East St. Joseph St., Rapid City, SD 57701.

Improved knowledge of the basic forces contributing to the adhesion of ice to highway surfaces was the objective of the research performed. Tensile and shear interfacial strength tests formed the main thrust of the experimental program. Tests were carried out over the temperature range - 0.5 deg. C to -20 deg. C for several concrete mixes, mortar and asphalt. Surface treatments included NaCl, CaCl₂, a silicone compound, a fluorocarbon compound and a mineral oil (#2 diesel fuel). The salts were effective in reducing adhesion above -8 deg. C; the other materials were more effective, especially at lower temperatures. In fact, diesel oil is a long term contaminant which must be avoided for tests on concrete. The wetting temperature of a clean substrate has been shown to be a factor. Modified concretes showed reduced adhesion. Results of numerical modeling of an ice/concrete interface show stress concentration factors greater than one, due to material dissimilarities, penetration of one material into the other, and non-homogeneous substrate. Tensile strength measurements for pure ice have been made, and failure criteria for the interface have been developed from them. Moisture adsorption and heat of wetting experiments for quartzite, limestone, sand, and P.C. mortar have been taken. Adsorption site areas and energies have been deduced. Data is being interpreted to disclose the role of capillary effects and the influence of fluorocarbon treatment. Results obtained indicate that both mechanical and chemical binding are important at the ice/concrete interface, and that the interfacial strength can be weakened by substrate modification, substrate treatments, or solute treatment.

2. Boies, D., and Bortz, S., "Economical and Effective Deicing Agents For Use On Highway Structures", Highway Research Board Nchrp Reports, pp 1-19, 1965. SUBFILE: HRIS

Research results are presented of an 18-month experimental program directed to the development of economical and effective deicing agents to minimize the corrosion of structural steel elements and vehicles, and the freeze-thaw deterioration of concrete. Corrosion experiments employing sodium chloride and calcium chloride were conducted under environments approximating critical field conditions for both vehicles and structures,

and corrosion rates for test experiments were observed. Subsequent studies were made to determine the potential of various materials as corrosion inhibitors. The studies of concrete deterioration by deicing chemicals was approached in a manner similar to that used for corrosion studies. A composite deicing agent of urea and calcium formate having an eutectic point of minus 3F is suggested to increase the corrosion rate. Formamide can be added if lower temperature performance is needed. The increase in corrosion rate encountered with chloride solutions may be eliminated by the addition of a polyphosphate-based material or a long-chain amine to the sodium chloride solution. Various materials added to the chloride deicer solutions reduced the rate of freeze-thaw deterioration. Typical additives were sequestering agents, such as the sodium salt of ethylenediamine tetracetic acid, and polyhydroxy sugar-type compounds, such as dextrose. Longer curing periods reduced the rate of cement mortar deterioration during freeze-thaw testing, and reduced the amount of additive needed in the chloride solution to afford protection. The cost of deicing is materially increased when the deicing methods found to be less reactive to steel and concrete are used.

3. Dahl-Jorgensen, E., Chen, W. F., Manson, J. A., and Vanderhoff, J. W., "Polymer-Impregnated Concrete: Laboratory Studies", May 15, 1974, 405776 PB-234 046/1, Report No. HRP-NCHRP-FEL-74-39006, Journal Announcement: GRA17420, Corp. Source Codes: 144000. See Also PB-233 047. NTIS Prices: PC A03/MF A01.

To aid in the development of polymer-impregnated Portland cement (PIC) for highway bridge decks and other structural applications, a laboratory study of several process and material parameters was conducted. It was shown that (1) stress-strain behavior could be varied over a wide range, from ductile to brittle, by using combinations of plasticizing and/or crosslinking comonomer with methyl methacrylate; (2) the presence of a realistic level of salt (up to 1%) in concrete has little effect on polymer loading and mechanical properties, but requires more rigorous drying; (3) while high temperatures (750F) accelerate drying but decreases strength, subsequent polymer impregnation essentially yields a PIC with properties similar to a conventionally dried material; (4) salt penetration (short-time, static) in mortars is reduced an order of magnitude by polymer impregnation, regardless of whether the polymer is glassy or rubbery. Thus, strong PICs can be prepared under a variety of drying and salt contamination conditions, and the mechanical behavior of PIC can be tailored to various specifications by varying polymer composition, without diminishing PIC's improved resistance to salt penetration.

4. Dubberke, W., and Marks, V., "The Effect of Deicing Salt on Aggregate Durability", Transportation Research Record, pp 27-34, 1985. SUBFILE: HRS available from: Transportation Research Board Publications Office, 2101 Constitution Ave., NW, Washington, DC 20418.

Since 1963, the Iowa DOT has been using the methods of rapid freezing in air and thawing in water to evaluate coarse aggregate durability in concrete. Earlier research had shown that the aggregate pore system was a major factor in susceptibility to D-cracking rapid deterioration. There

are cases in which service records indicate that on heavily salted primary roads, concrete containing certain aggregates show rapid deterioration while the same aggregates show relatively good performance on secondary roads with limited use of deicing salt. A five cycle salt treatment of the coarse aggregate before durability testing has yielded durability factors that correlate with aggregate service records on heavily salted primary pavements. X-ray fluorescence analyses have shown that sulfur contents correlate well with aggregate durabilities with higher sulfur contents that produce poor durability. Trial additives affecting the salt treatment durabilities would indicate that one factor in the rapid deterioration mechanism is an adverse chemical reaction. The objective of the current research is to develop a simple method of determining aggregate susceptibility to salt-related deterioration. This method of evaluation includes analyses of both the pore system and chemical composition. This paper appeared in Transportation Research Record N1031, Geotechnical Engineering Research.

5. Larson, T. D., Cady, P. L., Browne, F. P., and Bolling, N. B., "Deicer Scaling Mechanisms in Concrete", Dec. 1970, Corp. Source Codes: 388225. Prepared in cooperation with the Pennsylvania Dept. of Transportation and Bureau of Public Roads. NTIS Prices: PC A07 MF A01, Contract No. PDH-44242.

The objective of this research was to investigate the mechanism by which deicers cause deterioration of concrete. Previously proposed mechanisms based on thermal shock and direction of freeze were experimentally isolated. The effect of direction of freeze was found to be insignificant. Deterioration associated with saturated calcium chloride solutions was found to be dependent upon relative humidity and temperature. It has probably led to the observation that calcium chloride is generally more aggressive as a deicer than sodium chloride. The mechanism of deicer deterioration of concrete shown to be common for many deicers was found to exist only with weak concentrations and only under freeze-thaw conditions. The effect of low concentrations of calcium chloride on concrete was greater than that of water or of more concentrated solutions.

6. Mehta, H., Chen, W., Manson, J., and Vanderhoff, J., "Innovations in Impregnation Techniques For Highway Concrete", Transportation Research Record, pp 29-40, SUBFILE: HRIS available from: Transportation Research Board Publications Office, 2101 Constitution Avenue, NW, Washington, DC 20418.

Corrosion of reinforcing steel due to the penetration of deicing salts poses a considerable problem in bridge decks. One approach that has received much attention has been impregnation of the bridge deck with a liquid monomer followed by polymerization to effectively seal the capillary pores against salt intrusion. This approach is technically feasible in the field. The present impregnation techniques, however, are costly in terms of energy, materials, and time, and simplifications and improvement would be desirable. In this paper, results are described of preliminary experiments with sulfur, tar, and mixtures of the two as surface impregnants and with a pressure-mat technique for mechanically

assisting monomer or sealant penetration. It is shown that the impregnation of Portland cement concrete and mortar by molten sulfur, tar, and an 80:20 mixture of the two yields significant reductions in moisture absorption and increases in strength and that, in the case of concrete slabs, predrying may not be necessary. It is also shown that pressure mechanically applied to patterned rubber mats can effect uniform impregnation with a monomer such as methylmethacrylate or with a sealant such as tar or linseed oil. Such an impregnation could conceivably be effected by using rollers. Thus, initial feasibility of two potential improvements in concrete impregnation processes has been demonstrated.

7. Stratfull, Richard F., Spellman, Donald L., Halterman, Joseph, California State Div. of Highways, Sacramento Transportation Lab., "Further Evaluation of Deicing Chemicals", Jan. 1974. NTIS Prices: PC A03/MF A01, Contract No. FHWA-B-4-3.

Severe corrosion of reinforcing steel and concrete deterioration in reinforced concrete bridge decks caused by salt applied to the decks to control ice and snow has prompted a search for a noncorrosive deicing chemical suitable for maintenance use. Seventeen candidate chemicals have been evaluated. Tetrapotassium pyrophosphate (TKPP) exhibited good frost preventing properties, and two years of limited field testing on bridge decks is reported. A skidding car method of coefficient of friction is presented. The test results of sodium formate used as a deicer and its detrimental effect on concrete is evaluated.

(Same as II.7)

VI. RUBBER IN ASPHALT CONCRETE

1. Anderson, J., "Plusride and Bonifibers Pavement Evaluation", SR-530, Stanwood Vicinity. Post-Construction and Annual Report, Sept. 1987, Federal Highway Administration, 400 7th St., SW, Washington, DC 20590, Report No. WA-RD 147.1, Contract No. G06560 Task 9, Contract SUBFILE: HR1S available from: National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161.

Asphalt mixes modified with the addition of reclaimed rubber granules (PlusRide) and polyester fibers (Bonifibers) were used in a 0.12-ft overlay of a badly distressed section of AC pavement. The distress consisted of a transverse and longitudinal cracking which was reflecting through from the underlying old PCC pavement, and severe alligator cracking which was an age-related fatigue problem. A section of standard Class B dense graded ACP was also put down to serve as a control section for judging performance. The three sections are to be monitored over a period of three years to determine the effectiveness of the asphalt additive products in preventing the reflection of the distresses noted in the underlying pavement from showing through in the overlay. The first year inspection revealed that the PlusRide section was showing some longitudinal cracking over the old PCC lane edge. The Bonifibers section was also showing the same longitudinal distress over the lane edge of the underlying PCC plus a small amount of transverse cracking.

2. Carey, D.E., "A Laboratory Evaluation of Rubber-Asphalt Paving Mixtures", June 1974, 433456 PB-239 076/3, Report No. RR-79, LA-72-10B(E), Journal Announcement: GRAl7509, Sponsor: Federal Highway Administration, Washington, DC, NTIS Prices: PC A04/MF A01, Contract No. HPR-PR-1(11).

Several rubber-modified asphalts and their corresponding aggregate mixtures were evaluated in the laboratory with respect to their physical characteristics. Results obtained on the properties of those rubberized asphalt binders were compared to those of the original untreated asphalts. The data would seem to indicate that an acceptable cement can be expected provided the quantity of rubber additive is closely controlled. Bituminous mixtures were molded using the mechanical Marshall Hammer and also the Gyratory Compactor. The results obtained on the Gyratory compacted specimens would indicate that for the same binder content, rubberized asphalt mixes possessed higher Marshall stabilities, equal or lower flow values, and less tendency to flush or bleed. Certain rubberized asphalts showed a capability of being used at an asphalt level in excess of that found optimum for unmodified asphalt. In addition, no loss of compaction or adhesion was found for rubberized asphalt paving mixtures.

3. Esch, D., "Asphalt Pavements Modified With Coarse Rubber", August 1984, Federal Highway Administration, 400 7th Street, SW, Washington, DC 20590, Report No. FHWA-AK-RD-85-07, Contract No. F16322, Contract SUBFILE: HRIS available from: Alaska Department of Transportation and Public Facilities, 2301 Peger Road, Research Section, Fairbanks, Alaska 99811. Also, "Asphalt Pavements Modified With Coarse Rubber Particles: Design, Construction and Ice Control Observations", August 1984, Final Report.

A paving system was developed in Sweden in the 1960's in which relatively large rubber particles are incorporated into asphalt concrete pavements. The original purpose was to increase skid resistance and durability. This system, distributed under the trade names "Skega Asphalt" or "Rubit" in Scandinavia and "PlusRide" in the U.S.A., was also found to provide a new form of wintertime ice control because of the increased flexibility and the action of protruding rubber particles. The Alaska Department of Transportation and Public Facilities (DOT & PF) installed six experimental pavement sections using the PlusRide system between 1979 and 1983. Major modifications to normal asphalt pavement aggregate gradations, asphalt contents, and mix design procedures are considered essential to achieve durable non-ravelling rubber-asphalt pavements. Laboratory tests of PlusRide paving mixes also indicated a potential for greatly increased pavement fatigue life as a result of the elasticity of this material, particularly when finely ground rubber is added to the mix and the mix cured at a temperature for about one hour prior to compaction. The attainment of low voids in the pavement is the primary design and construction objective, and mix design and construction activities are discussed in this report. Observations of the skid reduction benefits under icy road conditions have been made with a British Pendulum Tester and a vehicle equipped with a Tapley Brake Meter. Tests indicate that significant reductions in city road stopping distance nearly always resulted from the use of the PlusRide paving system. For 21 testing dates over three winters, stopping distances were reduced by an average of 25 percent, with reductions on specific dates ranging from 3 to 50 percent.

4. Esch, D., "Rubber in Pavements For Ice Control", Alaska Department of Transportation and Public Facilities, Northern Engineer, 22, No. 4, 1980, p 34-39.

In the late 1960s, Sweden experimented with rubber particles in asphaltic pavements. A system incorporating 3 to 4% by weight of relatively large (1/16" to 1/4") rubber particles into asphalt pavement was developed to increase skid resistance and durability, and was found to provide a new form of wintertime ice control as well as a reduced noise level. The ice control mechanism is the flexing of the protruding rubber particles under traffic action, which causes surface ice deposits to breakdown.

"PlusRide" asphalt is now used to designate the material in the U.S.A.

Field trials in Alaska in 1979-1980 were encouraging.

5. Esch, D., Geophysical Institute, Alaska Department of Transportation and Public Facilities, "Rubber in Pavements For Ice Control", Northern Engineer, 1980, 12, No. 4, pp 34-39.

Successes and failures of these experiments are discussed herein. In general, the pavements had greatly improved skid resistance. However, they were not very durable, due to their high voids content. This can be rectified by asphalt contents and compactive efforts high enough to assure low filled voids. Additional pavement trial sections are necessary to evaluate fully the benefits of rubber-asphalt mixes and to develop further the proper specifications for assured success.

6. Gannon, C., and Majidzadeh, K., "A Laboratory and Field Study On The Use Of Elastomers In Hot-Mix Emulsified Asphalts", Highway Research Record, pp 34-41, SUBFILE: HRS.

Experimental data on four paving mixtures after 0, 1, and 2 years in service are examined. Mixture A is an emulsified hot-mixed asphaltic mixture with no latex additive. Mixtures B and C are emulsified hot-mixed asphaltic mixtures with 1.5 and 3% rubber additive. An 85 to 100 penetration asphalt cement with no additives was used in the control mixture D. The significance of rubber additives in the mixture behavior was investigated by performing compressive strength, creep, flexural fatigue, flexural strength, and Marshall stability tests on asphaltic mixtures. The extracted and recovered binders were also treated for physical characteristics. The following are conclusions reached from this study. (1) The evaluation of engineering properties of mixtures at 0 year in service indicates that mixture C with 3% additive is superior to the other mixtures. (2) The evaluation of engineering properties after 1 year in service indicates an age-hardening trend for mixture D. Mixtures A, B and C show slight age-softening effects. (3) The evaluation of engineering properties after 2 years in service indicates that mixture D has continued its age-hardening trend. Mixture A with no additive follows an age-softening trend. Rubberized materials in B and C appear to be approaching their initial engineering characteristics. (4) Mixture C, with 3% rubber additive, has remained superior to the other mixtures as related to temperature susceptibility. This mixture is the least temperature-dependent. The superiority of mixture C is also apparent from flexural strength and flexural fatigue data.

7. Huff, B., and Vallerger, B., "Characteristics and Performance of Asphalt-Rubber Material Containing a Blend of Reclaim and Crumb Rubber", Transportation Research Record, pp 29-37, 1981, SUBFILE: HRIS available from: Transportation Research Board Publications Office, 2101 Constitution Avenue, NW, Washington, DC 20418.

Asphalt cement, rubber extender oil, and a mixture of ground reclaim and crumb rubber, blended together at an elevated temperature in specific proportions and sequences, form a tough, durable, and adhesive membrane when hot-spray-applied to a surface and allowed to cool to ambient temperatures. This cast-in-place asphalt-rubber membrane has been found to be suitable for use in the construction of surface treatments for

existing pavements (chip seals), stress-absorbing membrane interlayers (SAMIs) in the placing of asphalt concrete overlays, and waterproofing membranes for bridge decks and hydraulic linings (ponds, canals, and reservoirs). When hot-poured into pavement joints and cracks and allowed to cool, it also serves as an effective joint and crack filler. The concepts and proportions of the formulation and preparation of this material are presented together with information and data on its properties and applications. A discussion is presented of the results of two analytic studies on the applicability of asphalt-rubber membranes (a) in minimizing reflection cracking when used as a SAMI, and (b) in producing a "multilayered aggregate structure" when used as a single-pass chip seal. A summary of the field performance observed to date on a number of installations of the asphalt-rubber material in its various applications is also included, together with observations on the efficacy of the material as a membrane and as a filler. This paper appeared in TRB Record 821, Bituminous Mixes, Concrete Pavements and Structures, Testing, and Construction.

8. Takallou, H., Hicks, R., and Esch, D., "Effect of Mix Ingredients On The Behavior Of Rubber-Modified Asphalt Mixtures", Transportation Research Record, pp 66-80, 1986. SUBFILE: HRIS available from: Transportation Research Board Publications Office, 2101 Constitution Avenue, N.W., Washington, DC 20418.

Presented are the results of a laboratory study to evaluate the effect of rubber gradation and content, air voids, aggregate gradation, mix, temperature, and curing conditions on the properties of rubber-modified asphalt mixtures. Twenty different mix combinations were evaluated for diametral modulus and fatigue at two different temperatures (-6 deg C; 21.2 deg F and 10 deg C; 50 deg F). Only the results of the tests at 10 deg C (50 deg F) are presented. The findings of this study indicate that rubber gradation and content, aggregate gradation, and use of surcharge during sample preparation have considerable effect on the design asphalt content and on the modulus and fatigue life of the mix. The laboratory data were used to develop guidelines for use of rubber asphalt mixes in Alaska. This paper appeared in Transportation Research Record N1096.

VII. SOLUBILITY PARAMETERS

1. Burrel, Harry, (Interchemical Corporation, 1754 Dana Ave., Cincinnati, OH), "Solubility Parameters For Film Formers", Official Digest, October 1955, pp 726-758.

This paper discusses the development of solubility parameters. The theoretical background and derivation of the constants is described, tables of values for many common solvents and film formers are given, and methods of calculation are presented. Examples are included which illustrate practical applications and demonstrate the validity of theory and practice.

2. Fedors, Robert F., (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA), "A Method For Estimating Both the Solubility Parameters and Molar Volumes of Liquids", Polymer Engineering and Science, February 1974, 14, (2), pp 147-154.

The solubility parameters and molar volumes of substances can be used, in conjunction with suitable theory, to provide estimates of the thermodynamic properties of solutions, the solubility characteristics of polymer-solvent systems, and the estimation of equilibrium uptake that are amenable to treatment. This paper proposes a method of estimating the solubility parameter based upon group additive constants.

3. Mellan, Ibert, "Compatibility and Solubility", Park Ridge, NJ: Noyes Development Corporation, 1968, c1968.
4. Seymour, Raymond B., (Professor and Coordinator of Polymer Chemistry, Dept. of Chemistry, University of Houston, Houston, TX 77004). "Plastics vs Solvents", Modern Plastics, October 1971, pp 150-154.

Discussion of the use of solubility parameters of solvents and polymers as a guide to the formulation of optimum systems for solutions. These parameters can also assist in selection of plastics for resistance to specific chemical environments.

VIII. STATE OF CONNECTICUT

1. State of Connecticut Bureau of Highways, Connecticut Department of Transportation. Snow and Ice Control Policy - 1988-89.

The purpose of the policy stated herein is to provide an acceptable standard of winter maintenance that will provide reasonably safe roads during and after adverse weather conditions throughout the winter season. Topics outlined in the policy include: General operating procedures, pre-season procedures, rented equipment, snow and ice control materials, spreading snow and ice control materials, and plowing operations.

IX. TESTING

1. ASTM D1559-82. "Standard Test Method for Resistance to Plastic Flow of Bituminous Mixtures Using Marshall Apparatus", 1982.

This method covers the measurement of the resistance to plastic flow of cylindrical specimens of bituminous paving mixtures loaded on the lateral surface by means of the Marshall apparatus. This method is for use with mixtures containing asphalt cement, asphalt cut-back or tar, and aggregate up to 1-in (25.4 mm) maximum size.

2. Page, B. G., "New Methods and Materials for Pavement Skid Resistance", July 1977. Source Codes: 040609016, Sponsor: Federal Highway Administration, Sacramento, CA, California Div. Report No. FHWA-CA-TL-3143-76-59; FHWA-RDj-78-145, NTIS Prices PC A06/MF A01, Country of Publication: United States, Contract No: DOT-FH-11-8480.

The report describes an evaluation and classification of pavement surfaces with respect to skid resistance. The study was conducted by means of a questionnaire survey of agencies within and adjacent to California, and by testing and examination of 45 existing pavement surfaces. The test program included standard skid tests at two speeds and additional tests with a smooth tire at one speed. Surface textures were measured by stereophotographs to obtain a "texture profile". The approximate cost of the surface, the amount of traffic exposure, and vehicle accident data were included in the evaluation. The pavement surfaces were ranked on the basis of skid number, speed gradient, and texture. Systems which ranked well under heavy or medium traffic included open-graded asphalt concretes with and without epoxy modification, textured cement concretes, and epoxy chip seals. Conventional and rubberized chip seals were found suitable for medium or light traffic. Dense graded epoxy-asphalt concretes generally ranked about the same as the control section of asphalt concrete. The corrective surface treatments considered new and innovative were all quite expensive compared to conventional treatments. Wet pavement accidents data did not provide any criteria for establishing minimum levels of skid resistance.

3. Wambold, J., "Evaluation of Wet Skid Resistance Using Four Deicing Salts", July 1983. Report No. PTI 8316, SUBFILE: TRRL, IRRD, HRS.

A series of tests was conducted, using the locked-wheel skid tester, to compare saturated solutions of water and calcium magnesium acetate, calcium chloride, and urea. The tests were then compared with plain water. All tests were conducted within 8 degrees F of freezing, and runs were made at various speeds both on concrete and asphalt surfaces. The results, presented in tables and graphs, show that concrete behaves differently than asphalt.

X. THEORY

1. Ashworth, T., Weyland, J.A., (South Dakota School of Mines and Technology, 500 East St. Joseph Street, Rapid City, SD 57701). "Investigation Of The Basic Forces Involved In The Adhesion Of Ice To Highway Surfaces", June 1982, 7807-7907. Federal Highway Administration Office of University Research, 400 7th Street, SW, Washington, DC 20590. Report No. DOT/RSPA/DPB50/82/5, Contract No. DOT-OS-70072, Contract SUBFILE: HRS available from: South Dakota School of Mines and Technology, 500 East St. Joseph Street, Rapid City, SD 57701.

Improved knowledge of the basic forces contributing to the adhesion of ice to highway surfaces was the objective of the research performed. Tensile and shear interfacial strength tests formed the main thrust of the experimental program. Tests were carried out over the temperature range -0.5 deg C to -20 deg C for several concrete mixes, mortar and asphalt. Surface treatments included NaCl, CaCl₂, a silicone compound, a fluorocarbon compound and a mineral oil (#2 diesel fuel). The salts were effective in reducing adhesion above -8 deg C; the other materials were more effective, especially at lower temperatures. In fact, diesel oil is a long term contaminant which must be avoided for tests on concrete. The wetting temperature of a clean substrate has also been shown to be a factor. Modified concretes showed reduced adhesion. Results of numerical modeling of an ice/concrete interface show stress concentration factors greater than one due to material dissimilarities, penetration of one material into the other, and non-homogeneous substrate. Tensile strength measurements for pure ice have been made, and failure criteria for the interface have been developed from them. Moisture adsorption and heats of wetting experiments for Quartzite, limestone, sand, and P.C. mortar have been taken. Adsorption site areas and energies have been deduced. Data is being interpreted to disclose the role of capillary effects and the influence of fluorocarbon treatment. Results obtained indicate that both mechanical and chemical binding are important at the ice/concrete interface, and that the interfacial strength can be weakened by substrate modification, substrate treatments, or solute treatment.

2. Bascom, W.D., Cattington, R. L., and Singleterry, C. R., J. Adhesion, 1, p 245-263, 1969.

Hydrophobic materials and coatings have long been considered effective ice removal agents, and an extensive search has been conducted in the hope of finding a "miracle coating" that would allow effortless ice removal. Bascom et al. performed a series of carefully prepared experiments, and found no clear correlation between the contact angle of water and the adhesive strength of ice, despite the generally accepted notion that adhesion of ice is weaker on a hydrophobic surface.

3. Forest, T.W., "The Adhesion of Ice To Low Energy Solids", ASME Publication, 80-WA/HT-19, July 12, 1980.

The relationship between the shear strength of an ice-substrate bond and the surface properties of the substrate is examined. A review of numerous experimental results on the shear strength of ice on low energy polymer solids is presented. The experimental data are correlated separately with the surface energy of the polymer solid and the work of adhesion of the ice-polymer interface. The two latter quantities are calculated using the surface equation of state approach. The measured strengths generally exhibit a linear relationship with both the surface energy of the polymer and the work of adhesion. A decrease in surface energy results in a decrease in shear strength. A statistical analysis of the data indicates that a significant portion of the variation in observed shear strength can be attributed to a variation in surface energy; however, other factors, such as roughness, play an equally important role.

Thus, ice adhesion is decreased by coating a surface with a hydrophobic material which lowers the surface free energy. However, roughness is a complicating factor. Some studies indicate that an increase in roughness can significantly increase the shear strength of the bond. A complicating factor is the fact that on a low energy surface which is rough, the ice may not completely penetrate the indentations on the solid surface. Thus, pockets of gas or vapour may be trapped in the crevices, which will act as points of stress concentration and lower adhesion.

4. Itagaki, K., (U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH 03755). "Adhesion of Ice to Polymers and Other Surfaces. Physiochemical Aspects of Polymer Surfaces", Proceeding of Int. Symposium, 1. 1988, pp 241-252, Plenum Publishing Corp., and Itagaki, K., "The Duplication of Surface Energy in Ice Adhesion", J. Adhesion, 16, p 41-48, 1983.

Since ice is weaker than its bond strength with the substrate, the apparent strength of the adhesive bond is controlled by the area of contact and the strength of the ice. Although the strength of ice is not a unique material constraint, but depends on various conditions, the values should remain within a relatively narrow range so that the main factor controlling bond strength is the area of "real" contact.

The assumptions are: (1) Water can penetrate an oil or grease layer before it freezes; (2) An oil or grease layer usually exists on a substrate unless its surface has been very carefully cleaned.

When a substrate is hydrophobic, the actual contact between a drop of water and its surface is limited to the edge of the drop. "Real" contact between ice and substrate when the drop is frozen, therefore, is also limited to the small area around the edge of the drop.

5. Raraty, L. E., Tabor, D., (Research Laboratory for the Physics and Chemistry of Surfaces, Department of Physical Chemistry, University of Cambridge). "The Adhesion and Strength Properties of Ice", Proc. Royal Society of London, Series A, 1958, 245, pp 184-193.

This paper describes a study of the adhesion of ice to various solids. If water is frozen on a clean metal surface, the interface is stronger than the ice, and fracture occurs within the ice itself. The detailed behaviour depends on the stresses developed near the interface. If tensile stresses are high and failure is brittle, the breaking stress is temperature independent. If the tensile stresses are below a critical limit, the failure is ductile and the breaking stress increases linearly as the temperature is reduced below 0°C. Ductile failure appears to be determined by the onset of a critical creep rate, and the variation of breaking stress with temperature may be explained in this way. This view is supported by the observation that small quantities of dissolved salts which increase the creep rate of ice produce a parallel reduction in the adhesive strength.

Surface contaminants on metals reduce the adhesion by a very large factor, and it is suggested that this is due primarily to a reduction in the area over which strong metal/ice adhesion occurs. The adhesion of ice to polymeric materials differs from the adhesion to metals. The interfacial strength appears to be less than the strength of ice, and failure occurs truly at the interface. Friction experiments carried out with clean and lubricated metals and polymers sliding on ice provide a measure of shear strength of the solid/ice interface. The results show a marked parallelism with those obtained in the adhesion experiments. This again emphasizes the close connection between the friction and adhesion of solids.

This study has some bearing on the deicing of aircraft and of ships sailing in polar seas. The results suggest that ice layers may be removed most readily if brittle fracture can be achieved. Constraint of the ice inhibits brittle fracture, and the forces to produce ductile failure are considerably greater. These forces may, however, be reduced by adding small quantities of suitable salts, since these reduce the resistance to ductile flow if the system is above the eutectic temperature. Finally, hydrophobic materials show a very low adhesion; this is particularly marked in the adhesion of ice to polytetrafluoroethylene.

6. Trost, S.E., Heng, F. J., and Cussler, E.L. "Chemistry of Deicing Roads: Breaking The Bond Between Ice and Road", Journal of Transportation Engineering, Jan. 1987, 113, No. 1, pp 15-26. American Society of Civil Engineers Report No. ASCE Paper 21144. SUBFILE: HRS available from: American Society of Civil Engineers, 345 East 47th St., New York, NY 10017.

The rates for breaking the bond between ice and road surfaces are measured as a function of temperature, type of road surface, and chemical application. Surfaces of asphalt, concrete, and brick give indistinguishable results. Chemicals used include sodium chloride, calcium chloride, urea, and calcium magnesium acetate (CMA). The results

are analyzed in terms of the maximum areas undercut and the rates at which the areas are undercut. The areas for all chemicals can be correlated with arguments based on freezing point depression. The rates seem consistent with diffusion controlled melting.

XI. THERMAL HEAT GAIN

1. Esch, D.C. (Alaska Department of Transportation and Public Facilities Research Section, 2301 Peger Road, Fairbanks, Alaska 99701). "Permafrost Prethawing By Surface Modification", Dec. 1982, (Final Report), Federal Highway Administration, 400 7th Street, SW, Washington, DC 20590, Report No. FHWA-AK-RD-83-23, Contract No. F16142, HP&R SUBFILE: H11S available from: Alaska Department of Transportation and Public Facilities, 2301 Peger Road, Fairbanks, Alaska 99701.

To minimize post-construction settlements of roadway embankments in thaw stable permafrost areas, one approach is to thaw and consolidate the permafrost soils as far as possible prior to, or during construction. Six test plots were established near Fairbanks in April of 1980, to determine how various surface modifications may be used to accelerate thawing of permafrost by increasing the solar heat gain. The various surface modifications examined included surface clearing and stripping, thin gravel pad construction, gravel pad surface darkening with asphalt, and the use of clear polyethylene film to create a "greenhouse effect" on both gravel pad and stripped sections. Each section simulated a 60 foot roadway width with adjacent uncleared vegetation. Instrumentation used to monitor performance included heat flow meters, windspeed and radiation recorders, and thermocouples for subsurface temperature observations. Thaw depths and surface settlements were recorded monthly at nine points on each section. Differences between thaw depths achieved with the different treatments were as great as 28% during the first thawing season, and 31% during the second and third seasons. At the study site, total surface settlements averaged one foot during the study period. Benefits of this approach would include reduced post-construction settlements and the use of thinner thermally stable embankment structures. The benefits are indicated to far outweigh the costs of the prethawing modifications.

XII. VERGLIMIT

1. Arnevik, A., "Asphalt Pavement With Salt Added To The Bituminous Mixture To Prevent Icing On Roads", Vaare Veger, 2, pp 8-9, March 1979. SUBFILE: TRRL; IRRD; HRS:

The City of Oslo road authorities has established four test roads with salt added to bituminous mixture in the pavement. For the tests, Verglimit, a Swiss product mainly consisting of calcium chloride, has been used. The results obtained so far show that icing was prevented, especially with regard to condensation of humidity on the road pavement, but that the wearing quality for the pavement was not satisfactory. On the latest test road established, a more durable mixture was used, but in order to obtain the desired effect from the salt, some wear must be present, and on this particular test section the wear has probably been too small.

2. Augeri, F., (Connecticut Dept. of Transportation, Wethersfield Bureau of Highways). "Placement of an Experimental Bituminous Concrete Mixture Utilizing an Asphalt Additive - Verglimit", Nov. 8, (Construction Report), Corp. Source Codes: 029800001, Sponsor: Federal Highway Administration, Hartford, CT, Connecticut Div. See also PB87-118857. NTIS Prices: PC A03/MF A01, Country of Publication: United States, Contract No. HPR-1085.

The pavement overlay incorporated the additive "Verglimit". Composed of calcium chloride and sodium hydroxide encased in linseed oil, this capsule-like material is added to the bituminous mix during production. Once in place as pavement, the Verglimit is designed to retard the formation of ice on the friction surface, particularly on bridge decks. ConnDOT has placed approximately 85 tons of Verglimit mix on one side of a newly constructed bridge, using the other as a control. The pavement durability and ice-retardant capabilities of the Verglimit mix will be evaluated for a period of five years.

3. Dohaney, W., "Verglimit/Asphalt Concrete Performance Analysis", Multiscience Publications Limited, 1253 McGill College, Suite 175, Montreal, Quebec, Canada, 0-919868-16-9, pp 60-69, Nov. 1981. SUBFILE: TRRL; IRRD; HRIS; RTAC.

Verglimit, an agent to retard ice formation on asphaltic concrete surfaces, was added to the asphaltic concrete overlays that were placed on

the Hillsborough River Bridge and the approach causeways in Charlottetown, Prince Edward Island. The agent was effective in retarding the formation during the first and second years of the installation. Removal of ice that did form was easier. Skid resistance measurements on the overlays did not show any significant deviation from those taken on regular asphaltic concrete overlays. Temperature/depth relationships for Verglimit treated overlays are similar to the temperature/depth relationships in the untreated pavements.

4. Fromm, H. J. (Ontario Ministry of Transportation & Communication, Canadian Engineering Research and Development Branch, Downsview, Ontario M3M 1J8 Canada). "Anti-Icing Compound For Bridge Decks and Road Surfaces", (Progress Report). Report No. HS-026, SUBFILE: HSL available from: Ontario Ministry of Transportation & Communication, Canadian Engineering Research and Development Branch, Downsview, Ontario M3M 1J8, Canada.

A compound known as Verglimit has been marketed to lessen the hazard to motorists of bridge deck icing, which occurs in the late Fall or early Spring and is caused by a sudden temperature drop. The product is essentially calcium chloride flake, to which about 5% sodium hydroxide and a small quantity of an unknown chemical are added. Compounded flakes are coated with linseed oil which is polymerized to protect flakes from water. This material is incorporated into the asphaltic concrete surface course mix at the hot plant, and the mix is applied to the road in the normal manner. Verglimit has been used in many areas of Europe. In view of the good European experience, the material was tested on some roads in Ontario, Canada. Testing showed that Verglimit is effective in reducing the extent of bridge deck icing and in preventing snow from sticking to pavement. Since the material increased the flow value of asphaltic concrete surface course mix, it should not be used where vehicles are stopping, as at an intersection. Some surface raveling and stripping occurred where Verglimit was used, possibly reducing pavement life below that of a pavement without the material. No reduction in skid resistance occurred with use of the compound. It is recommended that Verglimit resurfacing be employed when bridge decks on which icing has been observed are being resurfaced.

5. Morian, D. and Arellano, J., "Verglimit De-Icing Chemical Asphalt Additive. Construction Report", March 1987, Federal Highway Administration, 400 7th Street, SW, Washington, DC 20590. Report No. FHWA-PA-86-041+83-39, Research Project: 83-39, Contract No. 83-39, Contract SUBFILE: HRIS available from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

The purpose of this project was to determine the effectiveness and feasibility of using the Verglimit de-icing chemical asphalt additive to minimize pavement icing problems. The Verglimit additive consists of calcium chloride flakes encapsulated in linseed oil. It was introduced into the bituminous mix at 5% of the aggregate by weight. This project consisted of a 1-1/2 inch Verglimit-modified ID-2 wearing overlay on a 2 inch binder course. No problems were encountered during construction. Normal paving techniques were followed except that a light spray of kerosene was used on the rollers instead of water because water strips the linseed oil from the calcium chloride flakes. The calcium chloride

content of the Verglimit was 75% by weight. The average density of six cores of the Verglimit-modified ID-2 was 99.6%. Skid tests taken in March 1987 indicate the skid resistance of the Verglimit-modified ID-2 is only slightly lower than that of the adjacent sections. The cost of the Verglimit-modified ID-2 material is three times that of standard ID-2 material. However, a reduction in application of de-icing agents (250 lbs/lane mile, 1985-86) and increased safety may justify this cost.

6. Nittinger, R. J., "Construction of An Ice-Retardant Overlay", June 1979, Sponsor: Federal Highway Administration, Albany, NY, Div. NTIS Prices: PC A03/MF A01, Contract No. NYSDT-143-1.

Among the most dangerous highway hazards is the formation of ice. It forms when moisture is present as the temperature drops below freezing. During icing, maintenance crews spread heavy applications of salt, which forms a strong sodium-chloride solution having a severe corrosive effect on reinforcing steel, bridge superstructures, and automobiles. A proprietary asphalt additive has been developed and tried in Europe to alleviate these conditions. Basically an encapsulated calcium chloride, it is introduced into asphalt concrete during mixing and is released by the action of traffic. In theory, the pavement wears gradually, continually exposing additional capsules. This is an interim report covering problems encountered in batching operations and laboratory testing, in addition to documenting construction procedures, skid resistance, and overall pavement appearance. It was found that automated batching could not be used because the additive was held in the mineral filler bin and added after the introduction of bitumen. Manual batching thus was required. Due to the additive's hygroscopic state, laboratory test results were erratic. No unusual problems were found during construction. The pavement became oily in appearance, but tests produced adequate skid numbers, and after two rainstorms and heavy traffic, the pavement appeared dry.

7. Rainiero, J.M., (National Research Council Transportation Research, Washington, DC). "Investigation of Ice Retardant Pavement (Verglimit)", 1988, 37 pp. SUBFILE: UCITS; TLIB John M. Rainiero Illustrated Paper Presented at the 1988 Annual Meeting of the Transportation Research Board, Washington, DC, Paper No. 870482.

One of the hazards confronting motorists is slippery conditions caused by snow and ice. In an effort to investigate the potential of maintaining roadway safety during these conditions, the New Jersey Department of Transportation, Bureau of Maintenance has installed a de-icing asphalt. This de-icing material is Verglimit, derived from the French expression "limite' le verglas", (end slippery ice). It was developed in Switzerland in 1973 and has been in use for fourteen years for ice control in Europe, ten in Canada, and nine in the United States. This de-icing material is essentially calcium chloride flakes, to which about 5% sodium hydroxide is added. The flakes are coated with linseed oil, which is polymerized to protect the flakes from water. This material (flakes) is introduced into asphalt concrete mix as part of the aggregates during the mix cycle. The treated mix is laid and compacted using conventional paving equipment.

Thus, Verglimit flakes are exposed as traffic wears away the pavement surface. This abrasion should amount to approximately 1 mm. per year, essentially creating a continuous ice free surface for the life of the overlay.

The project involved the design, application, and evaluation of an asphalt concrete mix, made ice retardant by the addition of encapsulated calcium chloride pellets (Verglimit). This de-icing asphalt was placed along an eight tenths of a mile section of Route 173, Clinton, NJ. The agent was very effective in retarding icing of the pavement and made removal of snow accumulations easier. Skid resistance values taken over the past ten months are as good as other Mix I-4 asphalt concrete pavements.

8. "Safe" Roads Too Deadly", Michigan Roads and Construction, 85, p 3, December 1988. SUBFILE: HRS available from: Baker Publishing Co., P.O. Box 25007, Lansing, MI 48909.

A mixture of asphalt and a chemical deicing compound called Verglimit, that was used on two county roads in New Jersey, is being removed. The roads became super-slippery, resulting in accidents, including one in which eight people were hurt and one person killed. The compound has been used successfully in New York state for a decade. Engineers are now studying the cause of the New Jersey failure. Some experts believe contractors failed to adequately compress the mixture, leaving gaps in the Verglimit pellets which let moisture in and prevented the compound's ability to prevent ice from bonding to the road surface.

9. Tanski, J., "Performance of Two Ice-Retardant Overlays", Final Report, (May 1986). Federal Highway Administration, 400 7th St., SW, Washington, DC 20590. Report No. FHWA/NY/RR-86/132; FOP 4119-044, SUBFILE: HRS Available from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

Prevention of ice- and snow-related accidents is a major concern of the New York State Department of Transportation. A significant portion of these occur when temperatures drop just below freezing, before the first application of deicing chemicals by maintenance crews. A proprietary product has been developed in Europe that is intended to prevent formation of ice and to reduce adhesion of snow to the pavement surface during this critical period. This additive, which is blended into plant-mixed asphalt concrete, was tested at two sites in New York State. The first, built in Albany during the summer of 1978, demonstrated that durability of an asphalt overlay containing this additive is equivalent to normal asphalt overlays and that it continues to perform as an ice-retardant after 7 years. The second, on Rte 17 near Binghamton -- site of numerous wintertime accidents -- was resurfaced in 1983. Two years of accumulated data show an 86% reduction in the rate of snow and ice-related accidents, while two control sites (one resurfaced with a high-friction aggregate overlay in 1983) on the same roadway had increases in such accidents for the same time period.

APPENDIX B

CHEMICAL NATURE OF THE ADDITIVES

Acryloid 710	Polyacrylate
Armid HT	Fatty amide
BASF 380	Polypropylene glycol 6000 molecular weight
Carbowax 300	Polyethylene glycol
DC 200 - 1000 CPS	Dimethyl silicone oil
DER 331	Epoxy (bisphenol diepoxide)
Eastman SAIB	Sucrose acetate butyrate
Eramide	Erucamide (22 carbon mono unsaturated)
EMA	Ethylene maleic anhydride copolymer
Flexol 4G0	Tetraethylene glycol di-2 ethyl hexaoate
Fyrol 6	Phosphated polyol
Gantrez M154	Polyvinyl methyl ether
Ice-B-Gon	Calcium-Magnesium Acetate, 91% (Chevron)
Indopol H 1500	Polyisobutylene (2060 mol. wt.)
Indopol 150	Polyisobutylene (420 mol. wt.)
Kenamid P 181	Palmitramide (16 carbon, saturated)
Ketjenflex 8	Toluenesulfonamide
Lipowax C	Ethylene diamine distearamide
Maldene	Butadiene maleic copolymer
Oleamide	Amide of oleic acid
Paraplex G25	Sebacate polyester
Plastolein 9717	Polyester (solidification at -8°C)
Plastolein 9789	Polyester (solidification at -29°C)
Paraplex G54	Adipate polyester
Poly PPG 425	Polypropylene glycol
Poly G71-530	Sucrose amine based polyol
Poly G75-442	Methyl glucoside polyphenylene oxide
Pluracol 824	Aromatic polypropylene glycol
Pluronic L61	Block copolymer 10% polyethylene glycol/90% polypropylene glycol
Santicizer 160	Butyl benzyl phthalate
Verglimit	Calcium Chloride (and 5% NaOH) coated with polymerized linseed oil

APPENDIX C

ICE ADHESION VERSUS VISCOSITY AND FREEZING CHARACTERISTICS

It has been demonstrated that only water soluble or hydrophilic additives, either coated onto the surface of asphalt concrete or blended into the asphalt concrete, reduce ice adhesion. One question that could be asked is, "What is the role, if any, of viscosity or freezing characteristics of the oil in lowering ice adhesion"?

In Table 1, a series of oils is arranged in order of increasing ice adhesion, as measured by the surface impregnation test. One possibility is that an oil may become excessively viscous or even become hard or frozen and, therefore, not function to lower ice adhesion.

Viscosity was measured semi-quantitatively by filling a 1 oz. jar half full, storing at -20°C and then tipping it horizontally and measuring time to flow to the lip of the jar. The longer the time of flow, the more viscous. "Freezing" characteristics of the liquid at -20°C are also shown, ranging from very fluid to hard or frozen.

There is no apparent relationship between viscosity or freezing characteristics and ice adhesion at -20°C (Table C1) (also Figure C1).

Table C-1

Oil Fluidity and Freezing
Characteristics vs Ice Adhesion

Additive	Ice Adhesion ⁽²⁾⁽⁵⁾		Viscosity ⁽⁴⁾ Poises	Freezing Character- istics ⁽³⁾ At -20°C
	Shear Strength (psi)	Time ⁽¹⁾ Of Flow To Lip		
Flexol 4G0	4	1 sec.	1.5	1
Poly-G-71-530	9	3 hrs.	>10x10 ⁶	3
Pluracol 824	15	>4 hrs.	>10x10 ⁶	4-5
Paraplex G-54	15	>4 hrs.	>10x10 ⁶	4
Santicizer 160	25	1.5 sec.	24	2
Admex 525	24	6 sec.	136	1
Indopol L50	25	9 sec.	220	1
NIAx Polyol PPG425	28	3 sec.	60	2-3
Pluracol 873	29	55 sec.	1900	2
BASF 380	47	6 sec.	130	3
DER 331	>64	>>16 min.	>10x10 ⁶	6
Eastman SAIB	>64	>>16 min.	>10x10 ⁶	6

-
- (1) At -20°C using a 1 oz. jar half full, topped on its side.
 (2) Surface impregnated briquettes.
 (3) 1 - very liquid (fluid); 2 - liquid; 3 - thicker liquid; 4 - very thick liquid; 4-5 - gelled; 5 - hard; 6 - frozen.
 (4) From a plot of viscosity versus flow time.
 (5) Lbs/one inch diameter disk of ice.

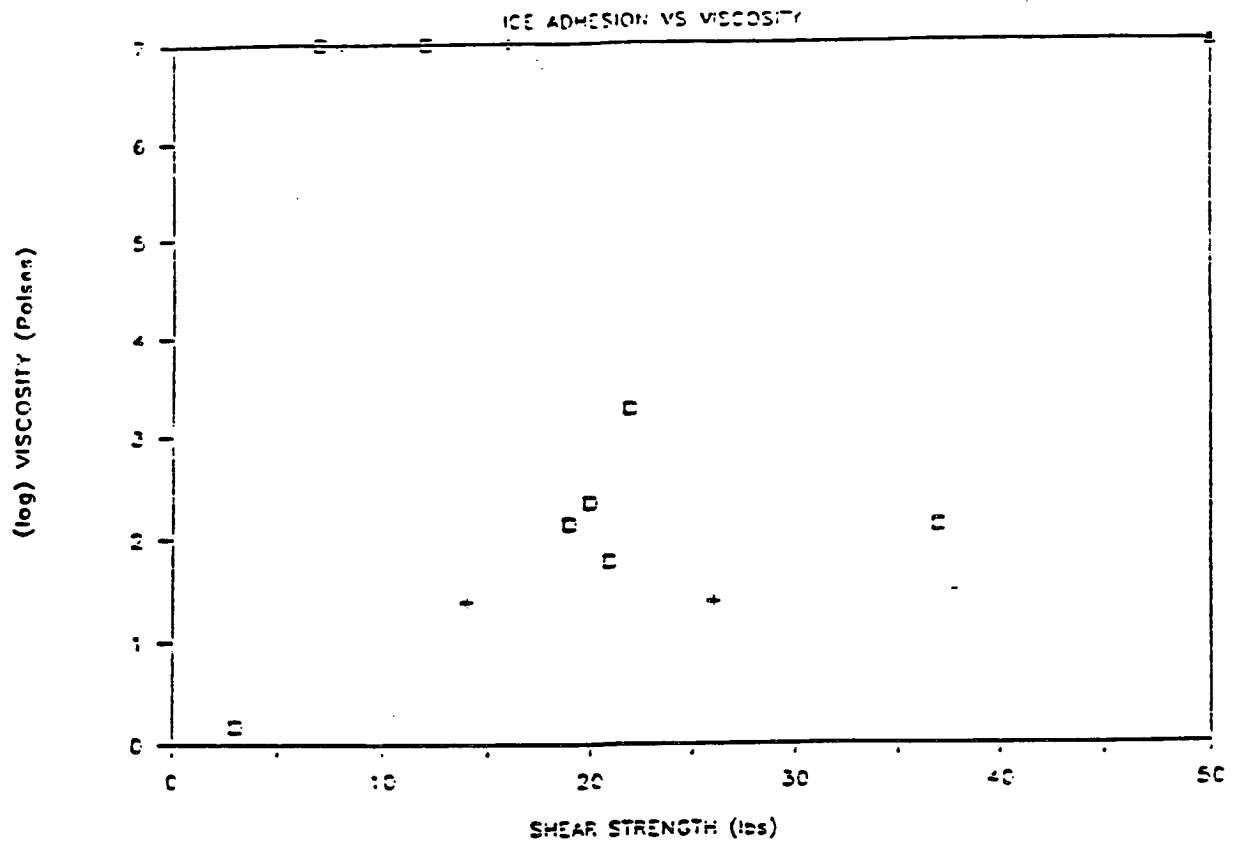


Figure C-1

Ice Adhesion vs Viscosity of Additive
Additive Used in Asphalt Concrete
Briquette.

- + SANTICIZER 160
- PARAPLEX G-54
- △ FROZEN AT -20°C
- × FROZEN AT -20°C
- ALL OTHER ADDITIVES

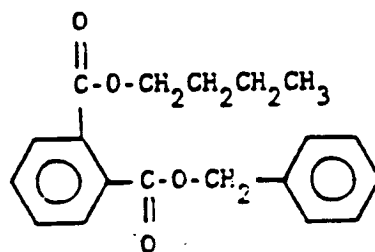
APPENDIX D

SOLUBILITY PARAMETERS

Known chemical composition:

Fedors' published method⁽¹⁾ was used to calculate solubility parameters of selected additive compounds. The calculations were based on the known structure of each compound. Experimental versus calculated accuracy of this method was reported to be within ten percent. The following is an example of how one additive, butyl benzyl phthalate, was calculated:

Structure:



Atom or group	Number of groups	$\Delta e_i^{(2)}$ cal/mole	$\Delta v_i^{(2)}$ cm ³ /mole
Carboxyl $\begin{array}{c} \text{O} \\ \\ \text{-C-O-} \end{array}$	2	8600	36
CH ₂	4	4720	32.2
CH ₃	1	1125	33.5
Phenyl C ₆ H ₅	1	7630	71.4
Phenylene (o,m,p) C ₆ H ₄	1	<u>7630</u>	<u>52.4</u>
Sum of the columns:		29705	225.5

Calculation:

$$\frac{29705}{225.5} = 131.7$$

$$(131.7)^{1/2} = 11.48 = \text{calculated solubility parameter}$$

(1) Fedors, R.G., "Polymer Engineering and Science", 1974, Vol. 14, No. 2, p 147-54; No. 6, Addendum, p 472.

(2) These values are given in Fedors' method.

Unknown chemical composition:

It is necessary to know the exact structure to calculate the solubility parameter of a compound using Fedors' method. Since asphalt is a mixture of many constituents, the direct calculation of the solubility parameter for asphalt would be very difficult, if not impossible, by this procedure. Consequently, the solubility parameter of the provided asphalt was estimated experimentally by evaluating the asphalt solubility in various solvents. Solvents used for evaluation were selected from a list of published solubility parameters⁽³⁾. The hydrogen bonding value versus the solubility parameter value were plotted for each solvent (see Figure 8). The solubility of the asphalt was noted at each point. From the plotted figure, it was possible to estimate the range of solubility or average solubility parameter value, based on the known values for solvents that dissolve the asphalt.

- (1) Fedors, R.G., "Polymer Engineering and Science", 1974, Vol. 14, No.2, p 147-54; No. 6, Addendum, p 472
- (2) Values taken from Fedors' Method
- (3) Mellan, I., "Compatibility and Solubility", Noyes Development Corp., 1968

APPENDIX E

STATISTICAL ANALYSIS - DEFINITIONS

PR > F Probability of a value greater than F (a tabulated statistic)

SAS Statistical Analysis System

REGWQ Name of a multiple comparison procedure designed to show
whether there are real differences between additives