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Table V. Carotenoids in Cigarette Blends

| | nmol/g of tobacco | | β-carotene/ |
	β-carotene	lutein	lutein
cigarette A	6.3	25.4	0.26
cigarette B	13.0	27.8	0.47
cigarette C	10.4	30.1	0.34

a trend toward a preferentially greater loss of β-carotene compared to lutein. While there is some variation in carotenoid levels among cured, aged tobaccos (Tables III and IV), the differences between freshly cured and aged tobaccos are greater. As might be expected, stems from cured leaves show the lowest carotenoid levels of all. Typically commercial cigarettes have carotenoid levels similar to those found in cured, aged tobaccos (Table V). These results suggest that the major decomposition of tobacco carotenoids occur during the curing process with continuous decomposition during aging. Such degradation of carotenoids may have important implications for flavor compounds formed from carotenoids by degradation (Fujimori et al., 1976).

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Preparation and Agronomic Evaluation of Long-Chain Crystalline Ammonium and Potassium Ammonium Polyphosphates

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Long-chain crystalline ammonium polyphosphates and potassium ammonium polyphosphates were readily produced by thermal dehydration of orthophosphate or short-chain polyphosphates in a stream of gaseous ammonia. The products were high in total P but low in available phosphorus (citrate + water soluble); however, greenhouse tests showed that they are highly effective sources of nitrogen and phosphorus.

Crystalline ammonium polyphosphates with a chain length greater than 50 have a composition approaching that of ammonium metaphosphate $(NH_4PO_3)_x$. They contain up to 14% N and 73% P_2O_5 and are the most highly concentrated fertilizers obtainable in the ammonium polyphosphate system. Several crystalline modifications have been prepared by heating urea with monoammonium orthophosphate (Shen et al., 1969), and a mixed cation polyphosphate was obtained by the reaction of urea, ammonium orthophosphate, and potassium orthophosphate (Lyons and Vandersall, 1970). The urea serves as a condensing agent by combining chemically with the water released by condensation of the phosphate. Because the urea is consumed in the reaction, a more practical process for the production of these long-chain polyphosphates is desirable. Thermal dehydration of ammonium phosphates produces an amorphous mixture of polyphosphates from which most of the ammonia has been lost (Margulis et al., 1966; Knorre, 1900; Terem and Akalan, 1949). However, laboratory research at TVA showed that long-chain crystalline ammonium or potassium ammonium polyphosphate can be made by simple thermal dehydration of orthophosphates in a stream of gaseous ammonia (Sheridan and McCullough, 1975; McCullough and Sheridan, 1975). Similar processes have been reported in the recent literature (Shen et al., 1969; Vol'fkovich et al., 1972; Hecht et al., 1974a,b).

This paper summarizes the preparation and crop response to N and P of these experimental products in comparison with standard fertilizer sources.

MATERIALS AND METHODS

Chemical analyses of the polyphosphates that were tested as potential fertilizers are shown in Table I. The preparation of these materials is described below.

Preparation of Ammonium Polyphosphates. The long-chain crystalline ammonium polyphosphates have the general formula $(NH_4)_nH_2P_nO_{3n+1}$, where n is about 50 or greater. These compounds are stable, nonhygroscopic, and sparingly soluble in water. They were prepared in the laboratory by thermal condensation of ammonium ortho-, pyro-, tripoly-, tetrameta-, or oligophosphates in a stream of ammonia. The ammonia promotes the formation of long-chain ammonium polyphosphates by preventing excessive loss of ammonia from the reaction bed and by sweeping away the water released by condensation of the ortho- and short-chain phosphates. The products were made in batches and also in continuous-type operations.

In the batch tests, samples usually were heated at 225–300 °C for 4–8 h in a current of ammonia. For example, 20.0 g of crude monoammonium orthophosphate prepared by ammoniation of wet-process phosphoric acid was heated at 225 °C for 8 h in a slow stream of ammonia at atmospheric pressure. The crystalline product weighed 13.4 g, and X-ray analysis showed that it was a mixture of forms I, II, and V long-chain ammonium polyphosphate. Form I has the shortest average chain length of several polymorphic forms having essentially the same chemical

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Table I. Continuous Preparation of Long-Chain Crystalline Ammonium Polyphosphates

	charge			operating conditions							yield		composit., %		mole ratio
	APP						sweep gas								
run	grade	g/h	product recycle, g/h	time, h	temp, °C	mL/g of raw mater.	% NH$_3$	retent. time, h	g of NH$_3$ charged/g of H$_2$O expelled		total g	rate, g/h	N	total P	N:P
1	12.1-61.7-0	24.9	0	0.83	250	1446	50.0	2.5	6.4		18.6	22.4	14.4	31.7	1.00
2	12.1-61.7-0	25.0	0	1.00	250	1440	66.7	3.1	6.5		19.7	19.7	14.3	30.5	1.04
3	12.1-61.7-0	9.3	0	2.25	250	3871	16.7	7.7	3.8		16.3	7.2	12.9	31.0	0.92
4	15-62-0	38.9	0	2.53	250	925	16.7	2.8	1.1		82.4	32.6	14.2	31.7	0.99
5	15-62-0	23.6	0	2.08	250	2034	12.5	3.6	1.9		40.2	19.3	13.8	31.3	0.98
6	15-62-0	26.4	0	4.25	270	886	100	3.4	8.3		87.3	20.5	13.7	30.7	0.99
7	15-62-0	22.2	0	7.30	275	1054	100	3.8	8.9		142.0	19.5	13.8	31.4	1.00
8	15-62-0	15.2	0	6.60	290	1828	49.7	4.3	6.9		91.8	13.9	14.1	31.4	1.00
9	12-57-0	12.5	0	7.00	275	1872	100	5.7	9.5		72.0	10.3	13.4	30.0	1.02
10	15-62-0	57.4	0	6.00	275	1411	100	3.5	10.6		326	54.3	13.3	31.3	0.94
11	15-62-0	29.8	6.0	16.20	275	4027	35.0	9.8	13.1		393	24.3	13.7	31.5	0.96
12	15-62-0	36.6	0	7.50	270	3279	35.0	5.0	9.9		239	31.9	14.0	31.4	0.99
13	12-57-0	50.8	0	7.20	300	2480	100	13.7	12.3		291	40.4	12.9	29.4	0.97
14	12-57-0	54.5	10.9	7.10	300	2312	100	8.7	11.1		318	44.8	12.7	29.7	0.95
15	12-57-0	91.0	30.3	6.60	300	1385	100	6.1	6.9		474	71.8	13.0	29.2	0.98
16	12-57-0	50.0	33.3	6.00	315	2520	100	8.9	11.7		255	42.5	12.8	29.2	0.97

composition; it is converted to forms II–V by tempering at 200–400 °C (Shen et al., 1969). In another batch test crude ammonium tetrametaphosphate (40.1 g) prepared by hydrolysis of P_2O_5 with aqueous ammonia was heated in gaseous NH_3 for 2 h at 240 °C. The product (39.2 g) was over 95% form I long-chain ammonium polyphosphate. Form II was obtained by heating crude ammonium tetrametaphosphate for 5 h at 225 °C in an ammonia stream, and form V was prepared by tempering form I or form II at about 400 °C in a closed tube for 3 h followed by quenching in liquid nitrogen. Both products were homogeneous as form II and form V, respectively.

Long-chain crystalline ammonium polyphosphates were also prepared in a continuous process by feeding ammonium phosphate to a tumbling bed of preformed granular product which was swept continuously with a stream of diluted or undiluted ammonia. The addition of pulverized recycle product to the feed helped to control the particle size of the product and usually lowered the retention time required for the reaction. The quantity of ammonia used to purge the reactor should be equal to or somewhat greater than that required to prepare the ammonium phosphate feed by neutralization of phosphoric acid. This amount of ammonia corresponds to 0.95 g for each gram of water to be expelled, and no recycling is required if this amount is used as the sweep gas because it can be absorbed in phosphoric acid to form more feed. Larger amounts of NH_3 were used in most of our tests, but run 4 (Table I) shows that the process can be operated with only a slight excess of ammonia. Pulverized reagent-grade monoammonium orthophosphate, ammonium polyphosphate from furnace acid (15-62-0) containing 48% ortho-, 50% pyro-, and 2% tripolyphosphate, and ammonium polyphosphate (12-57-0) prepared from wet-process acid and containing 70% ortho-, 21% pyro-, and 9% tripolyphosphate were used as feed materials. Products prepared at 250–275 °C were mixtures of forms I and II, but the products made at 300 °C were almost homogeneous as form II ammonium polyphosphate. The operating conditions and results of several continuous runs are given in Table I.

Potassium Ammonium Polyphosphate. Long-chain crystalline potassium ammonium polyphosphate has the general formula $K_x(NH_4)_yH_2P_nO_{3n+1}$ in which n is greater than 10 and is probably between 20 and 400. The ratio of y/x ranges from 0.25 to 4.0 and $x + y$ is equal to n. The sparingly soluble compound is stable and nonhygroscopic and contains the three primary plant nutrients. Potassium ammonium polyphosphates were prepared by copolymerization of monopotassium orthophosphate and ammonium ortho-, pyro-, or tetrametaphosphates. Tests also showed that a variety of ammonium phosphates and potassium salts could be used, including potassium chloride, potassium carbonate, potassium polyphosphate, and ammonium tri-, tetra-, and long-chain polyphosphates.

The potassium and ammonium salts were mixed together by grinding and then heated at 250–300 °C in a stream of ammonia for 3–16 h. The charges melted and then crystallized after the water of condensation was driven off. Ammonium chloride and carbon dioxide also were evolved in the tests with potassium chloride and potassium carbonate. Paper chromatographic analysis of samples withdrawn from the melt showed that the orthophosphate content decreased rapidly as condensed phosphates formed. Large amounts of short-chain intermediates, mainly pyro- and tripolyphosphates, were formed initially; these species then decreased with time as the concentration of long-chain phosphate continually increased. Most of

Table II. Fertilizer Value of Long-Chain Crystalline Ammonium and Potassium Ammonium Polyphosphates (Measured in Greenhouse with Two 6-Week Crops of Corn on Mountview Silt Loam Limed to pH 6.4)

| material | crystalline form | composition, wt % | | | test no. | relative performance[a] | | | | | |
		N	P total	P avail.		nitrogen response DM	nitrogen response UN	phosphorus response granules DM	granules UP	fines DM	fines UP
Products Derived from Furnace Acid											
$(NH_4)_nH_2P_nO_{3n+1}$	I	14.4	31.8	27.8	A	99	85	125	119	108	107
$(NH_4)_nH_2P_nO_{3n+1}$	II	14.4	31.6	15.2	A	100	86	116	116	99	113
$(NH_4)_nH_2P_nO_{3n+1}$	V	14.2	31.7	8.6	A	98	80	114	120	103	106
$(NH_4)_nH_2P_nO_{3n+1}$	II	14.0	31.4	19.5	B	99	104	87	80	104	99
$K_x(NH_4)_yH_2P_nO_{3n+1}$[b]		6.2	28.1	11.5	A			121	118	109	107
Products Derived from Wet-Process Acid											
$(NH_4)_nH_2P_nO_{3n+1}$	I, II, V	12.5	30.2	12.9	A	96	82	98	100	90	92
$(NH_4)_nH_2P_nO_{3n+1}$	II	12.7	30.0	12.5	B	96	93	82	66	93	95
$(NH_4)_nH_2P_nO_{3n+1}$	II	13.0	29.2	15.0	B	95	95	83	71	96	89
$(NH_4)_nH_2P_nO_{3n+1}$	II	12.8	29.2	12.7	B	94	96	87	69	95	92
$(NH_4)_nH_2P_nO_{3n+1}$	I, II	13.4	30.0	22.3	B	95	94	95	73	108	102
reagent $NH_4H_2PO_4$		12.2	27.0		A			117	89	109	95
					B			106	87	117	110
no N or no P					A	39.3	30.8	19.5	21.8	19.0	20.6
					B	50.1	44.9	26.7	26.4	30.0	32.3

[a] Average of uptake by two crops from two rates of application, compared as N sources against NH_4NO_3 and as P sources against concentrated superphosphate (expressed as percent of yield or uptake of nutrient from standard source; DM = yield of dry matter, UN = uptake of N, UP = uptake of P). Granules were –6 +9 mesh, fines were –35 mesh. [b] Contained 19.0% K, and the ratio x/y was equal to 1.10.

the products were homogeneous crystalline solids with unique optical and X-ray diffraction properties. Only the products made from potassium chloride or ammoniated wet-process phosphoric acid contained impurities.

Most of the preparations were made in small batches; however, in other tests potassium ammonium polyphosphate was prepared continuously in 8-h runs. A mixture of ammonium polyphosphate (fertilizer grade 15-61-0) and monopotassium orthophosphate was added from a powder feeder to a tumbling bed of previously prepared product at 275 °C in a rotating 600-mL stainless steel beaker. The ammonium polyphosphate was a fertilizer made from furnace acid and contained about 50% orthophosphate, 45% pyrophosphate, and 5% tripolyphosphate. The reaction mixture was swept with a mixture of equal volumes of ammonia and nitrogen, and the retention time was 4.5 h. The product was collected as it spilled from the reactor as uniform, white granules. The granules had a high crushing strength, and their composition was that of potassium ammonium polyphosphate with a mole ratio N:K of 1.0. The granules contained 6.48% N, 28.59% P, and 18.26% K. The calculated composition for $K_x(NH_4)_yH_2P_nO_{3n+1}$ with x/y equal to 1.0 and n equal to 100 is 6.50% N, 28.75% P, and 18.15% K.

When mixtures of potassium and ammonium phosphates were heated in air or dry nitrogen, the charges lost ammonia and formed tacky, acidic glasses. Thus, ammonia vapor in the reactor is necessary for the formation of these long-chain polyphosphates.

The mole ratio N:K in the potassium ammonium polyphosphate was found to range from 0.25 to 4.0 with only minor changes in the X-ray diffraction pattern. The X-ray patterns were similar to those of one form of long-chain ammonium polyphosphate and the long-chain potassium polyphosphate known as Kurrol's salt. This behavior indicates that the unit-cell structure of the potassium ammonium salt is the same as that of the ammonium and potassium polyphosphates and that these salts are members of an isomorphous series. Plots of the X-ray data showed that shifts in selected diffraction lines are linear functions of the nitrogen or potassium contents of the polyphosphate. Thus, the ammonium and potassium ions are interchangeable in the unit cell.

Greenhouse Tests. The experimental fertilizer materials were evaluated in the greenhouse against ammonium nitrate as sources of nitrogen and against concentrated superphosphate as sources of phosphorus. The tests were made at two different times, and results were expressed in relation to those obtained with the standard fertilizer in the same test. All tests were made in triplicate in plastic pots that contained 3 kg of Mountview silt loam, an infertile acid soil from Tennessee, that had been limed to pH 6.4 with a mixture of two parts of calcium carbonate and one part of magnesium carbonate.

For evaluation as sources of nitrogen, the compounds were added in amounts to supply 200 or 400 mg of N per pot; and phosphorus (as concentrated superphosphate), potassium (as the sulfate), and a micronutrient mixture were added in amounts to ensure that only nitrogen was the limiting nutrient element. All plant nutrients were mixed thoroughly with the soil.

For evaluation as sources of phosphorus, the compounds were added in amounts to supply 60 or 120 mg of P per pot, and nitrogen (as ammonium nitrate), potassium, and micronutrients were added to ensure that only phosphorus was the limiting nutrient element.

The experimental fertilizer materials were applied as fines (–35 mesh) in the nitrogen tests and as both fines and granules (–6 +9 mesh) in the phosphorus tests. Granular P sources were layered at 2-in. depth, but all fines were mixed with the soil. The granules were prepared by pressing the fines in a laboratory press and crushing and screening the pellets.

The pots were planted with corn [*Zea mays*, Funk's G-76 (test A) or Funk's 4455 (test B)], and the forage was harvested 6 weeks after planting. A second crop of corn was planted 1–2 weeks after harvest of the first crop, and supplemental nutrients were added as required to ensure that only the nutrients under test were the limiting element. The forage of the second crop also was harvested 6 weeks after planting. The harvested forage was dried, weighed, and analyzed for nitrogen by a microKjeldahl method modified to determine nitrate nitrogen or for phosphorus by the vanadate method (Jackson, 1958).

Diclofop-methyl Metabolism in Oat and Wheat

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The results of the greenhouse tests are shown in Table II and expressed as a percent of yield or uptake of nutrients from the standard sources. The response to nitrogen or phosphorus of the standard fertilizers was two to five times that of the no-nitrogen or no-phosphorus controls, thereby assuring valid comparison among the different nutrient sources.

RESULTS AND DISCUSSION

These experiments clearly show that long-chain crystalline ammonium and potassium ammonium polyphosphates are effective sources of N and P. As shown in Table II, all of the long-chain polyphosphates were good sources of N, although N uptake tended to be slightly lower than from ammonium nitrate. The long-chain polyphosphates prepared from furnace acid gave responses equivalent to or higher than that of monoammonium orthophosphate, but those products made from wet-process acid were slightly less effective.

Most of the long-chain polyphosphates were low in available P (citrate + water soluble) and one sample contained only 27% of its total P in an available form, as shown in Table II. Thus, the conventional availability test indicates that these polyphosphates could not be useful sources of P for growing plants. In spite of their low rating in the availability test all were effective fertilizers, and the results from fine and granular sources showed the usual granule size response obtained from water-soluble P sources in Mountview soil. Apparently, the rate of dis-

solution in the soil was sufficient to give agronomic response typical of water-soluble sources. Therefore, the conventional availability test is not valid for these long-chain polyphosphates.

This investigation has shown that long-chain crystalline ammonium or potassium ammonium polyphosphates may be readily produced by thermal dehydration of orthophosphates or short-chain polyphosphates, and these highly condensed phosphates are effective sources of N and P.

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Metabolism and Selectivity of Diclofop-methyl in Wild Oat and Wheat

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Diclofop-methyl (methyl 2-[4-(2',4'-dichlorophenoxy)phenoxy]propanoate) was hydrolyzd rapidly to diclofop (2-[4-(2',4'-dichlorophenoxy)phenoxy]propionic acid) in resistant wheat and susceptible wild oat. Neither compound accumulated in the tissues of either species. The major reactions in wheat are the oxygenation of the 2,4-dichlorophenyl moiety of diclofop, followed by conjugation to an acidic aryl glycoside. In wild oat, diclofop was conjugated as a neutral glycosyl ester. The sugar moiety has not been characterized positively in either conjugate. Only limited symplastic and apoplastic translocation of diclofop-methyl and its metabolites occurred in wheat and wild oat. Herbicide selectivity between wheat and wild oat may be a function of its placement on the plant and the rate of herbicide metabolism, but the ability of wheat to irreversibly detoxify the herbicide by aryl hydroxylation may be the primary selective factor.

The experimental herbicide diclofop-methyl shows considerable promise for control of wild oat (*Avena fatua* L.) and foxtails (*Setaria* spp.) in cereal crops (Friesen et al., 1976; Miller and Nalewaja, 1974). Diclofop-methyl is used mainly as a postemergence herbicide but it also has preemergence activity (Wu and Santlemann, 1976). Root growth was severely inhibited in wild oat but only slightly in wheat (*Triticum aestivum* L.) when intact plants were root-treated in nutrient solution (Hoerauf and Shimabukuro, unpublished data).

Postemergence application of diclofop-methyl inhibited wild oat growth and caused extensive ultrastructural

damage to leaf cells. Growth of wheat was unaffected and ultrastructural damage was less severe than that observed with wild oat (Brezeanu et al., 1976). Diclofop-methyl was a stronger auxin antagonist than diclofop, but the free acid was more effective in inhibiting root growth than the ester (Shimabukuro et al., 1978). The presence of both forms may be necessary for herbicidal action in wild oat (Shimabukuro et al., 1977).

Little is known about the metabolism of diclofop-methyl in plants. Diclofop-methyl was hydrolyzed rapidly to diclofop in both wheat and wild oat (Shimabukuro et al., 1977). A major metabolite of diclofop-methyl in wheat was a conjugate of 2-[4-(2',4'-dichloro-5'-hydroxyphenoxy)-phenoxy]propionic acid (Gorbach et al., 1977). The purpose of our study was to determine the differences in metabolism of diclofop-methyl between wild oat and wheat and relate the differences to herbicide selectivity. This paper also describes the isolation and characterization of

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