

Deficiency in corn causes a shortening of the internodes of corn and a severe stunting. A typical zinc-deficient plant is shown in Figure 9. When the deficiency is severe, many corn plants will die in the seedling stage, with those recovering exhibiting several different colorations and symptoms ranging from a lack of green color in the upper leaves to interveinal striping in the upper leaves. Severe zinc deficiency in corn is known as "white bud."

Zinc deficiencies are corrected by soil applications of zinc sulfate and zinc chelates in the case of row crops, and by spray as well as soil applications for trees. Responses to zinc application are often marked (Figure 10).

Yield increases as large as 30% have been obtained with the application of zinc, without deficiency symptoms being present.

Acknowledgment

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Correction

Phosphine Residues from Phostoxin-Treated Grain

In this article by R. B. Bruce, A. J. Robbins, and T. O. Tuft [J. AGR. FOOD CHEM. 10, 18 (1962)], the following corrections should be made on page 20:

Column 1, line 7: (Table IV) should read (Table III). Column 3, line 4: maximum of 0.023 p.p.m. in one sample should read maximum of 0.029 p.p.m. in one sample. Column 3, line 6: (Table V) should read (Table IV). Column 3, fourth full paragraph, line 2: in Table II should read in Table V.

MICRONUTRIENT SOURCES

Metal Ammonium Phosphates as Fertilizers

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A number of divalent metals including magnesium, iron, zinc, copper, and manganese form ammonium phosphates having the general formula $MeNH_4PO_4 \cdot xH_2O$. These compounds are very slightly soluble in water and soil solutions. They are effective sources of nitrogen, phosphorus, and metals for plants through both foliar and soil application. When properly granulated they can be applied to soil at rates greatly exceeding those of conventional fertilizers without danger of burning plant roots, and they continue to furnish nutrients over long periods of time. In pulverized form, they may be applied to leaves of plants at high rates without burning.

SEVERAL DIVALENT METALS form ammonium phosphates having the general formula $MeNH_4PO_4 \cdot xH_2O$ (3). The most familiar of these compounds is magnesium ammonium phosphate. Others are the iron, zinc, manganese, copper, and cobalt ammonium phosphates. The most common form is the monohydrate. All are only slightly soluble in water.

The slight solubility of these compounds suggested their use as nonburning and long-lasting sources of nitrogen, phosphorus, and metals. Magnesium ammonium phosphate has been mentioned as a possible fertilizer material (2, 10-12), but has never been commercially available or widely used for fertilizer purposes. Magnesium ammonium phosphate is present in certain natural fertilizers such as guano (12). The other metal ammonium phosphates have not been used as fertilizers.

The present work has shown that metal ammonium phosphates when properly granulated are nonburning to plants even when applied at extremely

high rates, and they can be used to supply plant nutrients over predetermined periods of time by control of their particle size. They can be used effectively for either soil or foliar application.

These special properties of the metal ammonium phosphates make them particularly suitable in uses where conventional fertilizers are inefficient, burning is a problem, and long residual effects are desired. Applications in-

clude fertilization of ornamentals, orchards, nurseries, forest outplantings, turf, highway plantings, certain other crops, and seed coating.

Chemical and Physical Properties

Composition of Pure and Fertilizer Grade Compounds. The metal ammonium phosphates of interest as fertilizers are listed in Table I. All (except the molybdenum compound) exist as

Table I. Theoretical Composition of Metal Ammonium Phosphates

Compound	Color	Mol. Wt.	% N	% P ₂ O ₅	% Metal	% Ignition Loss
MgNH ₄ PO ₄ ·6H ₂ O	White	245.43	5.71	28.92	9.91 ^a	54.65
MgNH ₄ PO ₄ ·H ₂ O	White	155.35	9.02	45.69	15.65 ^b	28.36
FeNH ₄ PO ₄ ·H ₂ O	Green	186.881	7.50	37.98	29.89	19.29
ZnNH ₄ PO ₄	White	178.395	7.85	39.79	36.65	14.60
MnNH ₄ PO ₄ ·H ₂ O	Pink	186.023	7.53	38.16	29.53	23.68
CuNH ₄ PO ₄ ·H ₂ O	Blue	194.571	7.20	36.48	32.66	22.64
CoNH ₄ PO ₄ ·H ₂ O	Purple	189.971	7.37	37.36	31.03	23.25
(NH ₄) ₃ [P(Mo ₃ O ₁₀) ₄]	Yellow	1876.50	2.24	3.78	61.36	4.16

^a 16.43% MgO. ^b 25.95% MgO.

Table II. Composition of Fertilizer Grade Metal Ammonium Phosphates

Compound	% N	% Total P ₂ O ₅	% Avail. P ₂ O ₅	% Metal	% F	% Moisture at 100° C.
MgNH ₄ PO ₄ ·H ₂ O	8.3	44.6	43.1	14.8 ^a	0.5	1.0
FeNH ₄ PO ₄ ·H ₂ O	7.0	37.5	37.0	27.3	0.3	1.5 ^b
ZnNH ₄ PO ₄	7.5	39.0	21.0	33.5	0.5	1.0
MnNH ₄ PO ₄ ·H ₂ O	7.2	36.0	25.0	27.6	0.3	1.2
CuNH ₄ PO ₄ ·H ₂ O	7.0	36.0	35.9	30.0	0.3	0.8
CoNH ₄ PO ₄ ·H ₂ O	6.9	38.0	38.0	27.0

^a 24.6% MgO. ^b 70° C.

Table III. Winter Weathering of Magnesium Ammonium Phosphate Monohydrate

	Original	Calcd. for MgNH ₄ PO ₄ ·H ₂ O	8 Months after Application	Calcd. for MgNH ₄ PO ₄ ·6H ₂ O
% N	8.96	9.02	5.86	5.71
% total P ₂ O ₅	45.70	45.69	30.30	28.92
% citrate insol. P ₂ O ₅	13.88	...	0.00	...
% avail. P ₂ O ₅	31.82	...	30.30	...
% MgO	26.26	25.95	...	16.43
P ₂ O ₅ /N ratio	5.12	5.07	5.18	5.07

monohydrates. Although a monohydrate of the zinc ammonium phosphate is known, the compound under ordinary conditions exists in the anhydrous state. The other metal ammonium phosphates are not stable in the anhydrous state. The magnesium compound exists as both a monohydrate and hexahydrate; the monohydrate is of more interest for fertilizer use because of its higher analysis and greater stability. The cobalt compound also exists as a hexahydrate (3). Metal ammonium phosphates of nickel, cadmium, uranium, and beryllium have been prepared but are not under consideration as fertilizers. Ammonium 12-molybdophosphate (ammonium phosphomolybdate) does not belong to the type of metal ammonium phosphate having the general formula MeNH₄PO₄·xH₂O. However, it is similar to metal ammonium phosphates in that it contains a metal with ammonium and phosphate ions, and has the same order of solubility.

Phosphate Availability. The availability of phosphate in fertilizer grade metal ammonium phosphates was determined by the A.O.A.C. ammonium citrate method (Table II). Essentially all the phosphate in the iron, copper, and cobalt compounds is available. These metals are strongly complexed by citrate ions. Table II indicates that approximately 97% of the P₂O₅ in magnesium ammonium phosphate monohydrate is available. The zinc and manganese compounds have low citrate solubilities.

Although magnesium ammonium phosphate monohydrate is soluble in ammonium citrate solution, the P₂O₅ availability as determined by the A.O.A.C. method varies from batch to batch depending on purity, crystal size, and degree of hydration. The availability

of the hexahydrate, either reagent or fertilizer grade, is substantially 100%. It is higher than that of the monohydrate because of greater dilution with water of crystallization which decreases the ratio of P₂O₅ to solvent in the analytical determination. (The hexahydrate contains 44.0% water of crystallization whereas the monohydrate contains only 11.6%.)

When magnesium ammonium phosphate monohydrate contacts soil moisture at ambient temperatures, it gradually hydrates to the hexahydrate. The transition temperature is 56–7° C. (4). Hence, under cool moist climatic conditions all the P₂O₅ in magnesium ammonium phosphate monohydrate becomes available. To illustrate this, a pound of reagent grade magnesium ammonium phosphate monohydrate containing about 14% citrate-insoluble P₂O₅ (due primarily to large crystal size) was applied to 1 square foot of lawn in midsummer. The powdery white compound formed a layer approximately 1 inch thick in the turf, but was not mixed with the soil. The grass responded quickly to the fertilizer and continued to be green and healthy throughout the remainder of the summer and fall. Approximately 8 months after application, the magnesium ammonium phosphate was sampled and analyzed. Table III shows that the effect of winter weathering on magnesium ammonium phosphate monohydrate is hydration to magnesium ammonium phosphate hexahydrate and that all the P₂O₅ in the resulting hexahydrate is citrate soluble. Because there was essentially no change in the P₂O₅/N weight ratio, as previously reported (4), the magnesium ammonium phosphate was assumed to dissolve congruently.

Approximately 14 months after ap-

plication, the material on the test plot was sampled again to determine the effect of subsequent summer weathering. X-ray diffraction analysis indicated that the major component was MgNH₄PO₄·H₂O. A small quantity of MgNH₄PO₄·6H₂O and a still smaller quantity of MgHPO₄·3H₂O were also detected. Hence, most of the hexahydrate formed over the cold damp winter months was dehydrated during the hot, dry, summer months to form the monohydrate again. Conversion of the hexahydrate to the monohydrate is usually associated with a slight loss of ammonia, thus accounting for the presence of a small quantity of MgHPO₄·3H₂O.

Similarly, granules of magnesium ammonium phosphate monohydrate mixed with soil hydrate to the hexahydrate and dissolve congruently. Under extremely dry conditions, the hexahydrate will gradually lose water.

Solubility. The solubilities of reagent grade metal ammonium phosphates in water and dilute hydrochloric acid (0.001*N* and 0.01*N*) were determined (Table IV). One gram of each compound having a particle size of less than 50 microns was agitated with 250 ml. of solvent (water or dilute HCl) for 1 hour at 25° C. The mixture was filtered, and the filtrate percolated through a column of Dowex-50 cation exchange resin in the hydrogen form to remove the metal ions. The resulting phosphoric acid was washed from the column with water and determined in the combined column effluent and wash solutions by an electrotitrimetric method (16). The solubility of the compound was calculated based on the quantity of phosphate found, assuming that the compounds dissolved congruently.

The metal ammonium phosphates are arranged in Table IV in order of decreasing solubilities in water. They have very low water solubilities. Those of the magnesium, manganese, and zinc compounds compare favorably with solubilities reported (4, 13, 15, 17) by other investigators. Solubility increases with acid concentration, but the rate of increase varies from compound to compound. The copper compound is the least soluble in water, whereas the ferrous compound is the least soluble in 0.01*N* HCl.

The difference in the solubilities of the two hydrates of magnesium ammonium phosphate is primarily due to the difference in molecular weight. Their P₂O₅ solubilities are approximately equal. Although the solubility of magnesium ammonium phosphate in water is low, it is increased slightly by the presence of other salts, particularly ammonium salts (ammonium phosphate excepted because the common ion effect reduces the solubility) (15). The solubility of magnesium

ammonium phosphate in various salt solutions increases in the order: sodium chloride, ammonium chloride, ammonium sulfate, ammonium oxalate (7-1).

Thermal Stability. Thermograms of reagent grade metal ammonium phosphates are shown in Figure 1. All experiments were conducted at atmospheric pressure with a Chevenard thermobalance in air at a heating rate of 5° C. per minute. Sample sizes were selected on the basis that the maximum loss in weight would be in the order of 150 to 200 mg. The gross appearances of the curves are similar. The thermograms for the magnesium and manganese compounds are in general agreement with those previously reported (8, 9).

The final horizontal portion of each curve represents ignition to constant weight with the formation of metal pyrophosphates. (Ignition of metal ammonium phosphates to pyrophosphates is a well known analytical procedure in the determination of magnesium, manganese, zinc, and cobalt.) Although a number of intermediate compositions result during ignition because of loss of water of crystallization, water of constitution, and ammonia, no attempt was made to establish their identity.

Magnesium ammonium phosphate monohydrate is much more stable than the hexahydrate (78). Losses of ammonia from the monohydrate on standing are insignificant, whereas the hexahydrate gradually loses ammonia

even at 35° C. (7). The hygroscopicity of the monohydrate is also much lower than that of the hexahydrate.

Ferrous ammonium phosphate is subject to air oxidation at elevated temperatures, and its thermogram indicates decomposition even as low as 100° C. All other monohydrates are stable for short drying periods at temperatures to approximately 200° C. The anhydrous zinc compound is the most stable of the series. Decomposition does not occur until the temperature is nearly 300° C.

X-Ray Data. Because inorganic compounds are customarily characterized by both chemical and x-ray analyses, x-ray diffraction data were obtained for reagent grade metal ammonium phosphates. The interplaner spacings, $d(A)$,

and relative intensities, I/I_1 , of the diffraction lines of the compounds are given in Table V. Data for the magnesium and manganese compounds had previously been catalogued in the ASTM files on x-ray diffraction data and are included in Table V for completeness. Magnesium ammonium phosphate monohydrate and ferrous ammonium phosphate monohydrate (and perhaps cobalt ammonium phosphate monohydrate) are isomorphous.

The interplaner spacings were calculated using a wave length of 1.5418A (copper K- α -average). The radiation was nickel-filtered. All line positions were measured to within $\pm 0.1^\circ 2\theta$; the estimated errors in interplaner spacing are based upon a 0.1° error in angle.

Table IV. Solubility of Metal Ammonium Phosphates at 25° C.

Compound	Solubility, Grams per 100 ml. ^a		
	Water	0.001N HCl	0.01N HCl
MgNH ₄ PO ₄ ·6H ₂ O	0.018 ^b	0.033	0.178
MgNH ₄ PO ₄ ·H ₂ O	0.014 ^c	0.022	0.120
FeNH ₄ PO ₄ ·H ₂ O	0.0095	0.013	0.067
MnNH ₄ PO ₄ ·H ₂ O	0.0038 ^d	0.026	0.097
ZnNH ₄ PO ₄	0.0018 ^e	0.016	0.098
CoNH ₄ PO ₄ ·H ₂ O	0.0017	0.018	0.101
CuNH ₄ PO ₄ ·H ₂ O	0.0009	0.010	0.092

^a Based on phosphate analysis.

^b 0.014 gram/100 ml. at 25° C. based on magnesium analysis (75).

^c 0.011 gram/100 ml. at 25° C. based on phosphate analysis (4).

^d 0.0030 gram/100 ml. in cold water and 0.0050 gram/100 ml. in boiling water, Mellor (73) reporting data of Fresenius.

^e 0.0015 gram/100 ml. at 20° C. (77).

Table V. X-Ray Diffraction Data for Metal Ammonium Phosphates

MgNH ₄ PO ₄ ·H ₂ O ^a		FeNH ₄ PO ₄ ·H ₂ O		ZnNH ₄ PO ₄		MnNH ₄ PO ₄ ·H ₂ O ^a		CuNH ₄ PO ₄ ·H ₂ O		CoNH ₄ PO ₄ ·H ₂ O	
d (A.)	I/I ₁	d (A.)	I/I ₁	d (A.)	I/I ₁	d (A.)	I/I ₁	d (A.)	I/I ₁	d (A.)	I/I ₁
9.00	100	9.7 ± 0.1	1.3 ^b	8.9 ± 0.01	4	9.00	100	9.6 ± 0.1	0.5 ^b	9.7 ± 0.1	1.2
5.50	7	8.8 ± 0.1	100	6.28 ± 0.04	81	4.85	15	8.7 ± 0.1	100 ^c	8.8 ± 0.1	100
4.80	27	7.6(band)	0.8	4.65 ± 0.02	100	4.30	25	6.3 ± 0.1	100 ^f	8.3(band)	1.6
4.20	27	4.77 ± 0.02	0.5	4.48 ± 0.02	37	4.02	4	4.62 ± 0.03	0.2	4.72 ± 0.02	0.5
2.80	67	4.42 ± 0.02	0.8	4.40 ± 0.02	78	3.80	2	4.51 ± 0.02	0.3	4.40 ± 0.02	1.4
2.48	7	4.23 ± 0.02	0.7	4.11 ± 0.02	7	3.45	15	4.40 ± 0.02	0.7	4.21 ± 0.02	0.5
2.40	7	2.950 ± 0.009	0.4	3.99 ± 0.02	4	2.86	100	4.33 ± 0.02	0.7	3.36(band)	0.4
2.13	7	2.823 ± 0.007	1.7	3.93 ± 0.02	4	2.72	1	3.90 ± 0.02	0.2	2.931 ± 0.009	0.6
1.67	7	2.683 ± 0.007	0.2	3.47 ± 0.02	4	2.53	6	3.75 ± 0.02	0.2	2.805 ± 0.008	1.5
1.61	7	2.637 ± 0.007	0.2	3.43 ± 0.01	7	2.46	6	3.71 ± 0.02	0.2	2.501 ± 0.006	0.5
		2.515 ± 0.006	0.5	3.22	56	2.38	8	3.62 ± 0.02	0.1	2.398 ± 0.006	0.3
		2.411 ± 0.006	0.2	3.20	48	2.32	13	3.49 ± 0.02	0.7	2.332 ± 0.005	0.2
		2.356 ± 0.006	0.2	3.13 ± 0.01	15	2.17	13	3.44 ± 0.01	0.3	2.281 ± 0.005	0.5
		2.298 ± 0.005	0.6	2.988 ± 0.009	7	2.06	2	3.36 ± 0.01	0.5		
				2.788 ± 0.007	26	2.01	1	3.31 ± 0.01	0.2		
				2.722 ± 0.007	44	1.88	8	3.25 ± 0.01	0.6		
				2.675 ± 0.007	2	1.83	4	3.10 ± 0.01	0.2		
				2.622 ± 0.007	37	1.75	6	3.03 ± 0.01	0.4		
				2.501 ± 0.006	19	1.66	13	2.921 ± 0.009	0.9		
				2.475 ± 0.006	7	1.58	2	2.885 ± 0.008	0.5		
						1.44	5	2.840 ± 0.007	1.3		
						1.42	1	2.691 ± 0.007	0.5		
						1.39	1	2.637 ± 0.007	0.7		
						1.36	2	2.543 ± 0.006	0.2		
						1.32	1	2.475 ± 0.006	0.5		
						1.29	1				
						1.27	1				
						1.20	3				

^a Data from ASTM files.

^b Probably a beta line.

^c Halo with a sharp low angle edge.

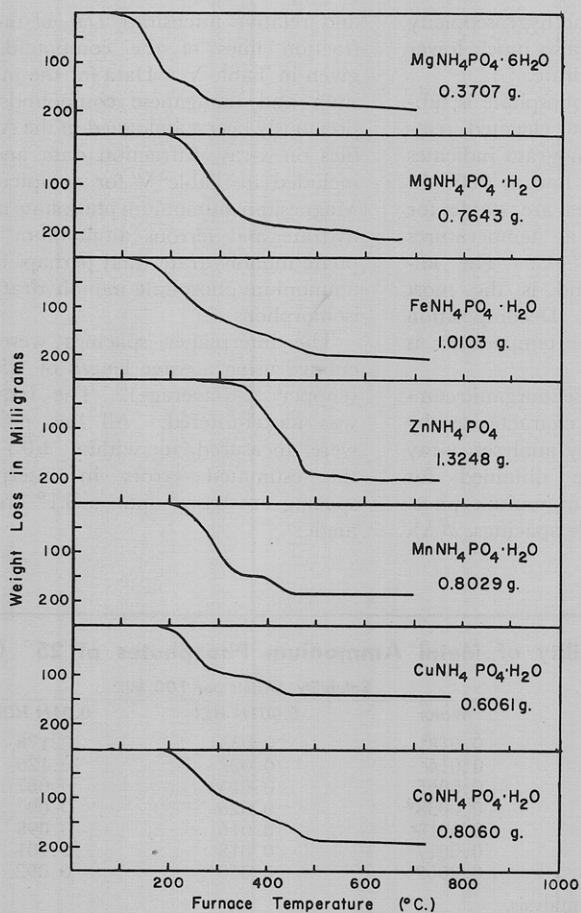


Figure 1. Thermograms of metal ammonium phosphates

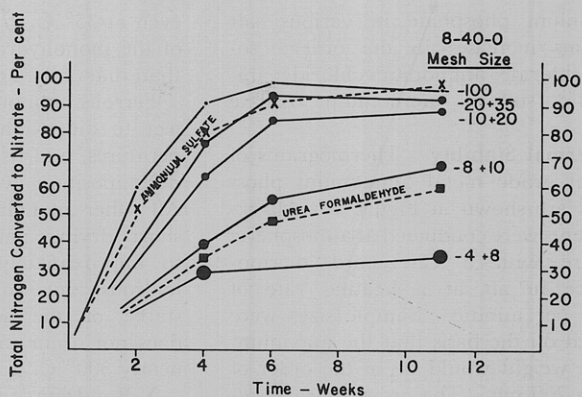


Figure 2. Nitrification characteristics of magnesium ammonium phosphate



Figure 3. Ryegrass germinated in soil (left) and in pure magnesium ammonium phosphate (right) after five weeks

Table VI. Effect of Fertilization on Cross Sectional Area and on Total Height of Certain Deciduous Broadleaved Evergreens and Coniferous Ornamentals

	Cross Sectional Area								Total Height					
	Treatments ¹								Treatments ²					
	No Fert.	2 Oz. 8-40-0		4 Oz. 8-40-0		1.6 Oz. 10-10-10		No Fert.	2 Oz. 8-40-0		4 Oz. 8-40-0		1.6 Oz. 10-10-10	
	$r,^2$ inches	$r,^2$ in.	% increase	$r,^2$ in.	% inc.	$r,^2$ in.	% inc.	Feet	Feet	% inc.	Feet	% inc.	Feet	% inc.
1 <i>Acer platanoides</i>	0.198	0.237	18.7	0.276	39.4	0.207	4.5	10.4	12.8	23.1	12.2	17.3	12.0	15.4
2 <i>A.p. 'Crimson King'</i>	0.314	0.336	7.0	0.336	7.0	0.354	9.6	9.1	10.4	14.3	10.7	17.6	10.0	9.9
3 <i>Betula alba</i>	0.722	1.538	113.0	1.716	137.7	1.932	167.6	12.7	15.3	20.5	14.5	14.2	11.6	-8.7
4 <i>Cercis canadensis</i>	0.624	0.931	49.2	0.504	-19.2	0.314	-49.7	9.7	12.0	23.7	10.1	4.1	8.4	-13.4
5 <i>Oxydendrum arboreum</i>	0.102	0.156	52.9	0.160	56.9	0.130	27.5
6 <i>Ulmus pumila</i>	0.819	1.188	45.1	1.428	74.4	1.664	103.2
7 <i>Colutea arborescens</i>	3.6	4.3	19.4	3.8	5.6
8 <i>Elaeagnus umbellata</i>	2.6	2.8	7.7	3.2	23.1
9 <i>Larix leptolepis</i>	1.9	2.6	36.8	2.3	21.1
10 <i>Magnolia grandiflora</i>	3.3	5.0	51.6	4.1	24.2
11 <i>Pieris japonica</i>	2.0	2.2	10.0	2.3	15.0	2.1	5.0
12 <i>Rosa virginiana</i>	1.6	1.7	6.3	2.1	31.3
Av. Response	47.65	...	49.4	...	43.7	18.0	...	20.4	...	5.4

^a Mortality compared to the unfertilized control for total experiment: 2 oz. of 8-40-0, 0.2%; 4 oz. of 8-40-0, 5.0%; 1.6 oz. of 10-10-10, 32.5%. Response data based on surviving specimens only.

Agronomic Characteristics

The metal ammonium phosphates have been extensively tested in greenhouse and field plots at the W. R. Grace & Co. Washington Research Center and in many other parts of the United States by agricultural experiment stations and commercial organizations. Complete data will be reported in appropriate journals.

Since metal ammonium phosphates contain not only secondary or minor elements but also nitrogen and phosphorus, it is necessary to isolate the response by compensating for the elements not under test. In some instances, this is impossible since suitable control materials are not available.

Nitrification. Laboratory incubation studies with heavy rates of pulverized metal ammonium phosphates in soil disclosed that the nitrate accumulation was much greater than could be accounted for by solubility of the salts. It was concluded that nitrification rather than solubility is under most conditions the dominant factor controlling availability to plants.

Nitrification studies with several of the metal ammonium phosphates were conducted following procedures similar to those described by Clark *et al.* (7). The results of one experiment are shown in Figure 2. Magnesium ammonium phosphate of small particle size nitrifies at a rate comparable with ammonium sulfate. Similar results had previously been obtained by Clark (6). With an increase in granule size, the nitrification rate is decreased. While virtually all of the ammonium sulfate and small granules of magnesium ammonium phosphate had nitrified in six weeks, only about 25% of the ammonia in the -4+8 mesh granule had been converted. Conversion of the large granules was less than that of a commercial urea-formaldehyde preparation (-12+35 mesh). Other metal ammonium phosphates and mixtures containing them also nitrified slower as particle size was increased.

As a result of these nitrification data, three particle size ranges were chosen for experimental production and agronomic tests: -16+35 mesh (for light applications and quick response), -6+16 mesh (for heavy applications lasting several months), and -3+6 mesh (for heavy applications lasting over a year). Also, a finely pulverized grade (-2 microns) was made for foliar application.

Nonburning Properties. To demonstrate that the material will not cause salt injury, seeds were germinated in magnesium ammonium phosphate monohydrate alone, and exceedingly heavy applications were made on turf and in the planting holes of many varieties of plants. Oats, corn, beans, wheat,

alfalfa, ryegrass, white pine, and several other varieties were successfully germinated in the fertilizer alone. After germination, some crops continued to grow well in the material for over 11 weeks. (Figure 3).

Broadcast applications of up to 2 tons of nitrogen per acre (equivalent to 1 pound of magnesium ammonium phosphate per square foot) on blue grass turf did not result in burning. One-year-old bare rooted peach trees, field planted in mixtures of up to 10 pounds of magnesium ammonium phosphate with 10 pounds of soil, were not injured and responded exceptionally well to the treatment. In other experiments, at least 20 species of field crop, grass, and shrub seeds were coated with magnesium ammonium phosphate. Germination was not impaired, and in several instances was improved in comparison with uncoated seeds.

Magnesium Ammonium Phosphate as a Source of Nitrogen and Phosphorus. Magnesium ammonium phosphate has been used in fertility work with many varieties of turf grasses, tree seedlings, ornamental plants, truck crops, field crops, flowers, and citrus. Most of the results reported here were on soils where magnesium was not believed to be a critical factor. Differences in yield can generally be attributed to the nitrogen and phosphate.

The response of many varieties in forest nurseries has been excellent. The convenience of a single application either mixed with the soil at the time of seeding or top-dressed is a distinct advantage. The amount used in top-dressing can be varied so that the single application lasts for either one or two years if necessary. The length and oven-dry weight of terminal growth of balsam fir in a nursery bed fertilized with magnesium ammonium phosphate were twice as great as that of the unfertilized bed at the end of one growing season. With red spruce under the same conditions, length and oven-dry weight were four times as great. White pine, American holly, multi-flora rose, Norway spruce, slash pine, Douglas fir, and several other varieties fertilized with magnesium ammonium phosphate in nursery beds had a much darker color and more growth than those treated with conventional materials.

A large number of experiments have been started with fertilization of forest seedlings during out-planting. The -3+6 mesh granule size of magnesium ammonium phosphate is placed at the bottom of the planting slit directly under the longest roots. At some locations, 1-, 2-, 4-, 8-, and 16-ounce rates have been used per seedling. Early results have generally been more satisfactory with the lower rates. This may be caused by the difficulty in properly placing the larger quantities.

An arrangement for dropping the fertilizer to the bottom of the slit was developed for use on a commercial tree planter. Depending upon the speed of the machine and the rate of application, the fertilizer was placed in a horizontal plane approximately 4 inches wide and 6 to 20 inches long. Depth of the planting slit was adjusted so that the seedling roots just touched the fertilizer.

A 30-acre experimental planting was made by the Washington Research Center using the method of placement described above. With rates up to 8 ounces of magnesium ammonium phosphate per seedling, survival of Norway spruce, black locust, loblolly pine, white pine, tulip poplar, red pine, larch, and Austrian pine was 92% during the first growing season. Survival of the no fertilizer controls was equal to that of the fertilized seedlings. All trees were measured for total height, new growth, and diameter after the first season in the field. Wood volume increases were determined by squaring significant radii measurements and multiplying them by the new growth. Preliminary data indicate growth increases in all varieties except Austrian and red pine. Most consistent results were obtained with 2 ounces of magnesium ammonium phosphate which resulted in typical responses of 75% wood volume increases on loblolly pine, 24% increases on white pine, 57% on tulip poplar, 27% on Norway spruce plus significant color differences, and 69% on black locust. All increases are expressed as per cent gain over the nonfertilized controls.

The survival data with forest tree plantings have not been consistent throughout the country. In one small planting, the survival of Lombardy poplars fertilized with magnesium ammonium phosphate at rates up to 1 pound per tree was 84% compared with 46% of those not fertilized. At the end of one growing season, those fertilized at the rate of 1 pound per tree had a trunk diameter 40% greater than unfertilized trees. Several other plantings with hardwoods have also had better survival with fertilization. With conifers, there have been instances ranging from slight depression of survival to severe losses generally in plantings where heavier rates were used in the dibble hole completely surrounding the roots. With placement such as this, losses can generally be attributed to lack of water rather than a burning effect. The magnesium ammonium phosphate monohydrate not only competes with the roots for water temporarily, but also creates a barrier which limits capillary movement of water from the soil to the roots. Losses using such placement are most severe in light

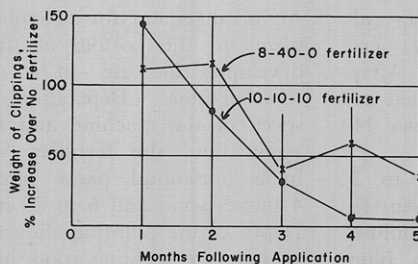


Figure 4. Response of five species of grass to 8-40-0 and conventional 10-10-10 supplemented with phosphorus and applied once at the rate of 2 pounds of nitrogen per 1000 sq. ft.

soils and during a prolonged drought immediately following planting.

Hardwoods seem to respond to fertilizer application much sooner than conifers. In some plantations, the height of hardwoods was as much as 200% greater with fertilization after the first growing season. Difference in height due to fertilization in conifers is generally less than 50% after one season. Differences in rate of fertilizer application above 1 or 2 ounces appear to have little effect in growth response during the first season. While it is difficult to estimate the long term value of this early response, it is expected that seedlings which grow away from their competition and produce a large root system earlier will also reach the harvest stage earlier.

In one experiment, 41 varieties of woody ornamentals were grown in nursery rows under clean cultivation. Treatments were 2 and 4 ounces of -3+8 mesh magnesium ammonium phosphate (8-40-0), 1.6 ounces of 10-10-10 (nitrogen equivalent to 2 ounces of 8-40-0) placed in the planting hole, and unfertilized controls. About 740 plants were used in the tests. About two thirds of the varieties gave growth responses to the two rates of 8-40-0, while responses to 10-10-10 were visible in only about one third of the varieties.

Data on growth responses after two growing seasons of a portion of this experiment are presented in Table VI as total height and for single stemmed plants, trunk radius squared. This latter measurement is proportional to the cross sectional area of the trunk and is more indicative of total growth than a diameter or height measurement. The three fertilizer treatments gave about equal trunk size increase on trees, but the 10-10-10 did not give height response equal to that from 8-40-0. The mortality data for the whole experiment are revealing. No increase in mortality over unfertilized controls occurred in the 2 ounces of 8-40-0 treatment, a 5% increase occurred at 4 ounces of 8-40-0, and a 32.5% increase resulted from the

10-10-10 treatment. The plants which survived responded to 10-10-10, but survival was poor. Foliage color at the end of the second growing season of plants fertilized with 8-40-0 was superior to plants fertilized with 10-10-10.

When graded according to commercial standards, these increases in growth reflected appreciable gains in grade size and, therefore, in dollar value. Gains from 10-10-10 fertilizer were offset by losses and lack of plant uniformity.

In one turf experiment with five separate species of grasses, magnesium ammonium phosphate was compared with conventional fertilizers at the rates of 2 and 10 pounds of nitrogen per 1000 square feet. A single application was made in spring. Responses of the treatments were measured as the dry weight of grass clippings harvested monthly and plotted as percentage increase over no fertilizer as shown for the 2 pound rate in Figure 4. The magnesium ammonium phosphate did not give as heavy a flush of growth as the conventional fertilizer immediately following application. It did, however, give considerably greater duration of response and total cumulative yields. Several other turf experiments, including establishment of new turf and fertilization of existing turf, gave results indicating that the magnesium ammonium phosphate becomes available gradually throughout the growing season.

Herbaceous flowers such as gloxinias, begonias, and many other varieties as well as most container-grown ornamentals gave excellent growth when fertilized with a single application of magnesium ammonium phosphate (Figure 5). A rate of 10 to 20 pounds of -6+16 mesh material per cubic yard of potting mixture appears to be quite satisfactory. Single applications of conventional fertilizers at rates great enough to last for one season invariably killed the plants. Higher rates of -3+6 mesh material can be used so that no additional nitrogen or phosphate need be added for two growing seasons; it may be necessary to add potassium.

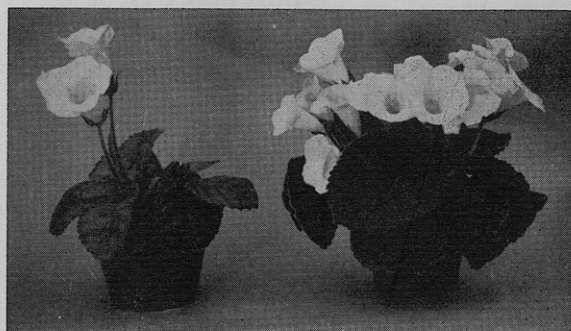


Figure 5. Gloxinia with no fertilizer (left) and a single application (right) of magnesium ammonium phosphate mixed with soil (1.5%) after 14 weeks

Tomatoes in a field test on sandy loam were fertilized with -6+16 mesh magnesium ammonium phosphate, commercial 5-10-5, urea plus triple superphosphate, and urea plus dicalcium phosphate. Rates of application varied between 0.5 and 15 pounds of nitrogen per 1000 square feet. The fertilizer was mixed with the soil and placed near the bottom of the planting hole which was about 5 inches deep and 6 inches in diameter. Comparisons were made at similar rates of nitrogen. With the exception of 5-10-5, phosphate rates were similar. No potash was added, since the soil potash level was high. Magnesium ammonium phosphate gave significantly greater yields than the other materials at all except the 5-pound rate of nitrogen. At the 0.5-pound rate of nitrogen, the yield with magnesium ammonium phosphate was 71% greater than with 5-10-5. This was due in part to a phosphorus deficiency with the 5-10-5 treatment. Combining rates of application, yields with magnesium ammonium phosphate were 100% greater than with the other sources, which were approximately equal.

Tomatoes in a large field experiment on fine sand subject to leaching were fertilized with a 1-2-2 ratio mixture formulated with magnesium ammonium phosphate and other mixtures of the same ratio formulated with conventional materials, applied at rates of 16, 36, and 56 pounds of nitrogen per acre at time of planting, side-dress, and lay-by, respectively. Yields were 37% greater with the mixture containing magnesium ammonium phosphate.

Magnesium Ammonium Phosphate as a Source of Magnesium. In a large potato experiment on soils where magnesium was deficient, 1-4-4 mixed fertilizers were formulated with magnesium ammonium phosphate, conventional materials with soluble magnesium, and conventional materials without magnesium. While the conventional mixture with soluble magnesium gave 20% more marketable potatoes than without magnesium, the

mixture with magnesium ammonium phosphate gave 42% more marketable potatoes. While this response to magnesium is excellent, additional yield from the magnesium ammonium phosphate was probably at least partially due to the presence of the slowly available nitrogen in this mixture.

Ferrous Ammonium Phosphate. Ferrous ammonium phosphate has been used as a source of iron on many varieties of plants. It may be used as a granulated material for soil application or as a pulverized material for application in sprays to foliage. While many varieties benefit from foliar sprays having a concentration as low as 2 pounds per 50 gallons of water, higher rates can be applied without danger of burning. Foliar applications indicate that bent grass shows an iron response in two days, tall fescue in four days, and many other varieties including bluegrass in five to seven days. Azaleas and rhododendrons respond to foliar applications in about one week. Field experiments with azaleas over a range of pH levels have been carried out for the last three years. Treatments have included fertilization without iron, granular ferrous ammonium phosphate in the soil only, as a foliar spray only, and as a combination application between soil and foliage. Iron chelates and other iron sources have been used in comparative treatments. Results have been measured in terms of growth response and differences in color read on Munsell color charts. The best results were usually obtained on treatments where granulated ferrous ammonium phosphate was applied to the soil, and the foliage was sprayed with pulverized material. Ferrous ammonium phosphate in soil gives a longer lasting treatment than application to the foliage alone. While the foliar treatment effectively cures iron deficiency on the leaves sprayed, later growth may still show iron chlorosis. The treatments with some of the chelates and other iron materials often resulted in a burning effect which sometimes caused defoliation and even death to the plant. In experiments where ferrous ammonium phosphate was added as a part of the soil treatment under peaches and many other ornamentals, the leaves were distinctly greener than untreated controls. In many species, leaf size was appreciably greater.

Some conifers have a tendency to become chlorotic in the fall. This is particularly objectionable with Christmas trees. Four year old Norway spruce, loblolly pine, and white pine were sprayed in a field test in July. Norway spruce trees sprayed thoroughly with a mixture of 4 pounds of ferrous ammonium phosphate in 50 gallons of water retained their green color much better throughout the winter than un-

treated trees. Loblolly pine and white pine did not tend to become chlorotic in this test and thus did not respond to treatment.

Zinc Ammonium Phosphate. Zinc ammonium phosphate has been applied in granular and pulverulent forms to several different soils and crops. The pulverulent form has also been applied in the form of a spray to some crops. Although yields of crops did not respond to zinc applications at some locations, zinc analysis of the crop gave indication of efficiency compared with other sources. In tests with corn, sorghum, and snap beans, yields or zinc uptake were in all instances at least as good as those from zinc sulfate. At some locations, differences favored zinc ammonium phosphate over zinc ammonium sulfite. At other locations where adequacy of sulfur was questionable, the zinc ammonium sulfite gave higher yields.

Manganese Ammonium Phosphate. Manganese ammonium phosphate has been applied to the foliage and the soil in several experiments on both inorganic and organic soils. Test crops have included sorghum, turnips, and radishes. Manganese uptake determinations were made on sorghum grown on limed and unlimed acid sand. Liming reduced the availability from manganese sulfate considerably, but did not affect the uptake from manganese ammonium phosphate. Since high lime is often a factor in inducing manganese deficiency, this may be an important observation.

Copper Ammonium Phosphate. Copper ammonium phosphate has been used for foliar and soil application on sorghum, turnips, radishes, and snap beans on both inorganic and organic soils. Uptake of copper by sorghum from copper ammonium phosphate was not depressed by liming as was the uptake from copper sulfate, on both an inorganic soil and an organic soil.

Ammonium Phosphomolybdate. Ammonium phosphomolybdate applied to an inorganic and an organic soil increased the molybdenum content of sorghum over the control. Ammonium phosphomolybdate compared favorably with molybdenum trioxide in this test.

Metal Ammonium Phosphates as Components of Mixed Fertilizers. Magnesium ammonium phosphate and ferrous ammonium phosphate have been tested as ingredients of mixed fertilizers. When other ingredients did not contain free acid, these materials retained their original properties. The mixtures did not cake. Laboratory tests indicated that nitrification rates were decreased with increased particle size. Agronomic tests with turf, vegetables, and ornamentals indicated the mixtures were more slowly available and more efficient than conventional mixtures. Residue analysis of large granules present

in soil for nine months indicated that the water-soluble components of the mixture had been occluded somewhat by the metal ammonium phosphates. Thus, rate of availability of the soluble portion was also reduced.

Caro *et al.* (5) concluded that addition of zinc ammonium phosphate did not induce caking of test mixtures. Several other conventional sources of zinc increased caking considerably.

Agronomic Applications. The metal ammonium phosphates, because of their low solubility, will not cause salt injury to seeds and plants. Thus, they can be used in many applications where conventional soluble fertilizers are unsuitable: seed coatings, placement near the seed, placement in the planting hole with seedling, and foliar spraying.

Rate of availability can be controlled by granulation. Due to the great variance in growing time of crops, this offers a means of increasing the efficiency of the fertilizer for a specific crop. Crops such as radishes which grow to maturity in a very short time can utilize the pulverulent form effectively, while very long term crops such as trees can utilize large granules more effectively. Nitrification of the compounds is the dominant factor in determining rate of availability. This in turn is controlled by the total surface of the granules. Fixation and leaching cannot then immediately begin on the whole mass as is common with soluble fertilizers. Depending on granule size, moisture, temperature, and other factors, nitrification of the insoluble material may proceed at a rate great enough to supply the plant with sufficient nutrients without building up concentrations susceptible to leaching or fixation. Since nitrification takes place most readily at temperatures and moisture levels favoring greatest plant growth, this should also lead to more efficient utilization of the fertilizer. Single heavy applications of large granules can thus be made under crops being grown for very long periods with some assurance that the nutrient supply will correspond with favorable growth periods and be effectively utilized.

The characteristics described also permit fertilizer particles to be enmeshed by roots after a short period of growth. As nitrification takes place, the plant is in a much better position to compete with fixation and leaching processes than if the fertilizer had already diffused into a large volume of soil.

All crops needing supplemental nitrogen, phosphorus, and minor elements, and especially those grown in areas where leaching and fixation of these elements are most pronounced, are logical candidates for use and further research with the metal ammonium phosphates. Situations in which crops could benefit from foliar application,

crops are susceptible to salt injury, and cost of labor for repeated fertilizer application is high would also be good candidates.

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MICRONUTRIENT GLASSES

Properties and Use of Micronutrient Glasses in Crop Production

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The chemical nature and particle-size characteristics of commercially available micronutrient glasses influence the nutrient content of crops. Suitable glasses release micronutrients more steadily than slowly soluble mineral substances, thus far investigated, and have more ability to minimize seasonal variation in elemental content of a crop. This control of release increases freedom to vary application, currently a principal factor limiting use in coarse-textured soils and in commercial fertilizers. Correct levels of reactivity, as measured by nutrient release in ammonium acetate, and pattern of release in soil are considered in terms of nutrient uptake.

INTEREST in slowly soluble micronutrient materials developed after 1927 when Brenchley and Warrington (4) demonstrated that boron is essential to plant growth. The high sensitivity of plants to this element was generally known because boron, as an impurity in certain potassium fertilizers, had caused heavy crop damage (23, 24). Glass products (75, 77) as well as mineral substances (6) were investigated during the 1930's. The results indicated that slowly soluble carriers would be superior to soluble forms under some conditions. However, significant use did not come until about 25 years later. Undefined causes of variation in nutrient content of crops presented much difficulty in evalu-

ating vegetative data. Experimental work was also hindered by a lack of suitable test materials. These obstacles have since been overcome and the information now available is sufficient to permit commercial applications.

Basic Problem

Coarse-textured acid soils, usually low in soluble nutrients, constitute the most compelling reason for development and use of slowly soluble carriers. Soluble nutrients when applied to sandy soils increase the nutrient content of a crop in early growth more than they do on loams or clay soils. Consequently, toxic concentrations are reached in the crop,

especially during germination, at relatively low levels of application. Later in the season, after the applied nutrients have been leached from the root zone (14, 19), deficiencies may develop. With seasonal variation in nutrient level being so great, there is little freedom to vary application, making it difficult to adjust the level of a single application to meet the needs of crops throughout the growing season.

The basic problem is inadequate control of dissolved supply by coarse-textured soils. The soil, being low in colloidal matter, has insufficient capacity to buffer solution concentration by sorption processes. In addition, capillary size is large, and water solutions move down-