

Pyrolysis of Urea Phosphate

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The pyrolysis of urea phosphate, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, was studied in the laboratory at temperatures up to 200 °C. Rate of pyrolysis was relatively slow below 126 °C, but at that temperature a rapid, exothermic reaction began and continued until the pyrolyzate was saturated with ammonia. Then, the reaction became endothermic and relatively slow. The reaction products contained ammonium ortho- and polyphosphates, urea, and small amounts of biuret. The distribution of phosphate species and composition of the pyrolyzates are described in terms of the average chain length. A general equation was developed for the stoichiometry of the pyrolysis of urea phosphate or mixtures of urea phosphate with ammonium orthophosphate, ammonia, or urea.

Concentrated solutions of ammonium polyphosphates are marketed as liquid fertilizers. They are economically prepared from wet-process phosphoric acid; however, impurities in the acid tend to form troublesome precipitates and impart undesirable color. A potential solution to the problems caused by the impurities is to treat the acid with urea to precipitate relatively pure, crystalline urea phosphate, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$. The urea phosphate then is pyrolyzed to form a highly soluble mixture of urea and ammonium polyphosphate (Gittenait, 1973; Nayar and Gopinath, 1971; TVA, 1972).

Schmeltzer and Birnbaum (1869) observed that urea phosphate decomposed upon heating with the formation of metaphosphoric acid, carbon dioxide, and ammonia. Later, Matignon and Dode (1934) found that the decomposition proceeded rapidly at 180 to 250 °C with the formation of insoluble ammonium polyphosphate; and Lundstrom and Whittaker (1937) reported that prolonged heating at 100 °C yielded mixtures of urea, ammonium pyrophosphate, and other condensed ammonium phosphates. More recently, investigators have concentrated on the thermographic analysis and the kinetics of decomposition of urea phosphate (Dusek et al., 1970; Sarbaev et al., 1971, 1972, 1974).

As part of Tennessee Valley Authority's (TVA's) research on solution fertilizers, a study was made of the pyrolysis of this compound as a function of time and temperature and in the presence of nitrogen, ammonia, urea, and monoammonium orthophosphate.

ANALYTICAL METHODS

Standard analytical procedures were used for determination of P_2O_5 , total nitrogen, and ammoniacal nitrogen (Official Methods of Analysis, 1970). Biuret was determined by a spectrophotometric method based on the formation of a colored complex between nickel and biuret (Makarevich and Koyander, 1970). Urea was calculated from the difference between total nitrogen and ammoniacal and biuret nitrogen.

The distribution of phosphorus between the various polyphosphate species was determined by ascending paper chromatography with Ebel's acidic solvent (Ebel, 1954). Chromatograms were eluted for 16 h at ambient temperature on Whatman No. 31 extra-heavy paper cut to the standard wick configuration. The chromatograms were developed under ultraviolet light after being sprayed with an ammonium molybdate-perchloric acid solution, and the

colored strips were cut out and analyzed for phosphorus (Woodis, 1964). The procedure clearly resolved linear polyphosphates up through hepta- or octapolyphosphate.

Most of the average chain lengths, \bar{n} , of the polyphosphates up to \bar{n} of about 2.5 were calculated from chromatographic data by use of the relationship

$$\bar{n} = 100 / \sum_{n=i}^{n=1} \%P_n / n \quad (1)$$

where n represents the number of phosphorus atoms in the different phosphate species. When \bar{n} was above about 2.5, an appreciable fraction of the phosphate existed as species too high to be resolved by the chromatographic procedure and \bar{n} was determined by pH titration (McCullough, 1973). Because ammonia and heavy metals from wet-process acid in the pyrolyzates interfere with the titration, they were replaced with sodium by passage through a column of the sodium form of IR-120 ion-exchange resin about 66 cm high and 3.8 cm in diameter. About 4 g of pyrolyzate dissolved in 10 mL of water was loaded onto the upper inch of the column and then eluted with distilled water at the rate of about 3 mL/min. Most of the sodium phosphate was contained in the 100- to 400-mL fraction of the eluent.

EXPERIMENTAL SECTION

To prepare pure urea phosphate, reagent-grade urea (5 kg) was dissolved by stirring and heating at about 60 °C in the stoichiometric amount of 68% reagent-grade H_3PO_4 . The hot solution was filtered and allowed to cool overnight to deposit crystalline urea phosphate. The coarse crystals were centrifuged, washed on the centrifuge with cold water, and air-dried to constant weight at room temperature. The product (8 kg) contained 17.6% nitrogen and 19.4% phosphorus (theoretical: 17.7% nitrogen and 19.6% phosphorus).

Impure urea phosphate containing 10% of the impurities in an equivalent amount of wet-process phosphoric acid was prepared to simulate the product expected from TVA's urea phosphate process. The material was prepared by evaporating to dryness under vacuum an equal molar mixture of urea and wet-process acid and blending the product with pure urea phosphate.

The pyrolyses were made in a 600-mL stainless steel beaker equipped with gas inlet tubes and a thermocouple well attached to the inside wall. A variable speed stirrer with stainless steel kitchen mixer-type blades was used to obtain efficient mixing and to dissipate foam. The beaker was heated in a constant temperature oil bath.

Samples to be pyrolyzed (50 to 75 g) were added to the reactor and heated to about 112 °C outside of the oil bath to obtain a fluid, partially molten slurry before transferring

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Table I. Regression of Mole Ratio [$R = 2(M - 1) + b(2/\bar{n})$]

Reaction conditions		b	2(M - 1)	S.E.e ^a	S.E.b ^b	r ^c	d.f. ^d
Atm	M						
Pure Urea Phosphate							
N ₂	1.000	1.026	-0.028	0.063	0.041	0.988	16
N ₂	0.800	0.953	-0.403	0.037	0.119	0.963	6
N ₂	0.667	1.019	-0.728	0.033	0.027	0.987	7
NH ₃	1.000	0.995	-0.045	0.057	0.038	0.973	10
Impure Urea Phosphate							
N ₂	1.00	1.164	-0.245	0.041	0.073	0.988	7
NH ₃	1.00	0.910	0.046	0.055	0.103	0.952	9
Overall							
N ₂ or NH ₃	1.00	1.010	-0.038	0.058	0.028	0.983	45
Theoretical							
N ₂ or NH ₃	1.00	1.000	0				
N ₂ or NH ₃	0.800	1.000	-0.400				
N ₂ or NH ₃	0.667	1.000	-0.667				

^a Standard error of estimate. ^b Standard error of regression coefficient. ^c Correlation coefficient. ^d Degrees of freedom.

to the oil bath—pure urea phosphate melts at 117.5 °C, but small amounts of decomposition products lower the melting point and mixtures of urea phosphate with urea or with NH₄H₂PO₄ melt at temperatures as low as 90 °C. The reactor then was transferred to the oil bath and heated at different temperatures from 135 to 200 °C for different periods from 2 to 85 min. There was considerable foaming from the initial fast evolution of CO₂ but the foam was effectively dissipated by the stirrer. In the initial tests, the melt was swept with nitrogen to exclude atmospheric moisture. Although subsequent tests showed that the reactions were too rapid for atmospheric moisture to have had a significant effect, the practice of using nitrogen was continued for the sake of consistency. In other tests, the melt was sparged with ammonia (1 g/min) while in the oil bath to test its effect on the pyrolyses. In some runs the temperature of the reaction mixtures was recorded on a strip chart. After heating for the prescribed period, the reactor was removed from the oil bath and quenched in ice water to stop the reaction and to fix the distribution of phosphate species. Both pure and impure urea phosphate were pyrolyzed. In other tests mixtures of urea phosphate, NH₄H₂PO₄, and/or urea were pyrolyzed.

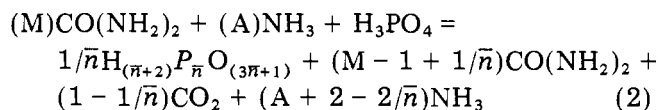
RESULTS AND DISCUSSION

Description of Melts and Products. Molten urea phosphate or molten mixtures of urea phosphate and NH₄H₂PO₄ are fluid and easy to pour or stir, and the melts can be held at temperatures up to 112 °C for several hours without appreciable condensation occurring. However, mixtures of urea phosphate and urea react relatively rapidly above 112 °C, and the rate of reaction increases with increase in the ratio urea:urea phosphate. Urea phosphate can be partially ammoniated at temperatures below 112 °C without appreciable condensation to form molten feed material for a main reactor. Pyrolyses of the melts produced viscous, foamy melts that became progressively more viscous with increasing time and temperature of heating. All of the reaction mixtures in these tests were easily stirred except for the most highly condensed products which formed a stiff, taffy-like mass on the mixer blades near the end of the run.

At room temperature, the products ranged from soft, taffy-like materials containing little condensed phosphate to hard, glassy substances containing large amounts of condensed phosphates. All of the products were mixtures of amorphous phosphates and microcrystalline urea as shown by microscopic examination. Long-chain crystalline ammonium polyphosphate is formed upon prolonged pyrolysis of urea phosphate, but none was detected in these products made at relatively short reaction times. The

pyrolyzates contained 18 to 21% N; up to 14% ammoniacal N; 0.2 to 1.3% biuret N; and 45 to 61% P₂O₅. All of the products were hygroscopic upon exposure to the atmosphere.

Stoichiometry. The general equation for the pyrolysis of urea phosphate or mixtures of urea phosphate with ammonium orthophosphates, NH₃, or urea can be written



M and *A* are the initial mole ratios urea:P and NH₃:P, and \bar{n} is the average chain length of the resulting polyphosphoric acid. *A* and *M* can have any value; however, in practice, values of *M* greater than 1 promote the formation of cyanuric acid and trimetaphosphate, especially when \bar{n} becomes greater than about 4. When *M* is equal to or less than 1, the value of \bar{n} may range from 1 to a maximum value that is determined by $1/(1 - M)$ when all of the urea is decomposed. Ammonia initially present and that released from urea combines with the polyphosphoric acid to an extent determined by stoichiometry and by the stability limitations of the ammonium polyphosphate under the reaction conditions. The equation assumes that no side reactions occur; however, a small amount of biuret is formed. Since water is not involved in the formation of biuret and it was shown experimentally that biuret reacts with phosphate as does urea, the condensation of phosphate is not affected. However, a mole of NH₃ is released for each mole of biuret formed and, thus, slightly more NH₃ is produced than is predicted by the equation.

Inspection of eq 2 shows that the mole ratio, *R*, of urea N to phosphorus in the pyrolyzates is given by the linear equation

$$R = 2(M - 1) + 2/\bar{n} \quad (3)$$

The validity of eq 2 and 3 is shown by results from the regression of mole ratio nonammoniacal N:P on $2/\bar{n}$ (Table I)—corrections for biuret in the regression analysis were not made after it was shown that they had no significant effect on the results. Comparison of the regression coefficients by Student's *t* test showed that there were no significant differences (99% confidence level) between the experimental values and the theoretical values. Also, there were no significant differences (95% confidence level) between pyrolyzates formed in nitrogen and in ammonia or between those prepared from pure and impure urea phosphates. These results show that under the experimental conditions no condensation of phosphate occurs without the decomposition of the stoichiometric amount

Table II. Distribution of Phosphate Species

$$\% N_x = A_0 + A_1(\bar{n} - 1)^{1/2} + A_2(\bar{n} - 1) + A_3(\bar{n} - 1)^{3/2} + A_4(\bar{n} - 1)^2 + A_5(\bar{n} - 1)^{5/2} + A_6(\bar{n} - 1)^3 + A_7(\bar{n} - 1)^{7/2}$$

$A_x^{a,b}$	N_x							
	Ortho	Pyro	Tri	Tetra	Penta	Hexa	Hepta	Octa
A_0	100.73	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A_1	0.0	-63.652	-12.090	0.0	0.0	0.0	0.0	0.0
A_2	-191.22	523.43	50.391	0.0	0.0	0.0	0.0	0.0
A_3	0.0	-732.18	0.0	0.0	0.0	1.9117	0.0	0.0
A_4	243.14	383.64	0.0	21.642	4.0904	0.0	0.84386	0.0
A_5	-171.67	-70.168	-15.804	0.0	0.0	0.0	0.0	0.38395
A_6	35.788	-0.0	0.0	-16.015	0.0	0.0	0.0	0.0
A_7	0.0	0.0	2.8803	5.4692	-0.49525	0.0	0.0	0.0
S	1.3	2.0	1.6	0.9	0.8	0.6	0.6	0.7
d.f.	119	117	116	97	85	57	37	10

^a All constants have Student's $t > 2$. ^b Equations are valid only over the experimental range (\bar{n} from 1.05 to 4).

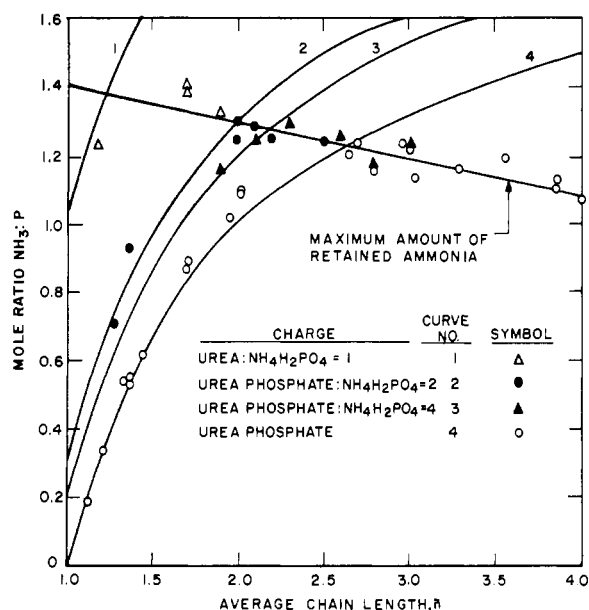


Figure 1. Effect of average chain length on the ammonia retained by the pyrolyzates.

of urea even in the presence of gaseous ammonia.

At the lower values of \bar{n} in urea phosphate pyrolyzates, all the ammonia released from the urea is fixed by the acid. At the higher values of \bar{n} more ammonia is released from the urea than can be accepted by the acid. This is shown by the plot (Figure 1) of the amount of ammonia originally present plus that theoretically released from urea during pyrolysis of mixtures of urea, $\text{NH}_4\text{H}_2\text{PO}_4$, and H_3PO_4 (shown in the figure as curved lines), and of the amount of ammonia retained by the pyrolyzates as a function of \bar{n} . As \bar{n} increases from 1, substantially all of the ammonia is retained by the pyrolyzates until a maximum ratio $\text{NH}_3:\text{P}$ is reached for each mixture where the polyphosphoric acid is saturated with ammonia. With further increase in \bar{n} , the ratio $\text{NH}_3:\text{P}$ decreases almost linearly as determined by the decrease in the ammonia fixing capacity of the acid with increase in \bar{n} (approximately defined in the figure as a straight line).

Between \bar{n} of about 2.6 and 4 urea phosphate pyrolyzates are saturated with ammonia and form aqueous solutions having a nearly constant pH of 6.2. The reason for the constancy of pH despite the decreasing ratio $\text{NH}_3:\text{P}_2\text{O}_5$ with increase in \bar{n} is that the weak acid function of the polyphosphoric acid also decreases with increase in \bar{n} , and the fraction of this weak acid neutralized by ammonia remains almost constant.

Distribution of Phosphate Species. The chromatographic data were treated by multiple regression

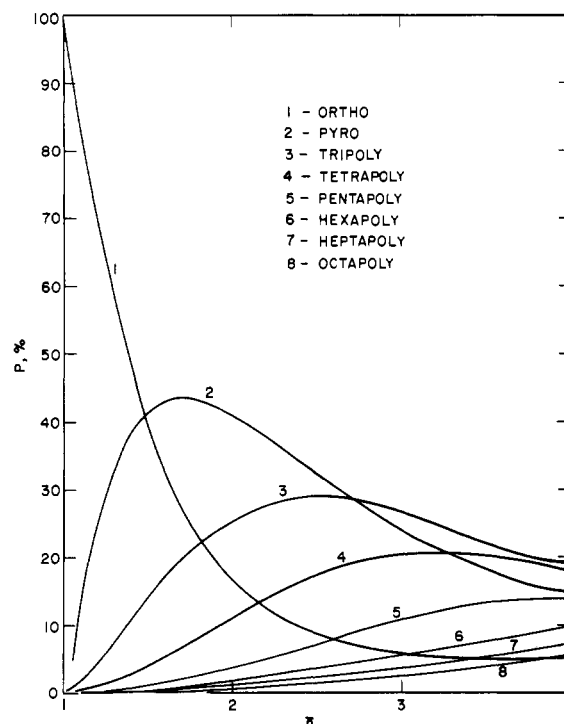


Figure 2. Distribution of phosphate species in quenched urea phosphate pyrolyzates (the temperature of the pyrolyzates before quenching ranged from 135 to 190 °C).

techniques to develop empirical equations for the fraction of phosphorus present as different species (ortho- through octaphosphate) as a function of \bar{n} (Table II). Included were data from pyrolyzates prepared at temperatures from 135 to 190 °C and from both pure and impure urea phosphate and with different amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ (M in eq 2 ranged from 0.67 to 1.0). Within the experimental error, neither the preparation temperature, the impurities, nor the amount of $\text{NH}_4\text{H}_2\text{PO}_4$ affected the results. The plot of the smoothed distribution of phosphate species (Figure 2) shows that polyphosphates in the pyrolyzates are reorganization polymers (Van Wazer, 1958) similar to polyphosphoric acid, and in the amorphous state the distribution is controlled by \bar{n} . Although the distribution pattern is similar to that for polyphosphoric acid calculated from the Jost model (Fleming, 1969), it is different in that the maximum amount of pyrophosphate and the amount of species greater than 4 is less and the amounts of tri- and tetraphosphate are greater.

Biuret. Multiple regression techniques were used to develop an empirical relationship for the biuret content of pyrolyzates as a function of \bar{n} and mole ratios urea:P and $\text{NH}_3:\text{P}$ in the starting material (Table III). The

Table III. Regression of Biuret on \bar{n} and Ratios Urea:P and NH_3 :P

Regression Equation								
$B = C_0 + C_1M + C_2A + C_3\bar{n} + C_4M^2 + C_5A^2 + C_6\bar{n}^2 + C_7M\bar{n} + C_8A\bar{n}$								
Variable					Symbol			
Biuret, mole ratio biuret N:P $\times 100$					B			
Average chain length					\bar{n}			
Mole ratio urea:P					M			
Mole ratio NH_3 :P					A			
Regression coefficient					C_x			
Regression Coefficients ^a								
C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
3.88	-11.22	-8.06	6.12	-2.54	10.57	-2.83	9.48	-4.74
Standard error of estimate					1.14			
Correlation coefficient					0.96			
Degrees of freedom					53			

^a All coefficients, except C_0 , are significant at the 95% or higher confidence level; C_0 is significant at the 70% confidence level.

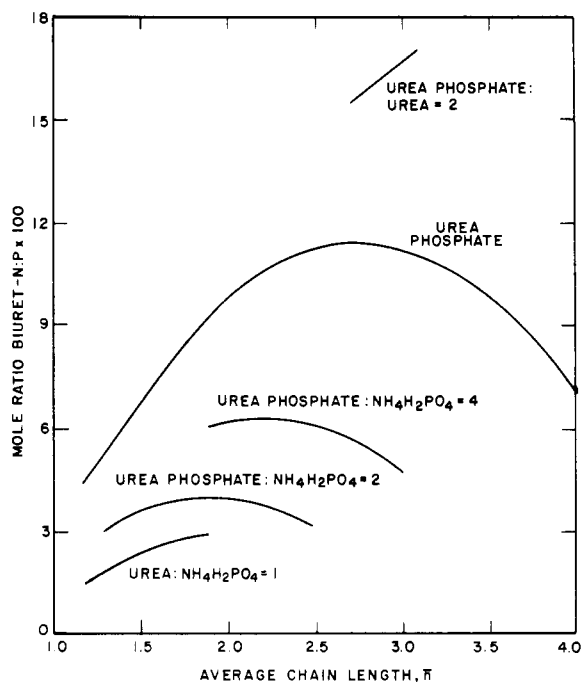


Figure 3. Relationship between average chain length and starting materials on biuret formation.

regression analysis was based on pyrolyzates prepared in nitrogen from pure and impure urea phosphate, mixtures of urea phosphate with $\text{NH}_4\text{H}_2\text{PO}_4$ and/or urea, and mixtures of urea and $\text{NH}_4\text{H}_2\text{PO}_4$. Pyrolyzates prepared in gaseous NH_3 were not included because of uncertainties in the amount of NH_3 and the time at which it was absorbed in the melt. The high value of the multiple correlation coefficient (0.96) and the relatively low standard error of estimate show that the regression equation fits the experimental data quite well. Caution should be used, however, in using the equation outside of the experimental range because it may be unreliable as shown by the high predicted values of biuret at \bar{n} near 1.

The predicted biuret content over the experimental range is plotted as a function of \bar{n} in Figure 3. The biuret content increases with increase in \bar{n} until maximum values are reached, and then it decreases with further increase in \bar{n} . Increase in the ratio urea:P increases biuret while increase in the ratio NH_3 :P decreases biuret. The highest amount of biuret was found in pyrolyzates made from mixtures of urea and urea phosphate. The next highest curve is for biuret in pyrolyzates made from both pure and impure urea phosphate alone—impurities at the level

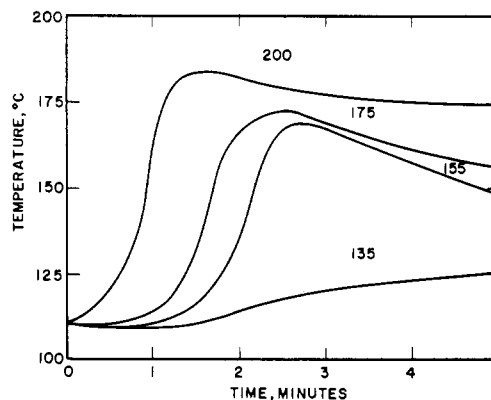


Figure 4. Typical time-temperature curves during pyrolysis of urea phosphate. (Numbers on curves denote temperature, °C, of bath).

tested had no effect on biuret content. In this curve the biuret reached a maximum value at \bar{n} of about 2.7. Pyrolyzed mixtures of urea phosphate and $\text{NH}_4\text{H}_2\text{PO}_4$ gave markedly lower amounts of biuret, and the least amount was produced by heating mixtures of urea and $\text{NH}_4\text{H}_2\text{PO}_4$.

Effects of Time and Temperature. Typical time-temperature curves for the pyrolyses of urea phosphate in nitrogen at different bath temperatures are shown in Figure 4. At the higher bath temperature, the melt temperature rose relatively slowly for the first 0.5 to 1.5 min until a temperature of about 126 °C was reached. The curves then rose steeply and reached maximum values within a period of about 1 min. The temperature then gradually declined on further heating. The maximum melt temperature usually exceeded that of the 155 °C bath and sometimes that of the 175 °C bath. This behavior is consistent with the exothermic nature of the initial pyrolysis, which occurs after the urea phosphate is melted and with the endothermic nature of the subsequent pyrolysis as reported by Sarbaev and Koryakin (1974). These investigators showed also that ammonia did not appear in the gaseous products of the reaction until the exothermic phase of the reaction was almost completed, which was interpreted to mean that the exothermic reaction was caused by neutralization of the acid by ammonia released from the urea. By extension of this logic, the pyrolysis becomes endothermic when the ammonia fixing capacity of the acid is satisfied.

Figure 5 shows plots of weight loss and \bar{n} against time at different bath temperatures. Both weight loss and \bar{n} increased with time and temperature; however, most of the increase occurred during the first 2 to 3 min at the higher

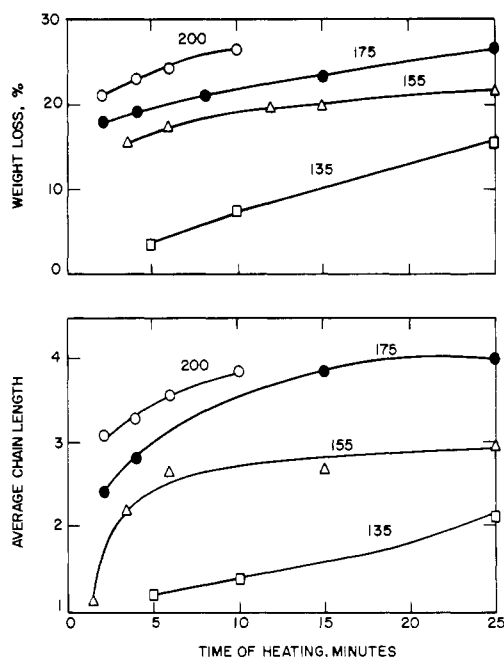


Figure 5. Effect of time of heating of urea phosphate in nitrogen on weight loss and average chain length of pyrolyzate. (Numbers on curves denote temperature, °C, of bath).

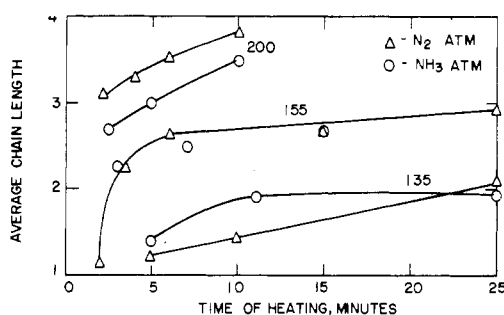


Figure 6. Pyrolysis of urea phosphate in nitrogen and ammonia. (Numbers on curves denote temperature, °C, of bath).

bath temperatures. Only a small weight loss occurred during the first 5 min in the 135 °C bath. Thus, most of the condensation occurred during a period of about 1 min while the melt temperature was rising rapidly. During this time the pyrolysis is exothermic, but after the maximum temperature is reached the pyrolysis becomes endothermic and condensation proceeds at a much lower rate. During the exothermic phase of the pyrolysis at the higher bath temperatures, products were obtained having \bar{n} from 2 to about 2.6 which corresponds to 83 to 92% conversion to polyphosphates.

Effect of Ammonia on Pyrolysis. Injection of anhydrous ammonia into molten urea phosphates while heating at 135, 155, or 200 °C had no visible effect on the pyrolysis. The pyrolyzates contained more ammonia at the lower \bar{n} 's, and the ammonia fixing capacity of the polyphosphoric acid was satisfied at lower \bar{n} 's. However, the relationship between \bar{n} and the ammonia fixing capacity shown in Figure 1 was unaffected. Other effects of the ammonia were to lower the biuret content and to alter the rates of condensation.

The effect of ammonia on the degree of condensation is shown in Figure 6 where the \bar{n} is plotted as a function of time in nitrogen and ammonia at different bath temperatures. At 135 °C, ammonia increased the rate of condensation up to \bar{n} of about 2. At 155 °C, ammonia had little or no effect over the time period studied. At 200 °C,

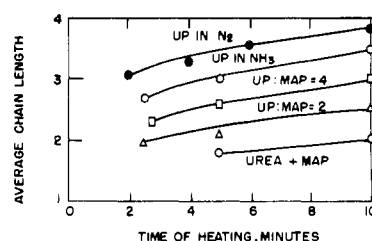
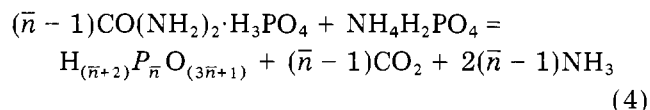


Figure 7. Condensation of urea phosphate at 200 °C in nitrogen, ammonia, and mixed with MAP.

the degree of condensation was decreased by the ammonia over the time period studied. This behavior is attributed to the release of additional heat during the initial phase of the condensation by the reaction of external ammonia with the acid. However, as \bar{n} increases, the degree of ammoniation of the acid becomes identical with or without external ammonia; hence, the total heat released also becomes identical. At \bar{n} 's where the acid is saturated with ammonia, external ammonia retards the condensation because it acts as a coolant.

Effect of $\text{NH}_4\text{H}_2\text{PO}_4$. In an effort to decrease the ratio of urea to phosphate in the products and to decrease biuret formation, mixtures of urea phosphate (UP) and monoammonium phosphate (MAP) were pyrolyzed. If the urea is completely decomposed as in the reaction



then the average chain length is given by the expression

$$\bar{n} = \frac{\text{moles of UP}}{\text{moles of MAP}} + 1 \quad (5)$$

Thus, it is theoretically possible to obtain any desired \bar{n} and to produce pyrolyzates containing no urea by using only the urea needed for the condensation reaction.

Mixtures of urea phosphate and monoammonium phosphate in mole ratios of 2 and 4 were pyrolyzed at temperatures of 150 and 200 °C for periods in the range 2.5 to 86 min. The equation predicts that these mixtures would yield maximum average chain lengths of 3 and 5, but these values were not reached because all of the urea was not decomposed even at the highest temperature and longest heating times. However, products with \bar{n} 's up to 3 were obtained, and there was a marked decrease in the amounts of biuret and urea in the pyrolyzates. This permitted the preparation of solutions higher in P_2O_5 than made from pyrolyzed urea phosphate only.

The \bar{n} 's of the urea phosphate- $\text{NH}_4\text{H}_2\text{PO}_4$ products increased with time and temperature of heating, but the values were lower than those obtained by pyrolysis of urea phosphate alone under the same conditions of time and temperature. The rates of condensation are shown in Figure 7 and compared with the higher rates for urea phosphate alone in ammonia and nitrogen.

Effect of Urea. In further study of the pyrolysis, mixtures of urea phosphate and urea were heated at 150 and 200 °C for periods ranging from 2.5 to 20 min. Mixtures of urea and urea phosphate in mole ratios in the range 0.5 to 1.5 were heated in dry nitrogen. The molten mixtures foamed mildly after 1 to 2 min and the melts were easy to stir during the runs. At room temperature, they were hard solids that crushed readily. The biuret content was higher than that in pyrolyzates of urea phosphate. Most of the products had about the same distribution of phosphate species, as found previously in urea phosphate

pyrolyzates having the same average chain lengths. A few products prepared at 200 °C contained more highly condensed phosphates than any pyrolyzate prepared from urea phosphate under the same conditions of time and temperature, but no long-chain crystalline ammonium polyphosphate was found. Most of these pyrolyzates contained some trimetaphosphate, a ring compound, and the pyrolyzate prepared at 200 °C from the high-urea mixture contained 45% of its phosphate as the trimetaphosphate.

Solubility. A detailed study of the solubility of urea phosphate pyrolyzates was not made, but a few general observations can be reported. Biuret is the first compound to crystallize with increasing concentration of pyrolyzate solutions, and urea usually is the next compound to crystallize, especially at the lower average chain lengths. The ammonium polyphosphates produced by pyrolysis are at least as soluble as those produced by conventional means. No metallic phosphates precipitated from pyrolyzate solutions containing 10% of the impurities in wet-process phosphoric acid. Therefore, the maximum concentration of clear solution fertilizers was limited primarily by the biuret content.

SUMMARY

In conclusion, several points should be emphasized. The pyrolysis of urea phosphate is rapid at temperatures above 126 °C. Most of the condensation of polyphosphate occurs during the first 1 to 2 min when the pyrolysis is exothermic. The addition of anhydrous ammonia enhances the reaction rate initially but later retards it. All water of condensation is released by means of urea hydrolysis and no free water is expelled. The distribution of phosphate species in the pyrolyzates is similar to but not the same as that in superphosphoric acid.

Small amounts of biuret are formed as a by-product. The biuret increases with increase in the average chain length of the phosphate, reaches a maxima at average chain length of 2.7, and then decreases with further increase in

the chain length. It increases with increasing urea in the product and decreases with increasing ammonia content. Pyrolysis of mixtures of urea phosphate and monoammonium phosphate gives products containing less biuret, but the rate of pyrolysis is decreased. The precipitation of biuret limits the grade of clear solution fertilizers that can be made from urea phosphate pyrolyzates.

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Heat Degradation of Carrageenan in a Milk Salt System

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A hydrolytic effect of heat sterilization on carrageenan (Seakem 2) was demonstrated in a synthetic milk salt system. The heat-induced changes in carrageenan included increased electrophoretic mobility on cellulose acetate and agarose, reduced viscosity, increased reducing power, and reduced molecular weight by sedimentation equilibrium centrifugation. The apparent weight average molecular weight decreased by 42% after 20 min of heat treatment at 122 °C. The hydrolytic process was a first-order random degradation with a velocity constant at 122 °C approximately twice as large as has been reported for heat degradation of carrageenan in aqueous solution at pH 7.0. The increased hydrolysis in the milk salt environment was attributed to a drop in pH which occurred during heating of that system which was greater than for normal milk. The ultracentrifuge analysis revealed that sodium carrageenate in 0.05 M sodium cacodylate buffer (pH 7) containing 0.25 M sodium chloride at 35 °C undergoes a reversible, pressure-dependent dissociation. At 20 000g species were produced with weight-average molecular weights of 8.5×10^4 for unheated samples and 5.1×10^4 daltons for samples previously heated in a milk salt system at 122 °C for 15 min. Extrapolation to zero speed indicated a molecular weight of 2.3×10^5 for the undissociated, unheated carrageenan aggregate.

Carrageenan is used as a stabilizer in a number of manufactured milk products, including evaporated milk

and sterilized infant milk formulas. The mechanism by which the products are stabilized is still not well understood, but appears dependent upon the protein reactivity and polymer size of carrageenan (Snoeren et al., 1975).

The heat degradation of carrageenan in aqueous solution has been studied by Masson (1955), Masson and Caines

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