FINAL REPORT

"PLEASE DESTROY ALL PREVIOUS DRAFT COPIES OF THIS REPORT."

DATE: September 30, 1999

TEMPERATURE AND HUMIDITY EFFECTS ON THE CO-EFFICIENT OF FRICTION VALUE AFTER APPLICATION OF LIQUID ANTI-ICING CHEMICALS

Prepared By:

TIMOTHY S. LEGGETT, P. Eng. Forensic Dynamics Inc. 230 - 1210 Summit Drive Kamloops, B.C. V2C 6C3

EXECUTIVE SUMMARY

The purpose of this research was to determine whether there existed a chemical "slipperiness" as a result of a transition from liquid to a solid, and vice versa, of typical anti-icing chemicals presently in use.

The number of reported slickness issues as a result of chemical treatments is infinitesimally small, (presently estimated at less than 1/1000th of 1% of all liquid anti-icing treatments). Prior research has shown that the slickness issues are often related to driver perception, contamination on the roadway other than from the chemicals themselves, and typical chemical dilution resulting in re-freeze. There have been some incidents reported where the chemicals themselves, prior to re-freezing, create a slipperiness for some unexplained reason. This research has shown that, indeed, when most chemicals transition from liquid to solid, and solid to liquid, a "slurry" phase is formed. This produces a relatively short-lived reduction in co-efficient of friction for most chemicals. This reduction is anywhere from essentially non-existent .4%, (FreezGard with Ice Ban) to a substantial 29%, (LiquiDow).

Most chemicals, however, upon continued dehydration, become solid and the solid co-efficient of friction returns to nearly the same value as liquid; (an exception to this was LiquiDow which had its friction value stay low) some chemicals such as CMA and LiquiDow Armor actually have a friction value which is superior when dry as compared to liquid.

The research has shown that all chemicals tend to be unstable in this transition phase, meaning that they pass through the phase briefly and unlikely maintain themselves in this region for a long period of time.

Temperature and humidity above those values required to cause the transition phase, appear not to affect the friction dramatically. However, at humidity levels in the high 20's to low 30's, most chemicals will begin to dry out, (after application as a liquid) potentially resulting in somewhat lower friction values during the transition phase.

Additional research is required before definitive conclusions can be made with respect to application on asphalt and concrete surfaces, but it appears that prudent use of the chemicals, (particularly with regards to application rate and frequency) bearing in mind incoming humidity levels, can further reduce the likelihood of slickness developing, particularly in the fall season when most incidents are reported to have occurred.

Experiments were carried out in May to August, 1999 in Kamloops, B.C. in a purpose-oriented climate-controlled test facility. The tests were necessary to fully establish the reliance of various anti-icing chemicals on temperature and humidity; specifically to determine what roll these, and other factors, play on the road co-efficient of friction.

Initially, the facility was run within the limits of 30% - 50% humidity, and -1E to 10E Celsius. Later, testing was performed at humidity levels in the lower range, (between 20% and 40%, with temperature held constant at 5E Celsius).

The climate-controlled test facility was specifically engineered and built for the testing purpose. It consists of a sandblasted glass surface laid inside a tray, upon which a B.F. Goodrich drag sled is pulled. Measurements are recorded via a Mettler-Toledo load cell with an accuracy of .001 lbs. force. Temperature and humidity are held at chosen levels via PC software, linked with a compressor and chiller unit, along with a 1.5 kilowatt electric heater. Humidity is controlled similarly with the use of a standard humidifier and evaporation tray, upon which a chemical used for drying, (ie. de-humidifying) can be placed.

Originally, four pure chemicals were tested. These included magnesium chloride, calcium chloride, calcium magnesium acetate and sodium chloride. Additionally, the following chemicals were tested: Ice Stop and Ice Stop 2000, MCP De-Icer, LiquiDow Armor, FreezGard 0, FreezGard 0 and TEA, FreezGard 0 and SHIELD LS, and finally, FreezGard 0 and Ice Ban. Additional testing is underway on other chemicals and will be reported on at a later date.

INTRODUCTION

The purpose of tests was to determine whether there existed an area, within the temperature and humidity range of 30% - 50%, and -5E to +10E Celsius, of reduced friction, which was the result of a chemical-only process, (ie. one related to chemical properties exclusively, as opposed to other external sources).

This experimentation flowed as a result of a technical working group meeting held on March 8th and 9th, 1999 in Minneapolis, Minnesota. At that time, the group reviewed approximately thirty (30) reported incidents in which roads reportedly became slippery after application of liquid chemicals, used in anti-icing operations. The meeting was sponsored by the Snow and Ice Cooperative Pooled Fund Program (SICOP) of the American Association of State Highway and Transportation Officials (AASHTO) At that time, it was determined that, based on the number of incidents which had been documented, and the volume of liquids now used in anti-icing, the likelihood of slickness occurring was likely less than 1/1000th of 1% of all applied liquid chemicals.

Of the thirty incidents recorded, the committee established four (4) explanations. Firstly, it was quite clear that, while in some cases the road was reported as being slippery, this in fact was not the case. This would be referred to as a user perception problem, not an actual slipperiness issue. In prior research¹, it was determined that even seasoned police veterans thought that magnesium chloride, applied as an anti-icing measure, did make the roads slick. In fact, the research showed otherwise. In one particular incident where the road was reported as being slick after application of liquid chemical, police investigation showed lengthy skid marks leading off the on-ramp of a highway. If indeed the road had been slippery, naturally, skid marks would not have been seen, (this indicates that excessive speed was a factor; not the slippery road, in the accident reported).

Secondly, many of the reported incidents were, in fact, simply roadways that had been allowed to freeze as a result of dilution. An example of this was one particular incident where an adjoining road was dry and bare, but another road treated with liquid chemical and allowed to stand in fog over the ensuing evening, became diluted to the point where the concentration levels dropped, (along with the ambient temperature), leading to pure ice.

The third reported source of some incidents, involved surface contamination. While some of these contaminates were unknown, it was reported that in at least one incident, the rust inhibitor used in the liquid chemical was indeed an oil-based product. Furthermore, other sources of contamination included oil, and the grease from routine traffic. In the absence of a previous rain, upon application of the liquid chemical, the water-based and oil-based products mixed together to form a "greasy" contaminated surface. An example of this was seen at airports, where, on ramp ways, upon first application in the fall, a thick foamy solution was formed, sufficient to actually spray onto the inner fenders of airport vehicles, (this was the result of liquid chemical anti-icing measures in combination with spilled grease, hydraulic fluid, oils, ethylene glycol and other products, and an apparent lack of rain to wash away the contaminants).

¹*The Effect of Magnesium Chloride as an Anti-Icing Agent on Tire/Road Friction Co-Efficient, Leggett, March 2, 1999.*

The fourth reason for slippery road conditions after application of liquid anti-icing measures, it was postulated, included the possibility that under certain conditions, the liquid chemicals could concentrate by evaporation, thus undergoing a crystallization phase change. At that time, it was hypothesized that crystals might give rise to a slick road surface which the committee referred to as "chemical slipperiness". The purpose of this research was to determine if this hypothesized condition has any basis in fact.

Test Equipment and Procedure

As indicated, it was necessary to construct a climate-controlled test facility in order to fully establish a complete matrix of temperature and humidity values, which might be encountered in real-world applications. In other words, simply relying on Mother Nature to provide the ambient conditions, would not guarantee or ascertain that all conditions would be appropriately tested.

Accordingly, a "box", fully insulated with a clear, "see-through" front for observation, was constructed. This allowed for direct inspection of the chemical throughout the testing process, in order to document any changes which correlated with areas of reduced friction, as measured. Because many of the reported slippery incidents involved humidity in the range of 45% and temperatures of approximately 8E Celsius, the majority of the initial testing was performed in this range. The friction was measured using an electronic drag sled, (equipped with a B.F. Goodrich tire) weighing approximately 20 lbs. The pull force was measured using a Mettler-Toledo 100 lb. load cell gauge, (with a sensitivity at .001 lbs.). The drag sled was pulled, using a constant velocity motor at a rate of approximately .3 metres per second, which allowed for data collection of approximately 33 points, (the sled was pulled over a 1 m. distance with a sampling rate of 10 measurements per second). The static friction, (that required to overcome the stationery position of the drag sled) was not measured in these experiments. Only after fluid motion commenced was the trace triggered. This allowed for a determination of the sliding, or dynamic, co-efficient of friction, exclusively, (the trace was removed before the motion of the drag sled terminated).

Between tests, the glass surface was triple-washed and triple-rinsed, then allowed to fully dry. Further, between tests, the drag sled was also triple-washed, then allowed to stand in water for 1 hour, then washed again and allowed to dry. This eliminated any possibility of cross-contamination between tests.

The output was tabulated by hand and internally with the use of testing software. Later, trends were established using graphical analysis techniques, and Quattro Pro spread sheets.

Unfortunately, during the removal of the glass surface for cleaning in early tests, a fracture occurred, rendering the surface useless for further testing. Accordingly, an additional glass surface was procured, with the instruction provided that it be sandblasted to the same extent. A review of the additional blast surface, both visually and through touch, indicated a very similar, if not identical, surface. However, under base line testing, differences were found. The first glass test bed was used for initial testing of calcium chloride, magnesium chloride, calcium magnesium acetate, and sodium chloride. The second glass surface was used for all additional tests, (pure compounds with inhibitor added). In order to directly compare the original calcium

chloride and $MgCl_2$ with the additional chemicals, the former two were "re-run" on the new test surface. Surprising differences were encountered in the re-run of $MgCl_2$ on the second surface. The second surface showed a "dry" friction value about 7% higher than the first surface, yet with $MgCl_2$, higher liquid and solid friction values were found in the first surface. This seems to stem from surface differences (asperities) between the two surfaces. It may also indicate why in the real world, surface texture might play a role.

Finally, at the end of testing, (involving well over 1,000 "runs"), baseline (wet and dry) tests were re-performed, to ensure that the surface, the drag sled, and/or the measuring equipment had not changed in any way.

Literature Research

Attempts were made to determine whether other literature existed, specifically with regard to the effect of liquid chemicals used as anti-icing agents on the road co-efficient of friction. A paper compiled by Persson and Ihs² was discovered. Here, the authors documented an earlier report completed by Kamplade and Sievert in 1989. The purpose of this study was to determine whether there was any risk that the road friction value would deteriorate by introducing calcium chloride in winter road maintenance. These experiments were also conducted in a climate chamber, where temperature was held constant and humidity varied. The tests were performed on pavement of differing textures, with a calcium chloride solution used exclusively. It was found that at extremely low humidity, the calcium chloride crystalized, as calcium chloride hexahydrate. Then, when humidity was increased, the calcium chloride was dissolved and gradually became all solution. This study showed that a special slipperiness developed when both the calcium chloride hexahydrate and the calcium chloride solution were present, (ie. in the transitional phase to or from the crystalized calcium chloride hexahydrate). It was also found, however, that the prerequisite for this condition rarely occurred in winter. In other words, at a temperature of 0E Celsius, the humidity must be less than 43%. It was also found that the friction value obtained was roughly comparable to that when oil is spilled on the road. As a result, the authors concluded that:

- slipperiness can occur at calcium chloride concentrations above 5 grams per meter² when the humidity drops below 40% 45%;
- at a relative humidity above 50%, even higher calcium chloride concentrations are not a problem, however, the concentration must be reduced by the effect of traffic run-off before the weather change produces a lower humidity;
- slipperiness develops both when the humidity drops, and the calcium chloride hydrate crystalizes, and when it rises again, and the calcium chloride hydrate goes back into solution.
- the thinner the hydrate layer, (ie. the lower the amount of calcium chloride on the roadway) the shorter the time when slippery conditions can develop by transition through the critical humidity range.

Additionally, the authors note that if calcium chloride is used in anticipation of incoming weather, and it does not occur, one should pay close attention to the relative humidity. If indeed the humidity drops, and part of the moisture in the calcium chloride solution evaporates, the

² "Calcium Chloride in Winter Road Maintenance: A Literature Study", VTI Report 829, 1998 from the Swedish Road and Transport Research Institute.

the concentration of the solution will increase accordingly. If the humidity drops to a level where equilibrium with the saturated solution is reached, and the humidity continues to drop further for a longer period of time, (2 - 5 hours) a portion of the calcium chloride solution on the road is converted into a solid form, (hexahydrate - CaCl₂ - 6 H₂0). This causes "ice to develop". In order for this to be a hazard on the road surface, the amount of calcium chloride on the pavement must be at least 40 grams of flakes per metre². If the amount of calcium chloride used during preventative treatment is in the range of 5 - 20 grams of flakes per metre², and additional spreading is not performed, there is no risk of icing. Finally, the authors note this is another reason why the application rate should not be too high in preparing the salt solution.

Other literature researched dealt exclusively with the effect of liquid chemicals on the road friction co-efficient of friction without any mention made of "a special slipperiness that can develop". Research has shown, for example, that the use of magnesium chloride does not diminish the road friction co-efficient beyond that which would be expected for pure water, but that it greatly enhances the co-efficient of friction typically experienced in winter time conditions if no application is made^{3, 4, & 5}.

Surprisingly, with the exception of the Persson and Ihs paper, the literature is essentially void of any research or testing on the subject of "special slipperiness" developed under certain chemical conditions. Perhaps this is because the occurrence of such slipperiness is, indeed, so rare.

Experimental Results

As a base line, pure water was initially used on the second test bed, both in liquid and in ice form. With an air temperature of -6.8E Celsius, a ramp temperature of -3E Celsius, (the ramp is the actual test bed) and an ambient humidity level of 51.5%, approximately 60 mm. of ice was present. This resulted in a co-efficient of friction of .088, (a very low friction value). When water was sprayed over top of the ice at similar ambient conditions, the value reduced to .070, reflecting the lubricating qualities of water on ice. The humidity was maintained at approximately 60%, and the ramp temperature was allowed to rise. With a ramp temperature of 1.0E Celsius, liquid patches began to appear and the resultant co-efficient of friction dropped, again reflecting the lubrication of water on ice. The lowest value (at 4.0E Celsius ramp temperature, with an air temperature of 14E Celsius) was determined to be .052, which is identical to the co-efficient of friction values for water on ice published in the literature⁶. For the second glass surface, a co-efficient of friction of .369 was

⁵ "Evaluation of Wet Skid Resistance Using Four De-Icing Salts, Pennsylvania Transportation Institute, July, 1983.

⁶ "Traffic Accident Reconstruction", Lynn B.Fricke, Northwestern University Traffic Institute

³ The Effect of Magnesium Chloride as an Anti-Icing Agent on Tire/Road Friction Co-Efficient, Leggett, March, 1999.

⁴ "Evaluation of Wet Skid Resistance Using Various Concentrations of Two De-Icing Chemicals", Schultz, Washington State Department of Transportation Materials Office, March, 1994.

measured for pure water at a temperature of 21E Celsius, and a ramp temperature of 12E Celsius, (the humidity was 44%).

Tests were also performed on a dry bed at 22E Celsius, and 42% humidity. The results of this pursuit indicated that the co-efficient of friction was .414, (second surface). The first glass surface produced a dry co-efficient of friction of .386, (ie. the second glass surface produced a dry friction value about 7% *higher* than the first glass).

Interpretation of Appended Graphs

Because there were three variables to all tests, (time, friction and humidity), two curves for each chemical are seen. To interpret the graphs, the reader must realize that every point on the friction curve, (represented by a triangle) corresponds to a point on the humidity curve, (represented by a square). When the humidity curve drops, this means the chemical is drying out. When it rises rapidly, moisture is being introduced into the chamber. Therefore, it is possible to immediately determine what the corresponding friction level is. Of importance, all chemicals start (on the left side of the graph) with liquid, dry out, then are returned to liquid.



1. Magnesium Chloride

The first chemical to be tested was $MgCl_2$, initially on glass surface #1. The test protocol involved altering the humidity from 30% to 50%, and the temperature from 2.5E Celsius to 10E Celsius. The first data point was 2.5E Celsius, and 30% humidity. This produced a co-efficient of friction of .347

upon application at a rate equivalent to 35 gallons per lane mile. Then, humidity was increased to 50%, where it was noted that the friction held fairly constant to .343. The temperature was then increased to 10E Celsius, and the humidity held constant at 50%, and the co-efficient of friction was determined to be .321. Each test was 15 minutes apart, (to allow for chemical equilibrium to be reached). In this set of experiments, no reliance on temperature and humidity was found, (ie. a "special slipperiness" was not observed). However, it should be realized the chemical stayed in liquid form, (ie. no "slurry" observed). Additional experiments were also performed holding the temperature at 10E Celsius and the humidity at 45% to determine the effect of time on the co-efficient of friction value. Upon application, the co-efficient of friction was determined to be .330. The co-efficient of friction showed a general decline, bottoming out at .312 approximately 1 hour and 10 minutes post-application. Then, the friction began to rise slowly, appearing to plateau at .325 approximately 6.5 hours post-application.

Further experimentations led to the solution beginning to dry out with an ambient humidity level of approximately 26% and a temperature of 19E C. This produced a co-efficient of friction of .278. The solution was allowed to fully dry, with an ambient humidity of 21%. At this time, white precipitate was seen with no liquid present. The co-efficient of friction increased to .342. At this time, re-hydration commenced, (humidity was introduced). A "slurry" was observed at an ambient humidity level of approximately 31%. With the temperature at a constant 10E C, the co-efficient of friction reduced to .235. Re-hydration was continued and when liquid formed, the co-efficient of friction value increased to .373. In another set of experimentations with MgCl₂ at 7.5E C, it was determined that the co-efficient of friction for solid precipitate, (no liquid present) was determined to be .321. With moisture added, a slurry again was formed, reducing the co-efficient of friction to .243. This involved a drop of roughly 25%. With liquid MgCl₂ at this temperature, a value of .324 was seen, (very nearly equivalent to the value for solid precipitate) and again, 25% better than the transitional phase.

As indicated previously, $MgCl_2$ was re-run with the second glass surface. Surprisingly, on initial application, (wet) A friction of .269 was found, (down from .373 from the first test; a drop of 28%). Further, in the transition, or "slurry" stage, a value of .25 was seen. This value was comparable to the initial results, where a value of .235 was observed. Finally, in the second set of tests, the "dry" (precipitate) friction value of .27 was determined; 16% short of .321 observed in the first set of tests, on the first glass surface.

2. LiquiDow

An equivalent application rate of 35 gallons per lane mile was completed with *LiquiDow*, (calcium chloride). The results of this analysis indicated that the co-efficient of friction, after application, was approximately .352, (at 10E C). The solution was allowed to dry, a "slurry" was formed at approximately 29%, and this produced a friction value of .210. The solution was then allowed to fully dry and white precipitate was observed with a crystalline structure. It appeared to resemble "ice", with large finger-shaped fracture sites. Under dry conditions, the co-efficient of friction remained low, at approximately .211

Additional tests with LiquiDow were completed on the second test surface. This resulted in liquid values of .275, (a drop from the previous .352), a "slurry" value of .243, (a slight rise from the previous .210), and finally, a dry of .21, similar to the previous .211 found on the first surface.

3. Calcium Magnesium Acetate

The liquid *calcium magnesium acetate* was tested. With application equivalent to 35 gallons per lane mile, a friction value of .367, (with temperature at 19E Celsius and humidity at 29%), was found. The temperature was then reduced to 10E Celsius, with the humidity at 32%, the coefficient of friction value actually increased to .377. At approximately 33%, at 10E Celsius, the solution began to dry, forming a heavy white precipitate. There were, however, no signs of crystals, nor was there any "slurry" observed. As the heavy white precipitate formed, the coefficient of friction rose sharply to .465. Even at 55% ambient humidity over a period of .5 hours, the precipitate would not re-enter liquid phase. Additional amounts of chemical were sprayed in order to allow the precipitate to re-enter solution, and this reduced the coefficient of friction to .350. Again, as time progressed, with ambient humidity levels at approximately 28%, precipitate began to form and the coefficient of friction again increased to a maximum of .442.

Similar tests were performed on the second surface, with seemingly similar results as the first surface.

4. Sodium Chloride

The last of the initial tests were performed with a *sodium chloride* brine. Initial conditions included 40% humidity and 15E Celsius. With liquid application, the co-efficient of friction was determined to be .394. White precipitate began to form at approximately 30% humidity and this reduced the co-efficient of friction to a minimum of .302. Once dry, the friction again returned to very nearly the same level as that seen on liquid application, (.404 at most). Upon rehumidification at up to 53%, the white precipitate would also not form back into a liquid solution.

5. LiquiDow Armor

Upon application of *LiquiDow Armor*, the friction value recorded is relatively high, (.34). Once humidity is dropped to approximately 26%, the friction also drops linearly to a low of approximately .28 at a time of 60 minutes after initial application. However, on maintaining the humidity levels at 23%, the solution completely dries and then attains a high level of approximately .44. During this time, a light brown precipitate drops out of the solution as the phase change occurs. This light brown residue increases the friction beyond the liquid friction value by approximately 30%. In the transition phase, between solid and liquid, a 24% drop in the friction, (to approximately .255) is seen. Once the humidity is re-introduced, the solution again forms liquid, and the value returns to that on initial application, (.34).

6. FreezGard 0 and Shield LS

On initial application, the co-efficient of friction is .257. Upon de-humidification, the solution begins to dry, forming a light brown gel with foam. This occurs at a humidity level of approximately 26%. As the material dries, the co-efficient of friction responds by increasing to .340. Upon humidification, the friction drops to .28. As liquid forms, the friction reduces again to very nearly the level at initial application, (.26).

7. FreezGard 0 and TEA

On initial application, the friction associated with liquid form, is .245. As de-humidification occurs, the friction rises linearly, and begins to form a crystal precipitate at a humidity level of approximately 23%. The associated friction value with this is .269. As drying continues, a value of .285 is seen. Upon introduction of moisture into the air, the friction drops to a level of approximately .25, (at approximately 40% humidity). As humidity is increased, all liquid is returned, and the value of friction levels off at approximately .244, (again, near identical with that on initial application).

8. Ice Stop

On initial application, the co-efficient of friction is .311. As de-humidification occurs, the friction drops marginally to .289. This occurs at approximately 26%. At 24%, the solution contains very little liquid and produces a friction of .333. When moisture is introduced, (ie. with the raising of humidity), the friction tumbles to approximately .25, which occurs at 34%. At this data point, a gel-like substance is seen. Then, with the introduction of more moisture, liquid returns and the value achieved is .312, (near identical to starting liquid conditions).

9. Ice Stop 2000

After initial application, at a relative humidity of 43%, the co-efficient of friction is determined to be .316. As de-humidification commences, the co-efficient of friction reduces nearly linearly until a low of approximately .284 is seen for a humidity level of about 26%. With continued dehydration, the formation of crystals is seen, and the corresponding co-efficient of friction rises marginally to approximately .287. On introduction of moisture into the system, the co-efficient of friction rises, and at approximately 38%, liquid begins to be seen. This corresponds to a resultant co-efficient of friction of approximately .305. All liquid is seen at approximately 44%, with resultant friction of .309. This is similar to initial conditions, (.316).

10. MCP De-Icer

Upon initial application, at a humidity of 41%, the solution provides a co-efficient of friction of .284. During de-humidification, the friction increases substantially as it dries and forms a white precipitate. The maximum value achieved under a full dry condition is .333. There is no reduction in friction as the solution transitions from liquid to solid phase. However, upon introduction of moisture into the system after it had stabilized in solid form, the friction drops to .287 as it begins to change to liquid, and stabilizes at .284 as a liquid, (identical to the value achieved on initial application).

11. FreezGard 0

On initial application as a liquid, (at 42%), the co-efficient of friction is .248. During dehydration, the friction value is maintained, until solid precipitates are seen, at which point the friction increased to .278. Once the humidity is increased, liquid reforms, and the solution produces a friction of .26. Importantly, no reduction below liquid or solid friction levels, (in the "slurry" stage) is seen.

12. FreezGard 0 and Ice Ban

The friction curve behaves nearly identical to *MCP De-Icer*. All liquid co-efficient of friction is .261. With the removal of moisture, friction increased to .308, when solid is formed. With the increase in humidity levels, the value of friction drops to .27 before stabilizing at .255 for liquid. During the "slurry" stage, only a marginal reduction in friction beyond the level of liquid friction is seen.

Comparative Results



De-Icer Chemicals

LEGEND

Solid Grey.... Liquid Hatch.....Slurry Light Grey...Solid

- 1. Magnesium Chloride
- 2. LiquiDow
- 3. Calcium Magnesium Acetate
- 4. Sodium Chloride
- 5. LiquiDow Armor
- 6. FreezGard 0 and Shield LS
- 7. FreezGard 0 and TEA
- 8. Ice Stop
- 9. Ice Stop 2000
- 10. MCP De-Icer
- 11. FreezGard 0
- 12. FreezGard 0 and Ice Ban

Overview

The purpose of this work was to determine whether there existed a chemical-induced slipperiness aside and apart from other causal factors which are believed to contribute to slippery road conditions. For example, it has long been known that the first rain after an extended period of no weather, produces a very slick road condition, as the moisture mixes with automotive fluid, to form a greasy, slimy solution. After a short period of rain, and continued traffic, this solution is worn away and the surface becomes clean once again.

The research was performed on an etched glass surface, (a typical window glass sandblasted to achieve a modelled, or rough-textured, surface with trough heights of approximately 1 mm., at most). The reason for this was to eliminate the effect of a cross-contamination which may have been introduced had an asphalt tablet been used. For example, if, under certain conditions, a slippery surface was noted, it would not have been possible to eliminate whether this was chemical activity, or simply a mixture with the oils impregnated in the asphalt surface itself.

The research has now confirmed that, using an inert surface such as the glass, there can be no doubt that some anti-icing chemicals themselves can, on occasion, produce a reduced friction surface. However, a very strong word of caution is urged to the readers with regards to this very important aspect. For example, it would be highly imprudent for a user to interpret the results of these tests, performed on a model glass surface, and extrapolate that data to use in another application, (ie. for asphalt or concrete road surface). Unless the user encounters a rubber tire travelling over a glass surface, the values presented in this paper would be inapplicable. Furthermore, as our own misfortune has shown, there are differences even between glass surfaces which appear to the touch and sight, very similar.

Therefore, it is expected that in the real world, differences in roadway surface texture will vary, resulting in various frictions when chemicals transition from phase to phase. Rough asphalt, or "chip seal", probably will be less affected, because the "slurry" will typically be found in a trough, where tire-road interaction does not occur.

Glass v. Asphalt

The level of repeatability and the level of accuracy of the friction tests is very high, thanks to the calibration of the Mettler-Toledo load cell. Therefore, even minor differences between the glass surfaces show up as surprisingly large differences in friction values. Perhaps, one surface had larger troughs, (ie. dips and valleys) at the microscopic level, than the other, over the surface being tested. This important observation can also be used to caution readers with regards to drawing conclusions between and amongst the various chemicals that have been tested. Whereas the graphs which accompany this report show fairly large differences between the co-efficient of friction values of various manufactured products, (particularly with the use of additives) in the real world, such large differences are likely to have a far less impact on the road co-efficient of friction value. The reason for this is undoubtedly that most asphalt and concrete surfaces would have far higher variations involving far greater trough depths. Therefore, since the chemical would typically sink to the bottom of those valleys, the surface encountered by the typical

passenger tire may not involve actual interface with the low part of the asphalt surface. In other words, interfacing with the crest of the asphalt at the microscopic level, there may not be the influence that is seen in the test chamber where the peaks and valleys are of infinitely smaller magnitude than that seen in the real world. Every parent knows that the application of talcum powder on a baby's skin produces a smooth, "low friction" condition when one rubs his/her hand across the child's skin. Would the same application rate of talcum powder on an asphalt surface reduce the friction similarly? Clearly not.

The proof of this lies in the differences seen between MgCl₂ testing on glass surface #1 and glass surface #2. While both surfaces were similar in appearance, touch, and dry friction, large differences in performance were seen with MgCl₂. For early tests, liquid MgCl₂ showed a .373 friction level compared to .269 for later tests. The transition phase for test #1 showed a level of .235 compared to .250, (test #2). Finally, for solid, initial testing showed a value of .321 compared to .27 for later tests. Why were "slurry" values so similar, but liquid and solid values so different? The tests were conducted about two months apart - could the solution have changed in that time? This seems highly unlikely. Everything was held constant, with the exception of the glass surface, which was changed, (by necessity). The second surface produced a "dry" co-efficient of friction of about 7% higher than the first surface, suggesting slightly higher asperities⁷ were present. This means the tire may not have made as much contact with the solution in the second experiments, as compared to the first. Importantly, the tire may have missed the "marbles" which were present during the "slurry" stage, because it was interfacing with the peaks of the glass which were not immersed in "slurry". This critical finding suggests that road surface texture probably plays as much, or more, of a role in determining whether drivers encounter a slippery condition, as the chemical themselves. Future work, with the present climate-controlled test facility on various roadway surfaces, will focus on this point.

That having been said, it is clear that the research has been very useful in ascertaining trends amongst chemicals as they transition from liquid to solid, and also to confirm that, indeed, this condition, which is incredibly rare in the real world, is a function of chemical composition and chemical properties. This is not to say that the chemicals are solely responsible for slickness issues and that other factors do not play a role. The writer's experience in reconstructing traffic accidents confirm that other factors, including those previously mentioned, and human factors, play a far greater role.

This research can also be used to identify the conditions upon which the probability or likelihood of chemical slipperiness developing exists. If this can be achieved, then by refining or rethinking the liquid chemical application, it may be possible for a maintenance manager to even further decrease the probability that such a chemical slipperiness can occur by either altering the quantity of application, the type of application, or by re-evaluating the application altogether.

The reader will note, as addendums to this paper, graphs are provided for most of the chemicals tested. No graphs for CMA or NaCl exist, because the early data collected for these chemicals was not processed time-dependant.

⁷ Asperities are the various "peaks and valleys" of the surface, seen at the microscopic level.

Further, the data output, (found on the graphs) was not smoothed, (using a Fourier transform or other method) nor has it been massaged in any way.

Limitations of the Test Facility

A final word of caution is in order with regards to the limitation of the testing apparatus. Most regrettably, as a result of the inability of available salinity sensors to correlate salinity levels with concentrations over a broad temperature spectrum, and also as a result of tables only being available for MgCl₂, it was not possible to equip the climate-controlled testing facility with a salinity testing device, which would have recorded the condition of the chemical as it transgressed between phases. Accordingly, whereas the ambient relative humidity levels were measurable with sophisticated humidity sensing equipment, a direct correlation with the condition of the chemical at that particular time (at the time the humidity value is received), was not possible. For example, whereas the appended charts may show a chemical slipperiness occurring at a certain humidity, it is not known whether it is the precise value of the chemical, or not. In fact, it is probably more likely that as a result of a time-lag, (relating to the inertial properties of the solution), the chemical lags the ambient conditions by some degree. The proof of this is that under conditions of 30% - 50% ambient humidity levels, LiquiDow did not appear to re-hydrate until a level of approximately 33% was achieved. According to the calcium chloride handbook from Dow Chemicals⁸, at the precise value tested, (15E Celsius), the relative humidity of air in equilibrium with a 30% calcium chloride solution at this temperature is approximately 36%. Therefore, it appears that the experimental results compared with that in the published literature, are approximately 3% apart. Again, it is considered likely that this relates to a time factor, which is difficult to account for in the testing method.

How Does It Get Slippery?

The mechanism for chemical-induced slipperiness as it relates to phase change from solid to liquid is, at present, not well explained. Future work will include the use of a high-power electron microscope so that during this important chemical transition, at the microscopic level, we will be able to observe the hydrates as they precipitate out. At this juncture, it is theorized that the mixture of some solids with liquid allows the mixture to act somewhat like "marbles" whereby the road tire is physically lifted from the surface and does not make as good a mechanical interaction with the peaks of the asphaltic surface as would be hoped for. Therefore, increased solution volume would expectedly decrease friction during the chemical slipperiness phase - ie. "more marbles".

Clearly, all chemicals follow their eutectic curve as they transition from liquid to solid. These can be seen as an inflection point on most curves, and it is at this point where "slurries" are formed, and this is sometimes associated with a decrease in friction.

⁸ A Guide to Properties, Form, Storage and Handling

Effect of Vapour Pressure

On the subject of vapour pressure of calcium chloride hydrates and solutions, it is of interest to note that in the temperature range typically used during winter time operations, (0E - 15E Celsius), the minimum water vapour pressure required for calcium chloride hydrates to deliquesce⁹ is very nearly the same, (hovering between 36% and 42%). However, as the temperature increases, specifically beyond the 20E Celsius mark, the saturated solution curve alters course and the vapour pressure curves are no longer parallel. Therefore, for example, at 30E Celsius, the vapour pressure required to liquify calcium chloride reduces to 22% relative humidity, or about half that required in winter time operations. For summer operations, any ambient humidity greater than 22% will allow the hygroscopic nature of the chemical to attract water molecules. Thus, in the summer time, since humidity is generally higher than 22%, calcium chloride will pick up water from the air and enter a dilution phase. It is this fact alone which makes it particularly useful for dust control. However, under winter operations, as indicated previously, the curve shifts and it is possible for the solution to dry out, (the reverse of hygroscopic activity). For example, according to the vapour pressure chart of 30% calcium chloride solution, at 5E Celsius, if the ambient humidity is less than 43%, (3 mm. HG \div 7 mm. HG x 100%), the solution will actually give off water molecules, (ie. evaporate), thus leaving calcium chloride hydrates behind. If this continues, all water molecules leave, creating a dry white precipitate solid. On asphalt, the dry white precipitate seen on glass may appear simply as a darker, slightly wet surface for some time. Once the humidity levels return above that required to re-hydrate the solution, the hygroscopic nature of the solution will again commence activity and the solid will become liquid once more. Our research shows that this activity, (drying and re-hydrating) can continue at infinitum without the chemical properties of the solution being altered. In other words, transition from liquid to solid and back to liquid on numerous occasions still allows the friction for liquid to be near identical.

Humidity Levels

Originally, the test procedure included focussing on the value of 45% relative humidity and 8E Celsius because it was synonymous with many of the reported incidents. The research now shows that at this level, slipperiness is generally not seen. Only after very low humidity values are achieved, (ie. less than 32%, and in most cases less than 28%) is reduced friction observed. Therefore, in the future, it is seen as being necessary that better documentation be procured with regards to determining the level of ambient humidity. As humans, we are poor at establishing factors relating to our own environment, (for example, time, distance, velocity, temperature and humidity) within any reasonable amount of accuracy. Therefore, it is insufficient to simply suggest that the ambient humidity levels are at a certain level simply because the sun is shining and that is a typical value for the area in question. Indeed, humidity levels vary widely and working with the climate controlled test facility on a daily basis, the author witnessed very large fluctuations in external humidity levels, (which were also closely monitored) even under similar conditions of temperature, sun, and wind.

⁹ Deliquesce is described as forming a solution.

The research also shows overwhelmingly that for some chemicals tested, (Ice Stop, LiquiDow Armor, LiquiDow, MgCl₂, CMA and NaCl) the reduced value of friction is found in the transition phase between solid and liquid, or vice versa. While there was a drop in friction of approximately 15% during the transition from liquid to the "slurry", for calcium magnesium acetate, when further dehydrated, it rapidly produced a greater co-efficient of friction value. In other words, the heavy white precipitate formed when calcium magnesium acetate dehydrates, produced a far greater co-efficient of friction value than either liquid or the liquid and solid mixture, (the solid produced an increase of about 22% greater than liquid phase, and about 34% greater than the transition phase). For sodium chloride brine, the co-efficient of friction for liquid was .394 and this reduced to a minimum of .301 as the liquid transitioned into a solid, forming a white "slurry". At this condition, ("slurry") a friction value of .301 was found, resulting in a drop of about 24%. Moreover, when solid formed, it, as well, showed a higher friction value at .404 than under the liquid conditions, (an increase of about 25%). Of interesting note, whereas the other chemicals were easily re-hydrated simply by adding moisture to the air, (through the use of a humidifier inside the test apparatus) the solid sodium chloride would not rehydrate unless moisture, in the form of pure water, was added directly to the dry crystal structure on the test bed. This factor, (the failure of the solid to attract moisture, enabling it to return to a solution) was also seen with CMA. With ambient humidity levels of 55% maintained for .5 hours, the very dry white precipitate remained, and would not re-enter liquid phase. Again, the only manner in which it was possible to re-liquify this solution was to physically spray it with liquid H₂0. This may suggest that salt brine and CMA, are apparently far less hygroscopic than the other chemicals tested, which readily and aptly accepted the introduction of moisture in the form of increased humidity levels.

There were numerous "surprises" seen in the testing, but none so obvious as the dramatic difference between the solutions that were only distinguished by the addition of an additive used for corrosion

inhibiting.

In some cases, the co-efficient of friction was unchanged in liquid form, however, in solid form, the friction was substantially higher with the use of an additive, (this was especially true, for example, with FreezGard 0 and Ice Ban and FreezGard 0 and Shield LS, as compared to straight MgCl₂). Generally speaking, all chemicals with additives performed better than their pure chemical counterparts. Also showing a substantially better liquid friction was Reilly Wendover's Ice Stop and Ice Stop 2000, the former which had levels of .310 seen as compared to straight MgCl₂ liquid value of .27. Of more importance, however, was the fact that MgCl₂, during its "slurry" phase, produced a co-efficient of friction of .25, whereas Ice Stop 2000, at its lowest value, (again during transition from liquid to solid, and vice versa) produced a lowest value of about .284. However, by far, the largest difference was seen between LiquiDow and LiquiDow Armor. For LiquiDow, (30% calcium chloride) the liquid co-efficient of friction was approximately .275. However, for LiquiDow Armor, the liquid co-efficient of friction was .342, for a difference of 20%. Furthermore, with LiquiDow, after it had dehydrated and dried, the coefficient of friction remained very low at approximately .196, (this was the lowest value tested). Unlike all other chemicals which typically had their friction curve rise as the solution became a more solid form, the LiquiDow maintained its very low friction level throughout its drying phase. However, unlike its cousin, LiquiDow Armor, when it solidified, increased friction dramatically to a maximum of .436, which was observed approximately 70 minutes after it began to dry.

These observations confirm the fact that it would be completely imprudent to measure the performance, in terms of co-efficient of friction, of a similar compound without actually testing an identical solution. Even trace amounts of inhibitor seem to dramatically affect the co-efficient of friction performance of all solutions. Another word of caution is urged with regards to LiquiDow and its apparent inability to respond after solidification to a higher friction value. According to prior research, which was performed on an asphalt surface¹⁰, the co-efficient of friction of solid calcium chloride was approximately .56 at 25% humidity. When re-hydration commenced, the friction drops to a low of about .38 at approximately 42%. This infers that in the real world, solid calcium chloride actually performs better when it is in the solid stage, which was not seen with testing on glass. Again, this likely relates to the surface texture of the roughened glass surface, which is no where near as abrasive and deep-textured as typical asphaltic surfaces.

These observations confirm that most of the time, when a chemical transitions from solid to liquid and liquid to solid, a "slurry" is formed. However, just because a "slurry" is formed does not mean it is associated with low friction ("slickness"). Whether a "slurry" will be slick depends on many factors, including surface roughness, application rate, product use, and humidity, etc.

Temperature - Humidity Dependance

With regards to temperature and humidity, there does not appear to be a substantial difference with the co-efficient of friction values in the range tested, (30% - 50% humidity, and -5E to +10E Celsius). The one caveat to this is clearly the fact that this is true so long as the solution does not begin to precipitate out, (form a "slurry"). If this occurs, then, indeed, some of the chemicals can be substantially slipperier than in their liquid or solid form. In one particular set of experiments which were initially designed to verify this, it was noted that with the temperature held constant at 2.5E Celsius and the humidity increased, there was a marginal decrease, (from .347 to .343). However, when a new temperature of 5E Celsius was held constant, and the humidity increased again, from 30% to 50%, the values also were lower, progressing with increasing humidity. As well, as the temperature increased, the co-efficient of friction value also tended to decline very slightly. There appeared to be, therefore, a trend towards slightly reduced friction as temperatures increased, and slightly reduced friction as humidity is increased.

In a further set of experiments, however, $MgCl_2$ at 10ECelsius, and 45% humidity was held constant, and over the course of approximately 6.5 hours, it was determined that indeed the friction did drop off during the first 75 minutes, (from a value of .334 to a low of .312). This relates to a reduction of about 6.5%. Therefore, it was determined that in the prior experiment, it was not the effect of raising the temperature or raising the humidity, which lowered the

¹⁰ Kamplade and Sievert, 1989

co-efficient of friction of value slightly, but rather the fact that the solution was placed in the tank and over the course of the experiment's time, the value descended marginally. Accordingly, there does not appear to be a temperature dependence on the reduction in co-efficient of friction for the chemicals tested in the *strict sense of the word*. In other words, humidity drives the chemicals between phases, and thus plays a far greater role in determining whether the potential for slickness is present.

As indicated previously, all chemicals have a vapour pressure curve, which allows for the calculation of dissociation pressures of their hydrates. For the example used previously, (calcium chloride) there is a slight difference in the values at which dehydration will begin to occur. For example, at 15E Celsius, at anything less than 36%, the precipitate will begin to form, given enough time. However, at 0E Celsius, the humidity level must be less than 43%. Considering these values, the effect of temperature is to lower the point at which a liquid will transition into a solid as temperature is increased. At the other end of the spectrum, under summer operations involving temperatures of say, 30E Celsius, the water vapour pressure needed to liquify calcium chloride reduces to about 22%, which is essentially not attainable in most areas of the country. Therefore, whereas temperature does not seem to play a role in the climate-controlled test facility, in the real world, it does come into play because it affects the value at which a solution will begin to precipitate out. Unfortunately, we have been unable to locate similar vapour pressure curves for other solutions in order to perform a similar analysis. However, for the magnesium chloride and calcium chloride based chemicals, it is deemed likely that a similar reasoning would probably apply.

Quantity of Chemical Used

As regards to quantity of application, the vast majority of tests were performed with an equivalent level of chemical as that which would be seen with an application rate of 215 litres per lane km. Prior research showed that for magnesium chloride, there was no discernible difference between application rates. In that research, however, the "slurry" stage was not seen. Other work has shown that for calcium chloride, increasing the amount tends to decrease the coefficient of friction¹¹. This is especially seen in the "slurry" stage, where with more solution used, (up to 22.5 grams of salt per metre²), the co-efficient of friction dropped to a value of about .36, (for rubber on asphalt). At lower levels of usage, (3.8 grams of salt per meter²) the lowest value of friction was .60. While we have yet to study the effect of varying the dosages of liquid chemical used, and how it interacts with the resultant co-efficient of friction, (this will be performed in further tests where the glass surface in the climate-controlled test facility is replaced with an actual asphaltic tablet) we have found that larger quantities of chemical in a given area require a greater time to initially transition into the "slurry" state, and also, once in the "slurry" state, greater quantities of solution typically stay at that state for an extended period of time. Again, it is considered that this relates to the inertial¹² properties of the solution.

¹¹ Kamplade and Sievert, 1989

¹² The ability and tendency of a solution to stay at any given state.

Time of Reduced Friction

On average, it was exceedingly difficult to maintain all of the chemicals in the "slurry" state for any extended period of time. It is considered that this state is one of unstable equilibrium, (ie. the solution prefers to either be in a liquid or solid form). An example of this occurs with boiling water. It is possible to keep the water warm, or to keep it boiling, but very difficult to modulate the heat source so that it stays on the verge of boiling. It is also considered that this factor alone is potentially most responsible for the incredibly few reports of slick conditions which are reported. (The other, of course, is that a requirement of very low humidity is necessary). In other words, when a chemical is seen to transform from a liquid into a solid, by definition, it must drop hydrates, according to its vapour pressure curve, and it has been found in the testing, that this condition for some chemicals, relates to a lowered value of friction. However, if this transition phase occurs over a very short period of time, as has been witnessed in the climatecontrolled facility, then a driver may well pass through this "zone", without even noticing that the reduced friction is present. A brief moment in time later, when the material solidifies completely, and for most chemicals, friction rises once again, the danger period has passed, and in all probability, without incident.

Review of Prior Instances of Reduced Friction

Our review of the documented instances of slipperiness, where other factors, previously mentioned in this report, have been ruled out, suggest the following.

Firstly, the location of incidents is not in one geographic area, (there have been reports of experiences in Montana, Idaho, Illinois, New Hampshire, Oregon, Kentucky, Kansas, Washington, Utah, British Columbia, and Texas, among others). From the data accumulated to date, it appears that these incidents seem to occur with warmer temperatures, (4.4E to 12E Celsius) and mid to low relative humidity, (less than 50%). Another characteristic which appears rather strong in the reports is that they occur in the fall, (there have apparently been a very few that have occurred during the winter months). As well, they appear to occur, more often than not, on bridge decks, although highway passes and other asphalt and concrete structures have experienced similar incidents. More often than not, there is an application of chemical made as an anti-icing measure, which was placed on a warm surface, (above 1.7E to 4.4ECelsius) in anticipation of a reported snow, or a frost event due within the next 24 hours. Applications were often made in the afternoon and within several hours, a slippery condition was seen. Another important commonality seems to be the fact that during fall applications, no rain fall had occurred for approximately two weeks before the application was completed. In a Washington State incident, two passes, near each other, were treated in identical ways with the same product and at the same application rate. Both were asphalt surfaces. One pass reported a slickness incident whereas the other did not. It was later determined that there had been appreciable rain fall on the one pass that had no concern, and the other pass had received no moisture.

Under initial investigation, it was considered more likely that the rain fall washed away the road grime left from passing motorists. After this research, it is now certain that, more likely than not, the area which did not receive moisture was slightly drier than the area which had. Accordingly, for the drier pass, the product simply dehydrated, allowing it to pass into the transition phase

from liquid to solid, (for the other pass which had received moisture, there was a sufficient local microclimate with excess moisture, so that drying out of the chemical did not occur, hence it stayed in the liquid form).

Humidity Prediction and Chemical Use

In Finland, humidity has been monitored for quite some time. In anticipation of anti-icing operations, forecasters pay as much, or more, attention to humidity levels as they do temperature levels, and apparently for good reason.

Users, therefore, would be well advised to procure humidity (minimum/maximum) charts for their area, showing historical humidity levels. For Kamloops, B.C., (considered a semi-arid location with less than 25 cm. of precipitation per year), the following data was reviewed:

Year	# of Days During Period November 15 - April 30 Where Humidity is Below 35%	Comments	
1996 - 1997	45 days	Only 3 days in December below 35%; remainder after March 7	
1997 - 1998	24	Only 4 days in November and December; under 35%.the rest were after April 4	
1998 - 1999	26	No days, November, December or January where humidity was below 35%	

For this location, from data on the past three years, it can be seen that the probability of low humidity in the fall is very low, but that later in the year, (March and April) it is virtually a given. However, in the spring, where showers occur, there may be sufficient surface moisture such that the chemical will not dry out, even if humidity levels are low. (In March and April, 1997, the humidity was between 17% and 35% for 37 out of 42 days).

Users should procure humidity data from prior years, for their area, and construct a humidity probability chart, as depicted above. In this way, a determination can be made with regard to when, or if, an application should be made.

As can be seen from the calcium chloride vapour pressure chart, at a relative humidity level lower than the vapour pressure of the solution, water will evaporate and the solution will tend to concentrate. In other words, it dries out, releasing moisture to the environment while retaining the solid material, (this is true for all chemicals tested, not just calcium chloride). On the other hand, if the ambient humidity level is above the vapour pressure of the solution, it will draw moisture from the atmosphere as a result of hygroscopic activity, (some solutions are far more hygroscopic than others, meaning they will attempt to draw and retain water more readily). Once the vapour pressure of the solution and the humidity levels equalize, (ie. chemical equilibrium is achieved) moisture will not flow either from or to the solution until the relative humidity levels of the immediate environment are changed, (either in the air or in the immediate surroundings). This process generally allows for a stability to be reached, either in the liquid or in the solid phase. The majority of chemicals tested do not appear to readily reach an equilibrium state that is in a transition period between liquid and solid, (ie. a "slurry").

REVIEW OF SPECIFIC CHEMICAL TRENDS

NaCl Brine

Upon application of the liquid, the co-efficient of friction value was .394, the highest of any liquid tested. This value reduced to .301, which was also one of the highest values found for a combination of a liquid and solid form. At this region of the curve, white precipitate began to form with liquid solution still present. As the material dried, substantial white precipitate, with no signs of crystallization, was observed. In its dry form, the co-efficient of friction value was .404, again, one of the highest of all the materials tested. Based on its inability to re-liquify, it appears NaCl brine is not as hygroscopic as other chemicals.

Magnesium Chloride

One of the first chemicals tested, (on the first glass surface) was MgCl₂. This chemical, because of its popularity, was used to assess time trends, humidity/temperature trends, etc. Early in testing, a very reduced friction was found in the transition from solid to liquid. Full liquid MgCl₂ produced friction values of .372, full solid MgCl₂ was determined to be .342. In the "slurry", or transition phase, a value of .235 was seen, (a drop of 31%).

For the tests on the second surface, with magnesium chloride put down as a liquid, a friction value of .269, is seen. This places it at about the mid-range of all liquid chemicals tested. However, on drying, the material formed a "slurry" of white precipitate and crystals. This produced a co-efficient of friction value of .250, which ranked it amongst the lower quarter of chemicals. The solution was then de-hydrated for approximately 1 hour, at which time it was very dry with no liquid present. The co-efficient of friction, as a result of this, was .264, however, as can be seen in the accompanying chart, it appeared to be still continuing to rise marginally. In hindsight, the material should have been allowed to dry further to see at what point it would have peaked. A value of .264 places it amongst the lower echelon of the chemicals, but in fairness, this may have been somewhat higher if the test had been allowed to continue.

The determined co-efficient of friction values for $MgCl_2$ differed substantially between the first and second glass surfaces. The second surface had a "dry", (no chemical) friction value about 7% higher than the first, yet for liquid MgCl₂, the first surface showed a value of .372 versus the .27 found on the second surface, (a difference of 27%). Apparently, the surface roughness, or asperities, have played a role. On a smoother surface (#1), for liquid phase, a phenomena known as "sticktion"¹³ might be responsible. For glass #2, the surface roughness might have been sufficient to eliminate the suction effect, thus lowering the measured friction levels. Clearly, far more testing is required on asphalt surfaces, before any conclusions can be drawn. Importantly, both surfaces produced fairly similar "slurry" friction values, however.

¹³ Sticktion refers to a suction-like retarding force causing increased pull force readings, (ie. like two sheets of glass with water placed in between)

Upon application of liquid, CMA produced a co-efficient of friction value of .368, which was the highest of all liquid values with the exception of the salt brine. Further, upon reduction of humidity, which allowed the solution to begin forming a heavy white precipitate, the co-efficient of friction reduced to just .312, again, the highest of all chemicals with regards to the transition phase between liquid and solid.

Surprisingly, once the de-hydration process continued, the solid CMA left on the glass surface became a heavy white precipitate and this caused a rather substantial retarding friction value of .474, which was also the highest of all solid chemicals tested. As a result, the average friction values obtained from the three phases suggest that calcium magnesium acetate, on glass, produces the highest overall average friction co-efficient of friction of all the chemicals tested.

Calcium Chloride (LiquiDow)

Upon application of the liquid, a value of .275 was observed, which ranked LiquiDow, 6 out of 12, (about the average of all chemicals tested). However, this value reduced rather substantially to a low of .196, which was at the point when both liquid and solid was present, (the "slurry" phase). This was the lowest value tested of all chemicals. A value of just .223 was seen for solid LiquiDow, which again, was the lowest of any solid measured. As a result, the LiquiDow had the lowest average co-efficient of friction of all the chemicals tested.

<u>LiquiDow Armor</u>

This product has a liquid co-efficient of friction of .342, which ranked it amongst the top of all the chemicals tested, just behind CMA and salt brine. Furthermore, the value achieved for the "slurry" was .280, which was also in the top quarter of all chemicals tested. More importantly, unlike straight LiquiDow, the solid value was determined to be .436, nearly double that for straight LiquiDow. The value of .436 was second only to CMA at .474, and this allowed LiquiDow Armor on average, to be ranked third overall, behind salt brine and CMA.

MCP De-Icer

This product recently received, is a new liquid from Minnesota Corn Processors. It provided a liquid co-efficient of friction of .284, also placing it at about the middle range of the chemicals tested. The low friction value of .274 again placed it in about the middle of the pack. However, it had a strong showing when the precipitate fully formed, providing a co-efficient of friction of .333. As can be seen in the accompanying chart, there was no slickness found upon the phase change from liquid to solid, however, upon re-hydration, the liquid co-efficient of friction value is somewhat lower than that for solid value. There is, however, no "slurry" seen in the re-hydration process, either.

Ice Stop and Ice Stop 2000

Both chemicals had very nearly identical liquid co-efficient of friction values, (.311 and .312) which ranked them in the top one third of liquid chemicals tested. However, Ice Stop showed a rather large friction drop as the solid was allowed to re-hydrate. This produced a low co-efficient of friction of .249, which was among the lower one quarter of chemicals tested. However, Ice Stop 2000 did not show this tendency upon re-hydration, as the accompanying charts clearly show. (Please note the one low value taken at 150 minutes, producing a co-efficient of friction of approximately .283 should be viewed as an errant data point, and thus not considered). Unfortunately, the Ice Stop 2000 did not attain the levels of Ice Stop under solid conditions, (a value of .288 versus a value of .333 was seen).

FreezGard with Additives

Four samples were received with FreezGard as a base ingredient, and additives used as rust inhibitors. These included FreezGard with TEA, FreezGard 0, FreezGard with Shield LS, and FreezGard with Ice Ban. All FreezGard with additives produced liquid co-efficient of friction values of .245 - .261, (the product with Ice Ban was slightly better than the others). This ranked them among the lowest of the chemicals tested. The graphs of FreezGard 0 with Shield LS and FreezGard 0 with Ice Ban were similar, as were the FreezGard 0 and FreezGard 0 with TEA. All four chemicals showed higher values as solid as compared to liquid. The lowest values recorded for the transition phase were with regards to FreezGard 0 with TEA at .239; FreezGard 0 at .278 was amongst the highest of these particular four chemicals tested. For solid phase, a surprising difference was seen with FreezGard 0 with TEA showing a .292 and FreezGard 0 with Shield LS showing a rather substantial .343. FreezGard 0 with Ice Ban also showed a relatively high .331, (ranking it about 6 of the 12 chemicals tested). On average, of these four, the FreezGard 0 with Ice Ban appeared to produce the highest average co-efficient of friction.

CONCLUSIONS / RECOMMENDATIONS

At this point, it should be realized that this research is in its infancy. Whereas factors such as highway flushing of oil-based debris, winter leaves and other elements, have been blamed for slippery road conditions, it is now known that indeed a chemical slipperiness can be developed just through chemical activity alone, (ie. during the phase change from a liquid to a solid, and solid to a liquid). How this affects users and how they must re-think the way liquid chemicals are to be used is a complex subject and will not be addressed in this paper. That having been said, as a result of this preliminary research, we are in a position to offer the following thoughts.

- 1. Firstly, as most of the slickness occurrences appear to be happening in the fall when temperatures appear to be higher, and potentially, humidity levels lower, great care must be used at this time of year. Particularly, if no appreciable rain fall has occurred, or, if a dry spell is experienced, it is possible that many of the chemicals tested, as a result of this research, will begin to dry out. Theoretically, for calcium chloride, at the freeze point, this would occur at around 43%. Our research has shown, however, that for the majority of chemicals, the humidity must be in the high 20's to low 30's before drying out occurs. Naturally, with site specific irregularities that exist, (for example, solar radiation, wind effects, and so forth) it is possible that a particular chemical could transition from liquid to solid at values outside of this humidity range. Also, our research shows that relative ambient humidity levels can change rather dramatically, even in the course of 24 hours.
- 2. The amount of chemical used should be closely monitored, particularly at this time of year. Smaller amounts of chemical have been shown to reduce the co-efficient of friction less in some studies, (calcium chloride - this was not seen with magnesium chloride testing). If the solution, however, does begin to precipitate out, the more solution, the greater the time it will be in that transition; (relating to chemical inertia) this will provide an extended period, or prolonged time of potential slipperiness. For applications made in early fall, (particularly for those used in anticipation of frost conditions) a relatively minimal amount of chemical is required to overcome these conditions, as opposed to the amount of chemical required for heavy winter snowfalls.
- 3. If moisture is present on the ground nearby, it is unlikely a difficulty with drying will be experienced, even if the ambient humidity levels are low. The hygroscopic ability of the majority of chemicals tested, will enable them to "pull" moisture from a neighbouring source and thus, dehydration will not occur.
- 4. Since the anticipated slippery conditions occur when a solid takes on moisture, or a liquid gives up moisture, the problem theoretically can occur over an extended period of time after initial application. Whereas most incidents have been reported to have occurred within the first few minutes, up to several hours later, because the solutions freely move from one phase to another and back again, it is possible that, for example, a solution that has passed through the "slurry" stage, into a solid, can become slippery days later, once moisture is absorbed. However, because, to the author's knowledge, there have been no such reported incidents, it is apparent that upon re-hydration, this "slurry" state must also exist for a very brief period of time, with most motorists simply not being aware that it exists.

- 5. Most chemicals, when transitioning from liquid to solid and vice versa, pass through a "slurry" stage where precipitates are suspended in solution. Further, with some chemicals, there is no reduction in friction at this point. Other chemicals show reduced friction levels in the transition, but it appears surface texture, (roughness) is also a factor. Smoother surfaces seem to show greater tendencies of more reduction in friction perhaps because the chemical stays on the surface, interacting directly with the road tire.
- 6. The largest single factor driving the chemicals toward a potential "slipperiness" is humidity. Temperature seems to play a very minor, if any, role.
- 7. The research shows that on glass, the "slurry" stage which is associated with reduced friction is numerically less than pure water, but certainly nowhere near as reduced as that associated with ice or worse yet, wet ice.

Future tests must be performed on asphalt and concrete, and with varying concentrations and application rates of solution. Only then will we be in a position to determine whether the chemical slipperiness that has now been documented, produces a concerned level of friction. If it does, additional work must be performed in the chemistry lab to locate additives which either eliminate the tendency for chemicals to become slippery entirely, or in the alternative, minimize the effect, and/or time, of the chemical induced slipperiness.

ACKNOWLEDGEMENTS

The research reported to date has involved well over 1,000 friction tests, each performed dutifully by Casey Dundass, E.I.T. The author wishes to thank Casey for the accuracy of the data, and the entire FDi staff for compiling same.

Additional thanks are due to Mr. Dale Keep of Ice & Snow Technologies, LLC, for firstly, having the vision to recognize that the circumstance that is described by this research can occur, (and more particularly, that it, indeed, occurs between the liquid and solid phase) and secondly, for participating in the research and reviewing this document before its publication, as well as arranging for the chemicals to be delivered for testing.

Initially, this research was supported by the Pacific Northwest Snowfighters, (including the Insurance Corporation of British Columbia, the State of Montana, the State of Washington, and the State of Idaho). More recently, some progressive chemical companies have furnished their chemicals for testing, (Reilly Wendover, IMC, Dow Chemical, and MCP) have also paid to have their products tested; the author wishes to sincerely thank all participants for their commitment to this project.

New chemicals have been received from Ice Ban, Cryotech and General Chemical. These will be tested soon, and reported on at a later date.



ICE STOP CI 2000





Freezgard 0 & Iceban













Magnesium Chloride



FRICTION TABLE (Rank Shown in Brackets)

CHEMICAL	LIQUID	TRANSITION	SOLID	AVERAGE
Salt Brine	0.394 (12)	0.301 (11)	0.404 (10)	0.366 (02)
MgCl2	0.269 (05)	0.25 (04)	0.273 (02)	0.264 (10)
МСР	0.284 (07)	0.274 (07)	0.333 (7.5)	0.297 (06)
LiquiDow	0.275 (06)	0.196 (01)	0.223 (01)	0.231 (12)
LiquiDow Armor	0.342 (10)	0.28 (09)	0.436 (11)	0.353 (03)
Ice Stop	0.311 (08)	0.249 (03)	0.333 (7.5)	0.298 (04)
Ice Stop 2000	0.312 (09)	0.284 (10)	0.288 (04)	0.295 (07)
FreezGard 0 w/ TEA	0.245 (01)	0.239 (02)	0.292 (05)	0.259 (11)
FreezGard 0 w/ Shield LS	0.257 (03)	0.27 (06)	0.343 (09)	0.29 (07)
FreezGard 0	0.248 (02)	0.278 (08)	0.281 (03)	0.269 (09)
FreezGard 0 w/ Ice Ban	0.261 (04)	0.26 (05)	0.331 (06)	0.284 (05)
СМА	0.368 (11)	0.312 (12)	0.474 (12)	0.385 (01)

Any opinions, findings, and conclusions or recommendations expressed in this publication are those of Forensic Dynamics Inc. and do not necessarily reflect the view of the Pacific Northwest Snowfighters Association (PNS).

This report is the result of an impartial approach used to evaluate the co-efficient of friction of liquid chemicals used in snow and ice removal. The report addresses the co-efficient of friction on a lightly blasted glass panel and may not be representative of obtainable frictional values on pavement surfaces after chemical application.

The data presented are believed accurate and the analyses credible. The statements made and conclusions drawn regarding the product evaluations do not, however, amount to an endorsement or approval of any of the products in general or for any particular application