

# Alternative Highway Deicing Chemicals\*

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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 current extensive use of NaCl as a road deicer. All classes of chemical compounds were reviewed. Deletions from the sum total were made on the basis of pertinent criteria such as water solubility and freezing point lowering, corrosion, toxicity, relative cost or cost potential, effect on soils and plants, on water supplies, flammability, etc. Low molecular weight and high solubility were primary qualifications. Waste products were considered as possible raw material sources. Two candidate deicers have been selected which, if used, might result in total costs about one-half those associated with the use of NaCl. Both materials can operate at temperatures below that at which NaCl becomes ineffective. Both can be made from waste cellulose. Neither is corrosive. One of them, methanol, reacts almost immediately upon contact with snow and ice but is less persistent than the other candidate or 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. By strong contrast with NaCl, CMA is a corrosion inhibitor, is beneficial to most soils and has no potential for harming drinking supplies.

The well known corrosive effect of sodium chloride (NaCl) upon metals has long begged for replacement of this chemical as a road deicer. It has been demonstrated that this obvious defect is but one of many undesirable results attendant upon the use of NaCl for deicing purposes (1). Accordingly, the present search for viable alternates was initiated.

Chemical deicing depends upon the general effect of solutes on the melting point of the solvent in which they are dissolved. The effect is always to lower the melting point. The amount of lowering is almost solely dependent upon the number of molecules or ions present in solution, roughly proportional to this number and almost entirely independent of the nature, size or weight of these solute particles.

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Thus, low molecular weight materials produce the most freezing point lowering for a given weight dissolved in the solvent. Also, the solubility of the solute determines the degree of lowering it can exert on the melting point of the solvent in which it is dissolved.

## Preliminary Elimination of Chemical Deicer Possibilities

Since the primary requisite for a deicing chemical is water solubility, there are many substances to choose from. Selection of the best deicing chemical then becomes a process of elimination. There are a number of criteria by which to judge and eliminate candidate deicers. These were applied repeatedly each time additional information became available upon which to form a judgement.

The first round of judgements was based upon general knowledge of the elements in the Periodic Table, their scarcities, costs, and hazards of various kinds. The following groups were excluded:

1. Transuranum elements.
2. Actinide series.
3. Lanthanide series.
4. Elements in Periods 4, 5, and 6, excepting potassium (K), calcium (Ca), barium (Ba), manganese (Mn), iron (Fe), zinc (Zn), and bromine (Br).
5. The noble gases Group VIIIA.
6. The miscellaneous group, beryllium (Be), fluorine (F), and sulfur (S in the sulfide form).

The remaining chemical elements were then considered under the two headings, Inorganic Salts and Organic Compounds. Organic chemistry is concerned primarily with the chemistry of carbon (C) and includes most of its compounds, the most notable exception being the carbonates characterized by the carbonate anion  $\text{CO}_3^{=}$ . Inorganic chemistry includes the carbonates and most of everything that is not organic. For chemicals of deicing interest, namely water soluble ones, attention is centered upon the neutral ionic inorganic compounds or salts.

In making an evaluation of deicing potential, whether organic or inorganic, a formula was developed which takes into account the unit weight cost of the material in relation to sodium chloride, as well as its effectiveness per unit weight related to sodium chloride. In nearly all cases, the unit weight

costs were derived from the July 1976 issue of the Chemical Marketing Reporter. In a few instances, it was necessary to obtain quotations from suppliers for materials which were not covered in the Chemical Marketing Reporter. For the first round cost evaluations, the effectiveness of the various deicing candidates was calculated on the basis of freezing point depression theory, assuming a figure of 1.86° C for the freezing point depression of water per unit molal concentration of solute. The osmotic effects of ions and of molecular solutes were assumed to be equivalent. Osmotic theory teaches that this is approximately so in that freezing point depression by a solute is a function of the number of particles in solution primarily, rather than a function of their nature. With the final cost comparisons, however, actual performance data was substituted for this type of approximation.

This cost effective comparison of a candidate deicer to sodium chloride, or ratio of cost effectiveness, is defined by the following equation:

$$R = \frac{MC}{N} \times \frac{N_o}{M_o C_o} \quad (1)$$

where M = molecular weight of the candidate.

C = cost of the candidate.

N = the numbers of particles or ions into which a molecule of candidate breaks up upon going into solution.

Subscript o = the same quantities for NaCl.

To illustrate the quantity N, a solute such as methanol will have an N=1 because a molecule of methanol CH<sub>3</sub>OH exists as such without splitting up when put in aqueous solution. On the other hand, a salt like sodium chloride, for example, breaks up into two parts or ions when it is put into solution. The two ions are oppositely charged, Na<sup>+</sup> and Cl<sup>-</sup>. As already mentioned, each of them behaves much like a separate molecule insofar as freezing point depression is concerned. Accordingly, the value for N in this case is 2. Both calcium acetate and magnesium acetate are ionic materials like sodium chloride. They differ from it, however, in that the positive ion or cation is doubly instead of singly charged. Consequently, to satisfy the demands of electric neutrality, there must be two singly charged acetate ions or anions. In other words, when calcium acetate or magnesium acetate dissolves in water each molecule, as it were, splits up into three charged particles, one doubly charged positive ion and two singly charged negative ions. The value of N in these cases is 3 accordingly.

#### Evaluation of Individual Deicer Candidates

##### Inorganic Salts

Using the R-Value system and a criterion of R equal to 20 or less, several more chemical elements were eliminated as constituents of deicers to replace sodium chloride. These were barium, manganese and zinc. Partly for reasons of cost and partly for reasons of corrosion, chlorine and bromine, the last two members of Group VIIA, were eliminated as components of inorganic deicers. Sulfur was eliminated as a component for reasons of toxicity (sulfide) and corrosion (sulfate, the only other stable form). Several elements were eliminated because they required excessively high or low acidities to be soluble. Silicon, as silicate, and iron and aluminum fell into this category. Lithium was found to be much too expensive. Boron, in the form of the borates, appeared to be too costly and too toxic to consider. The nitrate combination of nitrogen and oxygen was found to be intolerably corrosive. It appeared that even the ammonium ion might be unacceptable under conditions where trace nitrates

might be formed by bacterial action.

Thus, only nine elements were left for serious consideration as constituents of inorganic deicers (Table 1).

The three elements in the left hand column combine in inorganic salts as positive singly charged ions or cations, i.e., H<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, H forming with N an additional singly charged cation, NH<sub>4</sub><sup>+</sup>, the ammonium ion. The only inorganic negatively charged ions or anions to go with these cations are formed by various combinations of the four elements to the right, -C, N, O, and P.

There are several possibilities. The combination of O and H to give OH<sup>-</sup> is severely caustic and cannot be used. The anions, CO<sub>3</sub><sup>=</sup> (carbonate), PO<sub>4</sub><sup>=</sup> (phosphate), P<sub>2</sub>O<sub>7</sub><sup>=</sup> (pyrophosphate) though less so, are still too caustic for consideration unless they are partially neutralized to form appropriate amounts of HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>=</sup> and H<sub>2</sub>P<sub>2</sub>O<sub>7</sub><sup>=</sup> respectively. The various viable salt combinations are tabulated together with some pertinent properties (Table 2). The freezing point data, in this case, were obtained from the literature or experimentally determined rather than calculated from theory.

Sodium Bicarbonate-Sodium Carbonate. Working from the top of the table downward NaCl is included as a reference point, it being the currently most used chemical deicer. Neither sodium bicarbonate nor sodium carbonate has sufficient solubility to be an effective deicer, having eutectics (temperatures at which all mixtures freeze solid) with water of -2°C and -3°C respectively. These salts, thus, are ruled out of consideration.

Sodium Monohydrogen Phosphate-Sodium Dihydrogen Phosphate. Of the three sodium salts of orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) none could be used alone as a deicer for different reasons. The dihydrogen phosphate salt (NaH<sub>2</sub>PO<sub>4</sub>) produces aqueous solutions which are too acid, pH = 3 to 4. The monohydrogen phosphate salt (Na<sub>2</sub>HPO<sub>4</sub>) is too insoluble and the tribasic salt (Na<sub>3</sub>PO<sub>4</sub>), as already mentioned, is too strongly alkaline, pH ≈ 13.

The composition of the triple eutectic of water NaH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub> is perhaps still too acidic, pH ≈ 4. The eutectic temperature of this salt combination is -9.9°C, which is certainly borderline from the point of view of utility (2). Its cost to produce an equal deicing effect at -10°C is 26 times that of sodium chloride. The damage inflicted on plants and animals by sodium ion, as well as the hypertension in human beings have been well documented (3, 4). All of these factors combined make the sodium salts of phosphoric acid, as a group, a poor candidate as a road deicer.

Potassium Bicarbonate-Potassium Carbonate. The mixture of potassium bicarbonate (KHCO<sub>3</sub>) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) looked promising at first, since the substitution of K for Na not only brought about lower eutectics with water but overcame most of the environmental objections associated with Na. The system was finally rejected, however, when it was found that the proportion of KHCO<sub>3</sub> required to temper the caustic nature of K<sub>2</sub>CO<sub>3</sub> resulted in too low a solubility, i.e., too high a eutectic.

The Environmental Protection Agency (EPA) has established pH 6.5 to 9.0 as optimum conditions for aquatic biota (5) with a somewhat wider range (pH 5.5 to 9.5) as the maximum tolerable pH range (6). Water pH is maintained by buffering capacity, which is primarily due to the bicarbonate-carbonate system. Alkalinity resulting from the presence of carbonates appears to have little harmful effect on aquatic life as long as it does not increase the pH above the optimum pH. Such a system is, of necessity, predominately a bicarbonate (as opposed to a

Table 1. Elements Remaining for Consideration as Constituents of Chemical Deicers Arranged in their Order in the Periodic Table.

Group Period	IA	IIA	IIIA	IVA	VA	VIA	Etc.
1	H (Hydrogen)						
2	--	--	--	C (Carbon)	N (Nitrogen)	O (Oxygen)	
3	Na (Sodium)	Mg (Magnesium)	--	--	P (Phosphorus)	--	
4	K (Potassium)	Ca (Calcium)					
Etc.							

Table 2. Deicing Performance Data for Inorganic Deicer Candidates.

Candidate Deicer	Eutectic with Water		Cost (\$/Lb <sup>a</sup> )	Deicer Needed to Liquify Ice at -10°C		Approximate pH of Aqueous Solutions
	Composition (wt.% Deicer)	Temperature (°C)		Lb/100 Lb of Ice	Cost Relative to that of NaCl	
NaCl	23.3	-21.1	.014	16.0	1.0	Neutral
NaHCO <sub>3</sub>	> 6.	~- 2.	.08	b		8
Na <sub>2</sub> CO <sub>3</sub>	7.	- 3.	.024	b		12
NaH <sub>2</sub> PO <sub>4</sub>	35.6	- 9.7	.107 <sup>c</sup>	~55.	26.4	3-4
Na <sub>2</sub> HPO <sub>4</sub>	1.56	- .5	.101 <sup>c</sup>	b		9
KHCO <sub>3</sub>	19	- 8.8	.14	b		8
K <sub>2</sub> CO <sub>3</sub>	41	-36.	.10	~19.	8.5	12
KH <sub>2</sub> PO <sub>4</sub>	11.6	- 2.7	.134 <sup>c</sup>	b		4-5
K <sub>2</sub> HPO <sub>4</sub>	36.8	-13.7	.145 <sup>c</sup>	47.0	30.4	9
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	~60.	~-39.	.35	37.4	58.4	10-11
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	18.5	- 6.	.08	b		4-5
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	35.	-14.	.067	32.5	9.7	8-9
NH <sub>4</sub> HCO <sub>3</sub>	10.6	- 9.5	.03 <sup>d</sup>	11.9	1.6	8
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	30.	-14.6	.04 <sup>d</sup>	31.6	5.6	9
NH <sub>3</sub>	<20.	<-77.	.09	8.1	3.3	12

<sup>a</sup> All prices are bulk and derived from the 7.5.76 issue of Chemical Marketing Reporter except that for CO<sub>2</sub> which was obtained 10/6/76 from an Airco representative in Chicago.

<sup>b</sup> No liquid phase at -10°C.

<sup>c</sup> From H<sub>3</sub>PO<sub>4</sub> and the carbonate.

<sup>d</sup> Mixed gases CO<sub>2</sub> and NH<sub>3</sub>.

carbonate) system (7).

Potassium Monohydrogen Phosphate-Potassium Dihydrogen Phosphate. Of the potassium salts of H<sub>3</sub>PO<sub>4</sub>, only one salt could be used alone as a deicer, K<sub>2</sub>HPO<sub>4</sub>. However, its eutectic is barely acceptable, -13.7°C, its cost for equal effect is thirty times that of sodium chloride and its pH is high, though perhaps acceptable. On the other hand, the tribasic salt is too caustic and the monobasic one too insoluble.

A mixture of the mono and dibasic salts in the weight ratio 27.3:72.7 produces a respectable eutectic, -16.7°C and a very desirable pH range of 7 to 8 (2); the cost for equal effect compared to sodium chloride at -10°C is 37 times. Environmentally, the potassium ion is fairly acceptable. Phosphate is a mixed bag. Far from being toxic to plants and animals, it can cause problems in lakes and rivers associated with overgrowth of unwanted species. On the other hand, it is an important constituent of many corrosion inhibitors (8).

The temperature of the water eutectic of the KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub> mixture can be lowered by 0.5°C and the cost for equal effect can be reduced from 37 to

36 times that for sodium chloride by inclusions of 2% of Na<sub>2</sub>HPO<sub>4</sub> (2).

The modest eutectic and undesirable environmental factors balanced by a rather high cost factor make the KH<sub>2</sub>PO<sub>4</sub>:K<sub>2</sub>HPO<sub>4</sub>::27.3:72.7 system a borderline case for further consideration. Nevertheless, this appears to be the best combination of the several possibilities involving the potassium salts of the orthophosphoric acid.

Tetrapotassium Pyrophosphate (TKPP). Though there may be some question as to the precise figure, there is little doubt that TKPP has a very satisfactory eutectic temperature with water. Its pH is high, 10-11, but this probably could be tempered by admixture with one of the less basic salts of pyrophosphoric acid. It possesses essentially the same environmental merits and drawbacks as the potassium salts of orthophosphoric acid, discussed above. It suffers from a high cost factor, however, nearly twice that of the potassium orthophosphate system -- borderline -- the much better eutectic offsetting the higher cost.

Ammonium Monohydrogen Phosphate-  
Ammonium Dihydrogen Phosphate. The respective ammonium and potassium orthophosphates are similar to each other in regard to water eutectic and aqueous pH. In both cases the monobasic salts are too insoluble and a little bit too acidic. The tribasic salts are too alkaline. In both cases, the dibasic salts show tolerable and nearly identical eutectics with water. The dibasic ammonium analogue shows a slightly more favorable pH range, 8-9, as opposed to approximately 9.

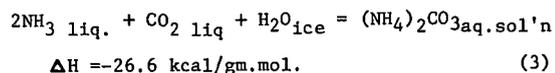
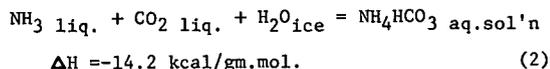
Probably the mono and dibasic ammonium salts would prove to exhibit a combined eutectic comparable to or possibly below that of the corresponding potassium salts, with a similarly favorable pH range. The biggest differences between the corresponding ammonium and potassium systems would appear to be in the environmental and cost factors.

Like the phosphates, the ammonium ion can serve as a nutrient to the point of causing unwanted proliferation in streams and lakes. In some circumstances, as already mentioned, it can be converted to nitrate with adverse corrosion effects (9). In addition,  $\text{NH}_3$  is extremely toxic to fish (see below). These potential adverse effects of ammonium phosphates, compared to the potassium salts, are offset to some degree by their much lower cost -- one-third to one-fourth or about ten times the cost of equivalent treatment with sodium chloride. Thus, depending upon priorities, the ammonium phosphate system would appear to be comparable to the preferred potassium phosphates and pyrophosphates, namely of borderline importance for further work.

Ammonium Bicarbonate-Ammonium Carbonate. On the basis of their water eutectics,  $\text{NH}_4\text{HCO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  are comparable though slightly better than the respective mono and dibasic ammonium and potassium phosphates. Similarly, they might be expected to exhibit a combined eutectic which is lower than that of either component, though this is yet to be determined. They exhibit similar near neutral solutions. Environmentally, they would be slightly superior to the ammonium phosphates and perhaps comparable to the potassium phosphates. They might trail the latter in this respect because of the absence of the generally beneficial potassium ion. On the other hand, the negative environmental aspects of the ammonium carbonates are lessened by virtue of their volatility.

The ammonium carbonates are far cheaper than either of these two phosphate salt systems on the basis of the weight to produce a liquidus of a given temperature (e.g.,  $-10^\circ\text{C}$ ). However, they are amenable to a unique method of dispensing which is capable of providing additional deicing benefits among which are more rapid and additional melting through heat of reaction.

The ammonium carbonates can be formed by reaction between two liquids in the presence of ice or liquid water:



The second reaction consumes 0.23 pounds of ice for each pound of the combined liquid reactants and the heat evolved is enough to melt 6.2 pounds of ice per pound of combined reactants. This ratio of weights corresponds to the liquidus at  $-5^\circ\text{C}$ . At lower temperatures, of course, the liquidus contains higher proportions of ammonium carbonate and consequently, the heat of reaction is in excess of that

necessary to melt the ice for the liquids. At  $-10^\circ\text{C}$  this excess heat amounts to 65%.

The technology for pumping, accurately metering and mixing reacting liquids is well known and the equipment is inexpensive and reliable. A considerable cost advantage accrues from making  $(\text{NH}_4)_2\text{CO}_3$  from liquid  $\text{NH}_3$  and liquid  $\text{CO}_2$  rather than purchasing it as the crystalline salt. In effect, the costs associated with crystallization, drying and sizing are eliminated.

Although both  $\text{NH}_3$  and  $\text{CO}_2$  have low boiling points ( $-33.4^\circ$  and  $-79^\circ\text{C}$  [sublimation] respectively) and therefore require pressurized storage, storage and handling techniques are convenient and economical due to well established large volume markets in both cases. The danger of freezing in the contiguous United States is nil since the freezing points are  $-78^\circ\text{C}$  for  $\text{NH}_3$  and  $-57^\circ\text{C}$  for  $\text{CO}_2$ . The manner of storage precludes the inconveniences sometimes associated with salt storage: caking, spillage, pollution of water supplies from runoff, corrosion of equipment, etc. Although ammonia is flammable, its flammability limits are narrow (from 16 to 27 volume percent in air) and its vapor density is one-half that of air. These, together with its manner of storage and handling, virtually eliminate the risk of fire. Leaks are detected by the pungent odor long before flammable concentrations are approached.

An important feature of forming the ammonium carbonates on the highway site is the fact that the ratio of the two reactant gases can be varied to suit the conditions. Thus, after a snow at the freezing point, where temperatures are not expected to drop below  $-5^\circ\text{C}$ , a bicarbonate mix would be preferred, i.e., equimolar  $\text{NH}_3$  and  $\text{CO}_2$  or 17 parts to 44 parts by weight respectively. For these temperatures the bicarbonate is the more economical, being only 1.5 times the cost of an equal performance application of sodium chloride. By the same token, in uninhabited regions when temperatures of  $-20^\circ\text{C}$  or below may be encountered, a ratio of ammonia in excess of that to produce  $(\text{NH}_4)_2\text{CO}_3$  might be employed. Ammonia is one of the most weight efficient freezing point depressants for water. Although its unit cost is higher than that of the stoichiometric  $(\text{NH}_4)_2\text{CO}_3$ , the resultant cost would be slightly less on account of the greater weight efficiency of the ammonia.

Even for a tenfold excess of  $\text{NH}_3$ , the pH would be raised only to about 10; this would then drop back to 9 as the excess  $\text{NH}_3$  gradually evaporated. The evaporation rate is too slow to produce a flammable concentration. With equipment adapted from the agricultural applicators for injecting  $\text{NH}_3$  directly into the soil and with the avidity of  $\text{NH}_3$  for water, including an appreciable heat of solution, there should be little difficulty in making it dissolve in road ice and snow.

Subsequent to the above findings, an additional serious drawback to the use of ammonium based systems was discovered. Actually, it is not the ammonium cation itself that causes the problem but rather the un-ionized ammonia which occurs when an ammonium salt dissolves in water of moderate to high pH. Waters containing as little as 0.2 ppm of un-ionized ammonia ( $\text{NH}_3$ ) have proved toxic to aquatic biota (5). The proportion of un-ionized ammonia varies with pH from about 0.04% at pH 6 ( $20^\circ\text{C}$ ) to 28% at pH 9.0 and increases even further with additional pH increases. Thus, at pH 6.0 a concentration of 500 ppm  $\text{NH}_4\text{CO}_3$  would produce a toxic concentration of ammonia. Since the pH of natural waters tends to be more alkaline than pH 6.0, the toxicity will generally occur at concentrations of 100 ppm of  $(\text{NH}_4)_2\text{CO}_3$  or less.

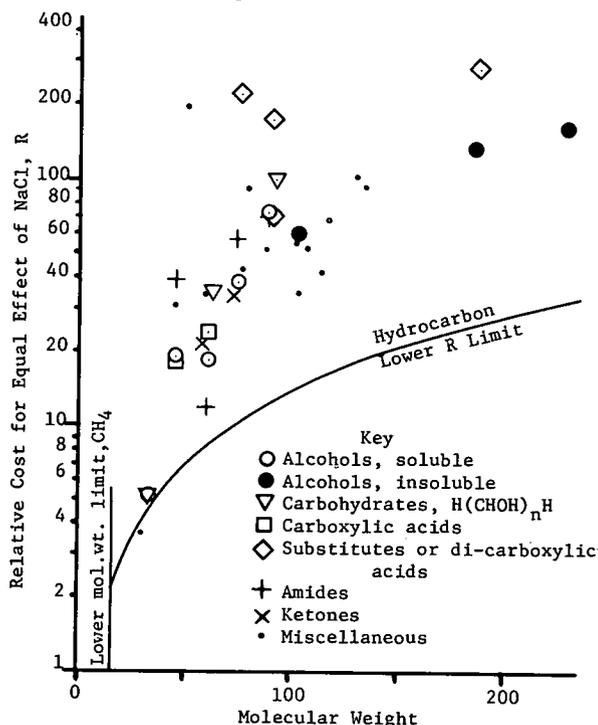
EPA has recommended a maximum level of 0.020 ppm un-ionized ammonia for surface water, one-tenth of the concentration deemed toxic to aquatic life. This would be impossible to maintain with extensive use of the ammonium carbonate-bicarbonate system as a deicer. Nevertheless, in arid regions where the

well being of aquatic biota are not a consideration, the ammonium carbonate system has unique and attractive features which merit its consideration.

### Organic Compounds

The prices of organic chemicals with molecular weights up to 248 were obtained from July and August issues (1976) of Chemical Marketing Reporter. Values of R were calculated and plotted versus molecular weight on semilog coordinates (Fig. 1). This figure helps to illustrate several constraints on the use of organic chemicals as deicer substitutes for NaCl. Although a plot on linear coordinates would illustrate more clearly the fact that R value tends to increase linearly with molecular weight, the semilog plot is more useful in making out distinctions in R values.

Figure 1. Relative Cost R of Organic Deicers versus Molecular Weight.



The price per unit weight of nearly all organic chemicals is higher than that of petroleum hydrocarbons for the simple reason that the latter are the cheapest source of carbon-hydrogen moieties for organic synthesis. Accordingly, although unsuited by water solubility and other reasons as deicing chemicals, hydrocarbons were included in Fig. 1 to illustrate the molecular weight and relative price limitations on organic chemicals to replace NaCl. It is seen that there is little hope of obtaining such a substitute having a molecular weight as high as 200 for less than 30 times the cost of NaCl to give equivalent performance. Synthesis costs must be considered and the maximum molecular weight for  $R=30$  would appear from the examples to be closer to 100. This corresponds to a maximum of seven or eight carbon atoms in the molecule. Methane, the hydrocarbon with only one carbon atom, has the lowest R value, and that is over two.

The question of solubility can only be resolved by the inclusion of oxygen, nitrogen or other polar atoms in the organic molecule. The simplest such modification of the hydrocarbon structure is the

alcohol series,  $C_nH_{2n-1}OH$ , represented by the circles in Fig. 1. A single hydroxyl group in the molecule will provide the requisite solubility only up to molecular weight 100. If the cost factor corresponding to  $R=30$  is applied, it is seen that only the three lowest alcohols fit, methanol, ethanol and i-propanol.

Solubility can be assured by attaching one oxygen to the molecule for each carbon atom,  $H(CHOH)_nH$ , the triangles in Fig. 1. Methanol is the first member of this series as well, then ethylene glycol and glycerol or glycerin. The cost factor rises with molecular weight, if anything even more rapidly than it does with the alcohols. It is already  $R=35$  with ethylene glycol and  $R=99$  with glycerol.

It is not always necessary to have one hydroxyl group for each carbon atom. The solubility can be improved over the alcohols by incorporating two hydroxyls per molecule, the glycols. Ethylene glycol is the simplest of this class and, as already mentioned, has an  $R=35$ . Both it and propylene glycol are infinitely miscible with water, the R value for the latter, 43, is larger as expected. Of the four butylene glycol isomers, molecular weight = 90.1, only the 1, 4 and 2, 3 isomers are completely miscible in water and the 1, 2 isomer is only slightly soluble. There is no reason to expect the butylene glycol R values to be anything but higher than that for propylene glycol.

Another type of oxygen linkage which might serve in an organic deicer is the ketone. The simplest of this class is acetone with  $R=21$ . The next higher homologue, methyl ethyl ketone, has an  $R=33$ . Higher homologues are insufficiently soluble for consideration.

Aldehydes can be ruled out on account of their chemical reactivity and particularly the irritant and toxic character of the more interesting lower molecular weight homologues. Were it not for these factors, the lowest member of the series, formaldehyde, would be of special interest because it appears to be the organic chemical with the lowest R value, 3.7.

The oxygen in ethers does not impart sufficient water solubility for this class of compounds to be considered as freezing point depressants. Esters are of no use for the same reason. Organic halogens are disadvantageous, since they add weight without imparting water solubility among other things.

Only a limited number of carboxylic acids are candidates and these only as their salts, on account of their corrosive power as free acids. Acetic acid with a molecular weight of 60 and an R of 23 is probably the most likely candidate. Propionic acid, whose R value is undoubtedly higher, is another possibility. The butyric acids would probably be unsuitable because of the powerful and objectionable odor of the free acid, which could not help but form from hydrolysis during actual usage conditions. Higher homologues would be ruled out because of excessive R values. Anhydrides are simply a precursor of the acids in the presence of water, with which they react only slowly and in which they are only slightly soluble. These and considerations based upon them make it difficult to see how the anhydrides can be of much use as deicers. Even considering the formation of two mols of acetic acid from one of the anhydride the R value for the lowest molecular weight homologue acetic anhydride is 27.

The amines are unsuitable because of their unpleasant powerful odor. Even as salts, this smell would be objectionable due to hydrolysis. The quaternary ammonium compounds are stable, very soluble and odorless, but too expensive for consideration. Amides, like the quaternary ammonium compounds, get around the malodor problem and are generally quite stable. Formamide, the simplest, has an  $R=38$ . Dimethylformamide has a much larger  $R=57$ . The most economical of the amides is the

diamide of carbonic acid, urea. Its R=11.8 and is the next most economical of the organic compounds discussed, being second to methanol at R=5.1.

The nitriles are generally insoluble and too toxic and accordingly, unsuitable.

It must be noted and emphasized that all of the R values determined thus far are based upon prices for compounds of technical purity, at least. The price usually includes an appreciable cost for purification and isolation as well as a base cost for raw material. Considerably lower R values, approaching those of the hydrocarbons, might conceivably be achieved where a reaction mixture can be used as is without further treatment. This possibility is, of course, open to the usage for deicing since, peculiarly to this purpose, the identity of the molecules and ions is not important, only their number.

The possibility of lowering the R cost ratio below those of the hydrocarbons and even below unity, the R value of NaCl, also exists in the usage of waste products whose value approaches or falls below zero. Solid waste, nitrogenous sewage sludge, nitrogenous tankage, and other waste materials were examined as possible raw material sources for these reasons.

The more cost efficient organic deicers shown on Fig. 1 were examined in greater depth and compared with NaCl (Table 3).

course, even higher than 60°F. The density of methanol vapor is only slightly above, while that of gasoline is several times that of air. Fires can be extinguished with water, by contrast to gasoline, because methanol and water are miscible in all proportions.

As with all substances, it has toxic limits. But these limits are relatively high, methanol having been cleared as a food additive (11). No ill effects have been found upon prolonged exposure to low concentrations or to short intermittent exposures to high concentrations of its vapors (12).

The cost of methanol is one of the lowest of the candidate deicers, being 5.5 times that of an equal effect application of sodium chloride at -10°C. If the cost of the harm caused by sodium chloride were included, the cost ratio of methanol could well be less (1). The methods of handling and dispensing liquids such as methanol are simpler than those for solids and subject to much finer control. Methanol appears to be the most promising of the simple organic compounds as a deicing substance.

Ethanol and Isopropanol. Ethanol and isopropanol are like methanol in nearly all respects; very low eutectics, neutral, noncorrosive, no nitrogen or phosphorus, volatile and flammable in nearly the same degrees, completely miscible with water and

Table 3. Deicing Performance Data for Organic Deicer Candidates.

Candidate Deicer	Eutectic With Water		Cost (\$/Lb <sup>a</sup> )	Deicer Needed to Liquify Ice at -10°C		Approximate pH of Aqueous Solutions	Flammability, Tagliabue			
	Composi-tion (wt. % Deicer)	Tempera-ture (°C)		(Lb/100 Lb of Ice)	Cost Relative to that of NaCl		Open Cup Pure Compound (°C)	Open Cup (°F)	-10°C Liquidus with Ice (°C)	Liquidus (°C)
Methanol	83	-125	.065	19	5.5	Neutral	15.6	60	43	109
Ethanol	93	-131	.17	23.5	17.8	Neutral	12.8	55 <sup>c</sup>	35	95
Isopropanol	≥80	≤-42	.127	29.9	16.9	Neutral	15.6	60	30	86
Acetone	>60	≤-27	.15	50	33.5	Neutral	-9.6	15	-3	27
Urea	33	-13	.08	34	12.5	Neutral	>100	>212	>100	>212
Formamide	65	-45	.35	34	53.5	Neutral	√100	√212	>100	>212
Dimethyl-Sulfoxide	>50	≤-50	.47	35.1	73.7	Neutral	95	203	>100	>212
Ethyl Carbamate (Urethane)	60	-6	.32	b		Neutral			b	

<sup>a</sup> All prices are bulk and are derived from the 7/5/76 issue of Chemical Marketing Reporter except as noted otherwise.

<sup>b</sup> No liquid phase at -10°C.

<sup>c</sup> Closed cup.

Methanol. Methanol exhibits a eutectic with water far below that of sodium chloride or any other inorganic deicer candidate. It is neutral and noncorrosive. It contains no nitrogen or phosphorus, thus contributes nothing to eutrophication problems. It has been used as an antifreeze for gasoline engines, but was replaced by the glycols because of its relatively high evaporation rate. At snow and ice temperatures volatility is much reduced. The remaining volatility, however, serves to minimize the concentration of methanol in the runoff and correspondingly, its contribution to BOD. It also facilitates housecleaning, since spills are self removing.

The flash point of methanol, 60°F, is nearly thirty degrees F above the freezing point of water while that of gasoline is fifty degrees below 0°F (10). The flash point of its aqueous solution is, of

only moderately toxic. Ethanol is probably the least toxic of the three alcohols. However, its apparent reaction with chlorine in water supplies to produce chloroform is a potentially serious drawback to its use wherever it might enter water supplies through runoff (13).

Both of these alcohols differ from methanol in having vapor densities appreciably heavier than air and each is approximately three times the cost of methanol. If anything, methanol is slightly superior to either of these two candidates and it is, of course, much cheaper.

Acetone. Acetone is similar to the above three alcohols in nearly all respects but flammability and cost. It is considerably more flammable in the pure state, though less so than gasoline and in water

solution still less so. It is double the cost of ethanol or isopropanol, six times that of methanol. It would not be purchased outright over any of the alcohols but would be acceptable as a constituent of a deicing mixture, as for example, one generated from waste products.

Urea. The water eutectic of urea is modest by comparison with those of the alcohols. It is comparable to but not quite, as low as that of  $(\text{NH}_4)_2\text{CO}_3$ . It is neutral but there is disagreement as to its corrosive effects (14, 15). The variable results may occur due to the tendency for urea to decompose and the resulting ammonia to be oxidized to nitrate which is, of course, corrosive. On the other hand, it is reported to adsorb tenaciously onto steel which, if not accompanied by decomposition and bacterial oxidation, might give rise to some corrosion inhibitory action. Its nitrogen content is a drawback from a eutrophication standpoint. It is nonvolatile, hence the full concentration is carried in runoff waters. On the other hand, it is nonflammable. Its cost, on an equal performance basis at  $-10^\circ\text{C}$ , is a little over double that of methanol and twelve and one-half times that of sodium chloride, not counting the cost of the latter's deleterious effects.

Urea:Ammonium Carbonate::52.4:47.6. The triple eutectic between water, urea and  $(\text{NH}_4)_2\text{CO}_3$  is a degree below that of sodium chloride with water (16). Neither component nor the mixture is flammable. The nitrogen content of the urea is more of a drawback than that of  $(\text{NH}_4)_2\text{CO}_3$  because of its lack of volatility. Although both compounds are solids, the one sublimates. Thus, storage of the already prepared solid mix might be difficult to achieve without some degree of disproportion due to thermal gradients, within the storage bin. On the other hand, mixing and dispensing solid urea along with the two liquid components of  $(\text{NH}_4)_2\text{CO}_3$  directly from truck to road is cumbersome and negates the convenience of liquid-liquid mixing and dispensing. Material cost was calculated nevertheless, on the latter basis. Preparations of the solid mix would be higher for the reasons already stated.

Despite the tempting lower eutectic it would seem that the added complications, cost and other disadvantages outweigh this combination system as compared to the ammonia and carbon dioxide system alone.

Formamide. Formamide has an excellent eutectic with water. It is neutral, nonflammable and its aqueous solution, corresponding to the  $-10^\circ\text{C}$  liquidus with ice, has the lowest viscosity of those tested. Its melting point,  $+2.6^\circ\text{C}$ , is disadvantageous, virtually assuring the necessity of dealing with it both as a liquid and as a solid, unless incorporated in solution with another ingredient.

It is an organic compound and so would increase BOD. It contains nitrogen which, on hydrolysis produces ammonia, with its attendant environmental problems. Its hydrolysis in aqueous solution, though very slow, probably accounts for its designation as a hazardous compound, since formic acid is also produced on hydrolysis. Acidic conditions such as occur on the skin surface tend to accelerate the hydrolysis, so skin irritation and perhaps even "burns" can be expected to occur if it is used in areas with foot traffic.

Its cost for equivalent treatment is ten times higher than that of methanol and 54 times that of sodium chloride. It would appear much less promising as a candidate deicer than methanol.

Dimethyl Sulfoxide (DMSO). DMSO, like formamide, has a very low eutectic with water, is

neutral, nonflammable below  $200^\circ\text{F}$  and has a melting point between room and water freezing temperature, namely  $18.6^\circ\text{C}$ . For an equal effect, it is even more costly than formamide, being over a dozen times more costly than methanol and 74 times more so than sodium chloride.

The compound contains no nitrogen or phosphorus and thus is free of the environmental liabilities associated with those elements. DMSO is considered to be relatively low in toxicity. It does dry and remove lipids from the skin when in contact at high concentrations. A more serious problem is its very high solubilization and penetration properties. DMSO solubilizes a wide spectrum of organic and inorganic substances, and it tends to carry them through the skin as it penetrates. The crude DMSO could itself contain impurities of questionable desirability, but it would certainly tend to solubilize other pollutants and carry them into whatever plant, animal or human it came in contact with (17, 18). This raises serious question as to the desirability of this material as a road deicer.

Considering its high cost and its possible toxic complications DMSO, like formamide, appears to be much less likely as a candidate deicing chemical than methanol.

#### Metal Organic Salts

All of the four metals picked in the initial screening, Na, K, Mg, and Ca and ammonium ion, form soluble salts with the lower organic acids mentioned above as candidate deicers. Of these possibilities, the Ca and Mg are preferred for several reasons, e.g., they are the cheapest when accepted as the naturally occurring mixture in dolomitic limestone (K is the most expensive); they are harmless to flora and fauna, by contrast to ammonium ion and they are beneficial to soils, in contrast to Na.

It has been shown that cellulosic solid waste can be converted to alkaline earth salts of lower carboxylic acids, predominantly acetic, by relatively simple technology and in yields sufficiently large to be interesting (see below). Most of these salts show sufficient water solubility to function as deicing agents. Other features of these compounds are attractive for this application.

A conservative cost estimate for producing these salts was based upon the process involving alkaline fusion of cellulosic waste. A more refined calculation will almost certainly yield a lower cost per unit weight. This same unit weight cost was used also for some of the other fatty acid salts produced by the same process in evaluating their respective costs for equivalent deicing effect (Table 4).

The water eutectics of the two primary products, calcium and magnesium acetates, are good and excellent respectively. Calcium propionate also shows a good eutectic. Although that of magnesium lactate is quite high, that of calcium formate is acceptable. It should be kept in mind that a combined eutectic such as would be encountered in a mixture will probably be lower than the lowest of the individual compounds.

The costs for an equivalent deicing effect are on the average about the same as that of methanol, around five times that for sodium chloride.

The aqueous solutions of these salts are not only neutral they exhibit pronounced inhibition of corrosion. In five month corrosion tests, the calcium and magnesium acetate solutions produced corrosion rates on iron strips an order of magnitude lower than rates in distilled water. None of these salts is flammable.

These salts do not contribute significantly to eutrophication. The anion decomposes to carbon dioxide and water. Usage as a deicer however results in minimal BOD stress because of the low temperatures. The calcium and magnesium cations are precipitated as the carbonates and thereby removed from

solution where their presence might otherwise influence water density and interfere with the turnover of the lakes.

Soils in the eastern half of the United States, where most deicing is done, are deficient in calcium and magnesium. Restoration of these ions to the soil in these areas as through a road deicer could be beneficial (19, 20). These divalent cations tend to improve the structure of the soil where, by comparison, sodium and to a lesser degree other monovalent cations (e.g., potassium and ammonium) tend to cause the breakdown of soil structure. Such breakdown results in a decreased permeability for both water and air, often a serious agricultural problem (21, 22).

Calcium and magnesium acetates and similar salts of other low molecular weight organic acids appear to be among the deicers which are ecologically the most desirable. On two counts, corrosion inhibition and soil building, far from being detrimental they are beneficial. For this reason, it is hardly accurate to compare these salts with sodium chloride on the basis of materials cost alone for the equivalent deicing performance. A proper comparison must include as well the attendant cost (or benefit) to the taxpayer's person and property (including that which he owns through the state) resulting from the application of the respective deicers. On this basis, the calcium and magnesium salts of the lower organic acids, instead of five times as costly, may prove to be half as costly as sodium chloride on an equivalent deicing basis.

This family of compounds would appear to be a primary candidate for further investigation as deicer substitutes for sodium chloride.

#### Deicers from Waste Materials

Alkaline Earth Organic Salts from Cellulose Waste. There are several processes for producing calcium and magnesium salts of organic acids, largely acetates from solid wastes and dolomitic limestone. These raw materials are of interest in part because one has a negative value and the other is one of the cheapest chemicals available. Four such processes are briefly described and evaluated below.

Enzymatic hydrolysis, involving fermentation steps through glucose and ethanol to acetic acid, suffers at present from low efficiency in breaking down the cellulose into glucose. Also considerable technological know-how is required to operate the process and then there is always a danger of enzyme poisoning from the very heterogeneous feed stock.

Destructive distillation of cellulosic solid waste at 400-1000°C in the absence of air produces, in addition to charcoal, a gaseous mixture containing about 2-6% acetic acid mixed with methanol, acetone, etc. Additional complex technology is required to convert the byproducts to acetic acid.

Oxidative pyrolysis involves heating in a limited supply of air to make producer gas which, in turn, can be converted to methanol, then acetic acid. Again, rather complex technology is required and very large plants are necessary (greater than 1000 tons solid waste per day) for economical operation. In this, as in the other two schemes above, the acetic acid and acetate production is in competition with other products of potentially greater value, e.g., methanol or ammonia.

Alkaline fusion is 19th Century technology which involves heating solid wastes in an excess of alkali (e.g., calcium, magnesium hydroxides) at a temperature of about 200-300°C for from one-half to three hours. The reaction produces a rather high yield of calcium magnesium acetate, which can then be extracted. The reaction is exothermic. Among its byproducts are methanol and acetone, either or both of which could be used as deicer or burned for pro-

cess energy. The insoluble byproducts, calcium and magnesium oxalates and carbonates could be allowed to remain or separated out by extraction. In the latter case they would be combined with makeup limestone and recycled in a kiln to produce the oxides and hydroxides with which to repeat the process.

While the literature on alkaline fusion of cellulosic wastes is old, none of it goes into as much detail as one could desire. Nevertheless, in preliminary experiments conversions up to 15% were obtained and there is every reason to believe that yields up to 20-40% acetic acid can be obtained, as claimed in 1895 by Cross and Bevan (23). Indeed, in 1892 Cross et al. had reported yields as high as 42% acetic acid from complex, largely cellulosic materials (24). Mahood and Cable reported yields of acetic acid -- up to 30% under optimum conditions -- with either calcium hydroxide or sodium hydroxide as the alkaline agent (1919) (25).

The alkaline fusion technology is simple, requiring only atmospheric pressure, relatively simple equipment and few steps. In these respects the process could serve the needs of smaller communities which could not afford the more sophisticated equipment or provide the trained personnel for the alternate methods of converting waste into deicing materials.

Approximately one-half of the United States population lives in communities too small to generate 200 tons of solid waste per day. If one-half of these, or 50-million people, live in the colder parts of the country, and if we assume solid waste production of two pounds per person per day, they generate  $1 \times 10^5$  tons of solid waste per day, or  $3.65 \times 10^7$  tons/year. If the production of acetic acid were approximately 30%, we would then be able to produce approximately  $1.4 \times 10^7$  tons of calcium magnesium acetates annually, as compared to  $0.9 \times 10^7$  tons of sodium chloride currently used on roads. The ratio of the weights is approximately that to produce equivalent ice melting effects. Thus, the deicer production capability via alkaline fusion of solid waste in the communities wherein it would most likely be employed is roughly equal to the current need for deicer of the nation as a whole.

#### Evaluation of Breakdown of Proteinaceous Wastes by Enzymes

Laboratory studies on this type of process were not carried out because initial evaluation appeared too negative.

It is assumed that proteinaceous wastes can, indeed, be broken down with enzymes into amino acids, and probably further treated to deaminate them. However, in light of the high value of proteinaceous feed and food supplements, it appears that edible usages would command a premium price which would make deicing usage economically unattractive.

In addition, a combination of nitrogen and carbon sources under conditions where bacteria can grow almost assures vigorous microbial growth -- and anaerobic growth produces putrefaction with all of the unpleasant odors implied by the term. Furthermore, nitrogen is usually a limiting nutrient for algal growth in lakes and streams, which means that a deicing chemical made from a protein source might have to be used with caution in some areas.

#### Prime Candidate Chemical Deicers

From the foregoing discussion it appears that the two best deicing candidates are methanol and CMA. CMA refers to the alkaline earth salts of the assorted low molecular weight organic acids derived from cellulosic materials (waste) by alkaline fusion.

Both of these deicer candidates have been and are still being tested. An elaborate program of corrosion testing is under way and preparations have been made for an additional road test. Heat of solution determinations revealed that by contrast with NaCl, which absorbs heat and gets colder as it dissolves, both methanol and CMA liberate heat upon going into water solution. This heating effect should speed up the melting process. Whether the effect on melting rate is appreciable is yet to be determined.

Preliminary sidewalk and road salting experiments reveal that CMA behaves very similarly to NaCl, the equiosmolar quantity producing about the same deicing effect and at about the same rate. By contrast to both of these, methanol acts immediately, producing its maximum effect within minutes after application. Again, by contrast its persistence is measured in only a few hours.

Some dynamic traction tests have been run on flat ice surfaces. These indicate as anticipated that if the deicer fails to bore through the sheet of ice to permit wheel contact with the pavement, the effect of applying either NaCl or purified CMA is to reduce traction. However, with CMA taken straight from the alkaline fusion reaction mixture without purification, the wheel traction on the ice appears to improve. This effect is probably due to the presence of insoluble byproducts of the reaction. The implication is that a purification step is not needed and that a superior CMA deicer may be produced without it at an even lower cost than anticipated.

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#### References

1. D.M. Murray and J.F.W. Ernst. An Economic Analysis of the Environmental Impact of Highway Deicing. EPA-600/2-76-105, 1976, 128 pp.
2. L. Van den Berg and Rose Dyson. Archives of Biochemistry and Biophysics. 81, 1959, pp. 319-329.
3. R.R. Hawkins and R.D. Herrigan. Runoff Quality in a Suburban Stream. Notice of Research Project Smithsonian Science Information Exchange, 1975.
4. G.R. Meneely. Toxic Effects of Dietary Sodium Chloride and the Protective Effects of Potassium in Toxicants Occurring Naturally in Foods. 2nd Edition, National Academy of Sciences, Washington, D.C., 1973.
5. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, D.C., Prepublication Copy, 1976.
6. Water Quality Criteria. Environmental Studies Board National Academy of Sciences and Environmental Protection Agency, Washington, D.C., 1972.
7. J.E. McKee and H.W. Wolf. Water Quality Criteria. Resources Agency of California, State Water Quality Control Board, 1963.
8. Corrosion Handbook. Ed. Herbert H. Uhlig, John Wiley and Sons, New York, 1948, pp. 9 & 10.
9. W. Lerch. Warning!. Use the Right Deicer. Modern Concrete, May 1962, pp. 66-67.
10. N.A. Lange. Handbook of Chemistry. 10th Edition, McGraw Hill Book Company, Inc., New York, 1961, pp. 41 & 42.
11. N.I. Sax. Dangerous Properties of Industrial Materials. 4th Edition, Reinhold Publishing Company, 1975, pp. 908-909.
12. U.S. Bureau of Mines Information Circular 6415. 1930, 7 pp.
13. T.A. Bellor et.al. The Occurrence of Organohalides in Chlorinated Drinking Waters. EPA-670/4-74-008, 1974.
14. A.G. Timms. Action of Deicing Agents on Concrete. Modern Concrete, May 1962, pp. 29-35.
15. M. Mellor. Snow Removal and Ice Control. Cold Regions Research and Engineering Laboratory Publication CRS & E III, A3b, 1965.
16. I.N. Balyaev et.al. Russian Journal of Inorganic Chemistry, 11,#6, 1966, pp 787-9.
17. A.J. Buckley. Potential Hazards Involved in Using Dimethyl Sulfoxide. J. Chem. Ed 42:674, 1965.
18. McGraw-Hill Encyclopedia of Science and Technology. 1971.
19. Soil. 1957 Yearbook of Agriculture. U.S.D.A.
20. H.J.M. Bowen. Trace Elements in Biochemistry. Academic Press, New York, 1966.
21. E.W. Russell. Soil Conditions and Plant Growth. Longmans, Green and Company, London, 8th Edition, 1950.
22. L.D. Baver. Soil Physics, 2nd Edition, John Wiley and Sons, New York, 1948.
23. C.F. Cross and E.J. Bevan. Cellulose. 1895, 320 pages.
24. C.F. Cross, E.J. Bevan and J.F.V. Isaac. On the Production of Acetic Acid from Carbohydrates. J. Soc. Chem. Ind. 2:966, 1892.
25. S.A. Mahood and D.E. Cable. Reaction Products of Alkali Sawdust Fusion, Acetic, Formic and Oxalic Acids and Methyl Alcohol. J. Ind. and Eng. Chem, 11:651, 1919.