Figure 1. Infrared curves

a. 4-Hydroxymethylproline
b. Peanut acid crystals
c. N-methylhydroxyproline

Nuclear magnetic resonance data confirmed this. The melting point of the peanut acid crystals was not depressed on admixture of the synthetic compound and infrared analysis showed the two compounds to be identical (Figure 1).

No record of the isolation of N-methylhydroxyproline from an edible source has been found. However, it was isolated from the bark of *Croton gubougia* (5) in 1919, and more recently from the heartwood of *Afrormosia elata* (10). *N*-methylhydroxyproline was synthesized by Leuchs and Felser (8) by methylation of hydroxyproline. Since the synthetic material from hydroxy-L-proline prepared by their method was proved identical with the material isolated from peanuts, the identity of the peanut product as N-methylhydroxyproline is established. Morgan (10) reports that the 4-hydroxy-N-methyl-L-proline isolated from *Afrormosia elata* is levorotatory. As the hydroxyproline derivative from peanut flour is also strongly levorotatory, it may be concluded that this compound is also 4-hydroxy-N-methyl-L-proline.

Since this material has never been reported as a constituent of an edible product, its role in nutrition as well as in plant metabolism should be determined. The new compound could possibly serve as a methyl donor.

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FERTILIZER STABILITY

Decomposition of Mixed Fertilizers during Drying

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LARGE scale continuous processes and the use of high proportions of ammoniating solutions containing heat-sensitive salts have led to considerable difficulty in maintaining nitrogen guarantees during the manufacture of high analysis mixed fertilizers. A survey conducted by TVA (6) showed that the nitrogen content of 10–10–10 (10–4.37–8.30 NPK) and 12–12–12 (12–5.24–

9.96) grade fertilizers was consistently low. About half of the samples were deficient in nitrogen to an extent that exceeded the tolerances set by state laws. In these cases the manufacturers gave assurances that the nitrogen input was at least equal to and usually more than that guaranteed.

As part of the same investigation, a pilot plant study on the manufacture of 12–12–12 (12–5.24–9.96) grade fertilizers disclosed that the loss of nitrogen, in a form that would explain why the losses

could not be detected by scrubbing samples of exhaust gas, resulted from the decomposition of ammonium nitrate to form N_2O or N_2. Near the distributors of the pilot plant ammoniator there were localized areas of high acidity and observed temperatures as high as 260° F. Such conditions favor serious loss of nitrogen by decomposition of ammonium nitrate.

Stability of pure ammonium nitrate has been studied extensively (3–5, 7), and in the temperature range 210° to

Rate of decomposition of fertilizer mixtures prepared from reagent grade materials increased rapidly with temperature from 85° to 180° C. and as the pH changed from 3.9 to 2.8. In the absence of chloride ion there was no significant decomposition but addition of only 0.05 weight % chloride caused substantial loss of nitrogen. When either the nitrate or ammonium ion was missing no nitrogen loss occurred. Decomposition was found to result from the hydrolysis of monocalcium phosphate to give dicalcium phosphate and phosphoric acid; the latter reacted with ammonium nitrate or chloride to release nitrous oxide, elemental nitrogen, and chlorine. Addition of ammonium or potassium sulfate to the mixtures inhibited decomposition by preventing hydrolysis and the formation of phosphoric acid.

500° F. 98% of the decomposition has been found to occur as follows:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad (1)$$
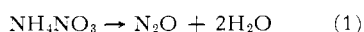
A reversible and endothermic dissociation reaction also takes place.

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \qquad (2)$$
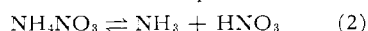
The presence of impurities has a significant influence on the decomposition of ammonium nitrate. Relatively small amounts of chloride and free acid may cause spontaneous decomposition at temperatures as low as 140° C.

Stability of ammonium nitrate in the presence of the salts commonly associated with it in commercial fertilizers and some of the factors influencing this stability were investigated by Borland and Schall (2), who gave particular attention to the effect of chloride, hydrogen, ammonium, and nitrate ions on stability. Decomposition was found to be extremely sensitive to the presence of chloride and free acid, but the presence of both ammonium and nitrate ions was required for significant nitrogen losses to occur. The stability of the fertilizer mixture was increased when sulfate-containing salts were present. Losses dropped markedly with increasing sulfate concentration and reached a minimum when the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. The fact that equimolar quantities of sulfate ion to ammonium nitrate were required was interpreted as evidence that the $NH_4NO_3.(NH_4)_2SO_4$ double salt may have been involved, but no data were obtained to support this.

The present investigation deals with stability problems encountered primarily during the drying and subsequent operations in the manufacture of mixed fertilizers. The effects of composition, pH, and temperature have been studied. A series of reactions has been proposed which accounts for nitrogen and chloride losses and explains the stabilizing effect of ammonium sulfate and potassium sulfate in fertilizer mixtures.

Experimental Method

Fertilizer mixtures made from reagent grade materials were prepared batchwise as needed. One hundred-gram portions were ground in a large mortar to ensure thorough mixing of the samples. The weighed samples were placed in a tared flask, stoppered with a vented cork, and held in a constant temperature bath at the desired temperature. Periodically the flask was withdrawn, allowed to cool, and after the adhering oil was removed, weighed and returned to the bath for another heating period. The loss in weight was recorded each time the sample was withdrawn, and the loss in weight of each constituent was determined from the initial and final analysis of the samples.

In a number of runs, the gaseous products were collected and analyzed to determine the amount of Cl_2, N_2, and N_2O produced. A schematic drawing of the apparatus is shown in Figure 1. The 500-ml. round-bottomed flask, which was used as the reactor, was connected to a series of absorbers fitted with fritted glass bubblers. The first absorber was charged with a 10% potassium iodide solution and the second was filled with potassium hydroxide pellets. From the absorbers, the gas passed through a U-tube, which was immersed in a dry ice-acetone bath, and then into the gas collector, a calibrated glass cylinder with a small opening at one end which was sealed with a serum cap. Gas samples were withdrawn from the collector through the serum cap with a hypodermic syringe and analyzed chromatographically.

Table I. Composition of 12-12-12 (12-5.24-9.96) Grade Fertilizer Control Mixtures

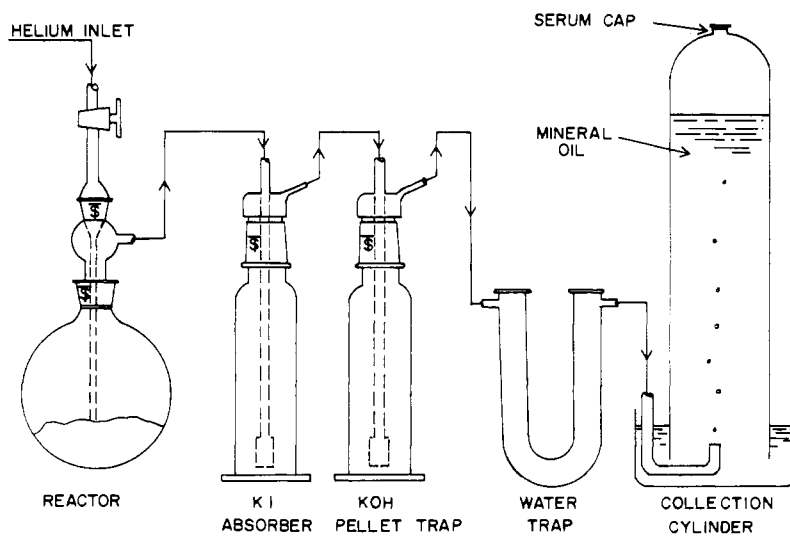| Ingredients	Mixture, G.					
	A	B	C	D	E	F
NH_4NO_3	12.40	12.40	12.40	...	...	...
NH_4Cl	29.50	...	29.50	45.90	...	37.80
$(NH_4)_2SO_4$	...	36.00	...	...	...	...
$NaNO_3$	...	...	...	...	59.70	13.20
$Ca(H_2PO_4)_2.H_2O$	21.30	21.30	...	21.30	21.30	21.30
$CaHPO_4$	...	...	23.00	...	...	...
KCl	19.00	...	19.00	19.00	3.40	19.00
K_2SO_4	...	22.20	...	...	...	...
KNO_3	...	...	...	...	15.60	...
Sand	17.80	8.10	16.10	13.80	...	8.70

Figure 1. Gas collection apparatus

In the first absorber, Cl_2 was removed from the gas by reaction with the potassium iodide to liberate free iodine. The second absorber removed all acid-forming gases such as HCl, NOCl, and NO_2 which may have been present in small quantities. Any water vapor in the gas was condensed as it passed through the U-tube to the collector. Only N_2 and N_2O were present in the gas collected in the cylinder.

At the beginning of a run a 25-gram fertilizer sample was transferred to the reactor and the system was purged with helium for 15 minutes to ensure complete removal of air. The delivery tube was then inserted into the collection cylinder, which was filled with light mineral oil, and the reactor was placed in the constant temperature bath. After heating for the desired time, the system was again flushed with helium to ensure complete transfer of the gaseous reaction products through the absorbers and into the collector. The reactor containing the sample was then weighed to determine the total weight loss. By chemical analysis, the amounts of chloride, ammoniacal nitrogen, and nitrate nitrogen lost were determined. From the gas analysis, it was possible to determine the amount of chloride recovered as Cl_2 and the amount of nitrogen recovered as N_2 and N_2O.

The chromatographic determination of N_2 and N_2O was carried out on an F & M Scientific Corp. Model 500-A linear - programmed temperature gas chromatograph. A $1/4$-inch o.d. copper tube, 2 meters long, and packed with Alcoa F-1 activated alumina, $-30+60$ U. S. standard mesh, was used to separate the two gases. Helium served as the carrier gas, and a flow rate of 30 ml. per minute was maintained through the column, which was kept at a temperature of 100° C. Under these conditions, the retention times were 5.8 and 12.3 minutes for N_2 and N_2O, respectively. Samples of the gas to be analyzed were injected into the column, and the amounts of N_2 and N_2O were determined by relating peak area and volume to the values obtained with known amounts of each gas under identical conditions.

The compositions of the 12-12-12 (12-5.24-9.96) grade fertilizer control mixtures are presented in Table I. Mixtures B to F are similar to control mixture A, except that from each formulation one of the four ions—Cl^-, H^+, NH_4^+, or NO_3^-—was eliminated in order to determine the effect of each ion on the stability of the fertilizer. Modifications of the control mixtures were prepared in which the concentrations of the chloride, hydrogen, and sulfate ions were varied, to gain some idea of the effect of concentration of these ions on the stability of the fertilizer samples.

Effect of Temperature

Samples of mixture A were heated in the constant temperature bath for up to 8 hours. Losses were determined at 85°, 100°, 120°, 130°, 140°, and 180° C. The results, shown in Figure 2, indicate that the losses increase rapidly as the temperature is increased. At 85° C. there was no loss other than moisture, but at 100° C. there was some loss of nitrogen and chloride, indicating that decomposition had occurred at this temperature. At 180° C. the losses leveled off at 16.80 grams after only 1 hour of heating. The losses included 90% of the nitrate nitrogen originally present. Chloride and ammoniacal nitrogen losses were substantial, but potash and total P_2O_5 content remained unchanged.

In addition to total P_2O_5, analyses were made to check the extent of reversion of the water-soluble monocalcium phosphate to citrate-soluble dicalcium phosphate. At 85° C. there was no reversion of the monocalcium phosphate, but at the higher temperature levels significant amounts of dicalcium phosphate were formed during heating. Almost 50% of the water-soluble P_2O_5 had reverted to the citrate-soluble P_2O_5 at 180° C. The reversion reaction is as follows:

$$Ca(H_2PO_4)_2 \cdot H_2O \rightarrow$$
$$CaHPO_4 + H_3PO_4 + H_2O \quad (3)$$
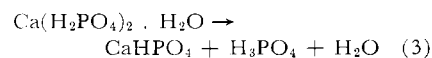
Equation 3 is important because the free acid formed enhances the decomposition of ammonium nitrate, particularly in the presence of chloride.

Experimental runs were made with mixture A in which the gas products were collected and analyzed. The studies were carried out at three temperature levels: 120°, 130°, and 140° C. The principal products were Cl_2, N_2, and N_2O. Table II shows that an average of 82.70% of the chloride lost from the samples was recovered as Cl_2. Material balances for nitrogen are presented in

Table III. An average of 86.78% of the total nitrogen lost was recovered as N_2 and N_2O. The weight ratio of N_2O to N_2 was constant at about 2.13 to 1.00 over the temperature range investigated. Although temperature effects the rate of decomposition, it does not alter the course of the reactions taking place.

The nature of the gas products indicates that the principal reaction involved in the nitrogen and chloride loss is between ammonium nitrate and ammonium chloride. Besson and Rosset (1) found that what actually occurs is a reaction between nitrogen dioxide, an intermediate in ammonium nitrate decomposition, and ammonium chloride as follows:

$$8NO_2 + 6NH_4Cl \rightarrow$$
$$4N_2O + 3N_2 + 3Cl_2 + 12H_2O \quad (4)$$
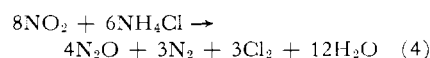
According to this equation, the weight ratio of N_2O to N_2 should be 2.09 to 1.00, very close to the weight ratio of 2.13 to 1.00 which was observed. In addition, Equation 4 indicates that the nitrate nitrogen loss should be slightly greater than the ammoniacal nitrogen loss, a fact which was also confirmed experimentally.

The nitrogen dioxide involved in Equation 4 is a product of nitric acid decomposition. Nitric acid can be produced in the fertilizer in several ways. The most important is probably the reaction of the free phosphoric acid formed by Equation 3 and ammonium nitrate.

$$H_3PO_4 + NH_4NO_3 \rightarrow$$
$$NH_4H_2PO_4 + HNO_3 \quad (5)$$
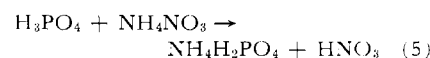
Another possibility is the dissociation of ammonium nitrate:

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \quad (6)$$
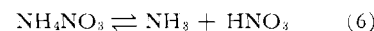
However, at the temperatures used in

Table II. Recovery of Chloride from 25-Gram Samples of Mixture A, Heated 8 Hours

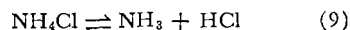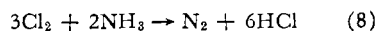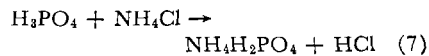| Run	Temp., °C.	Cl⁻ Lost G.	Cl⁻ Lost %	Cl⁻ Recovered as Cl₂ G.	Cl⁻ Recovered as Cl₂ %
A-3-R-5	120	0.4428	6.21	0.3614	81.62
A-3-R-6		0.3493	4.96	0.2887	82.65
A-4-R-5	130	0.7223	10.14	0.5753	79.65
A-4-R-6		0.7003	9.89	0.5902	84.28
A-5-R-4	140	1.0583	14.76	0.9029	85.32

Table III. Recovery of Nitrogen from 25-Gram Samples of Mixture A, Heated 8 Hours

| Run	Temp., °C.	N₂ Lost G.	N₂ Lost %	N₂ Recovered, G. N₂	N₂ Recovered, G. N₂O	Recovery, %	Weight[a] Ratio, N₂O:N₂
A-3-R-5	120	0.3324	11.15	0.1195	0.1595	83.94	2.10
A-3-R-6		0.2619	8.68	0.1000	0.1280	87.06	2.01
A-4-R-5	130	0.6606	22.09	0.2570	0.3465	91.36	2.12
A-4-R-6		0.6541	21.78	0.2204	0.3168	82.13	2.26
A-5-R-4	140	0.8814	29.26	0.3294	0.4588	89.42	2.19

[a] N_2 recovered as N_2O is converted to equivalent grams N_2O to calculate weight ratio.

this work, the dissociation may not be significant.

It is likely that most of the chloride not recovered as Cl_2 was lost as HCl. Several side reactions which would result in formation of HCl are:

$$H_3PO_4 + NH_4Cl \rightarrow$$
$$NH_4H_2PO_4 + HCl \quad (7)$$

$$3Cl_2 + 2NH_3 \rightarrow N_2 + 6HCl \quad (8)$$

$$NH_4Cl \rightleftharpoons NH_3 + HCl \quad (9)$$

Since the fertilizer is distinctly acidic, the following reaction may also occur:

$$HNO_3 + 3HCl \rightarrow$$
$$NOCl + Cl_2 + 2H_2O \quad (10)$$
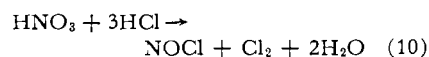
This reaction would also account for some of the nitrogen which was not recovered as N_2 or N_2O. Most of the nitrogen which was not recovered was probably lost as NH_3, HNO_3, or NO_2. No attempt was made to isolate these gases.

Effect of Chloride Ion

One hundred-gram samples of mixture B which contained no chloride were heated in the constant temperature bath at 130° C. for 16 hours. An observed loss of only 2.10 grams indicated that the presence of chloride was necessary for significant decomposition to occur. Modifications of control mixture B were prepared in which the chloride concentration was varied from 0.05 to 10% by replacing increasing amounts of ammonium sulfate with ammonium chloride. With the addition of only 0.05% chloride, the losses increased markedly and reached a plateau at the 0.50 level. The losses did not change as the chloride concentration was increased beyond 0.50% (Figure 3).
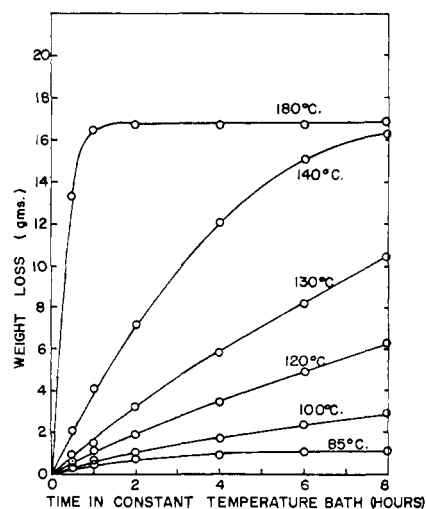
In the mixture which contained no

chloride, the nitrogen lost was almost all ammoniacal nitrogen. This is in contrast to the results obtained with mixture A, where the nitrate nitrogen loss was always somewhat greater than the ammoniacal nitrogen loss. It is evident that when chloride is not present, the reactions involved in the decomposition are not the same. The nitrogen loss in the absence of chloride in mixture B may be due to the decomposition of ammonium sulfate which is present in high concentration.

$$(NH_4)_2SO_4 \rightarrow NH_3 + NH_4HSO_4 \quad (11)$$
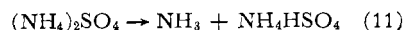
The addition of chloride even in trace amounts increases the nitrate nitrogen loss. At a chloride concentration of 0.50%, the total nitrogen loss is again divided between ammoniacal nitrogen and nitrate nitrogen in the same manner as in mixture A.

Effect of Acidity

The acidity of mixture C was varied by preparing 100-gram samples in which the relatively neutral dicalcium phosphate was replaced by increasing amounts of the acidic monocalcium phosphate. The samples, ranging in pH from 2.80 to 6.30, were heated in the constant temperature bath at 130° C. for 16 hours. The pH was determined by suspending a 1-gram sample in 10 ml. of water adjusted to pH 7.00.

A sharp drop in weight loss from 15.68 to approximately 1.00 gram was observed as the pH increased from 2.80 to 3.90. In the sample of pH 2.80, the weight loss included 89.63% of the nitrate nitrogen, 15.83% of the ammoniacal nitrogen, and 13.24% of the chloride present in the preheated sample. In samples of pH greater than 3.90, no losses were observed other than moisture.
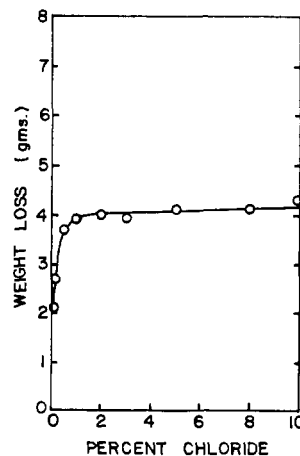
Effect of Ammonium and Nitrate Ions

Samples (100-gram) of mixture D from which the nitrate ion was absent and mixture E which contained no ammonium ion were heated in the constant temperature bath at 130° C. for 16 hours. The losses in weight were 1.54 and 1.49 grams, respectively. Analyses showed that these losses were moisture only. Mixture F, in which the nitrate ion was supplied by sodium nitrate and the ammonium ion by ammonium chloride, lost 15.31 grams upon heating at 130° C. for 16 hours. Thus, the presence of both ions is required for decomposition to occur. They need not be supplied by ammonium nitrate, since equivalent losses occurred when the ions were supplied by other ammonium and nitrate salts.

Effect of Sulfate Ion

Since the experiments with mixture B indicated that the sulfate ion tended to stabilize the mixture, this effect was further investigated. A series of samples containing increasing amounts of sulfate ion was prepared from a sulfate-free mixture G. The basic formula of this mixture was: 12.40 grams of NH_4NO_3, 29.40 grams of NH_4Cl, 21.40 grams of $Ca(H_2PO_4)_2.H_2O$, and 36.80 grams of sand. The sulfate content was varied from 0.0% to a maximum of 35.0% by replacing sand with increasing amounts of $(NH_4)_2SO_4$, K_2SO_4, or $CaSO_4$. One hundred-gram samples of the mixtures were heated in the constant temperature bath for 16 hours at 130° C.

Losses from the mixtures in which the sulfate was added as $(NH_4)_2SO_4$ or K_2SO_4 dropped sharply as the concentration of sulfate ion increased and reached a minimum of approximately

Figure 2. Effect of temperature on decomposition of 100-gram samples of mixture A

Figure 3. Effect of chloride concentration on decomposition of 100-gram samples of mixture B, heated 16 hours at 130° C.
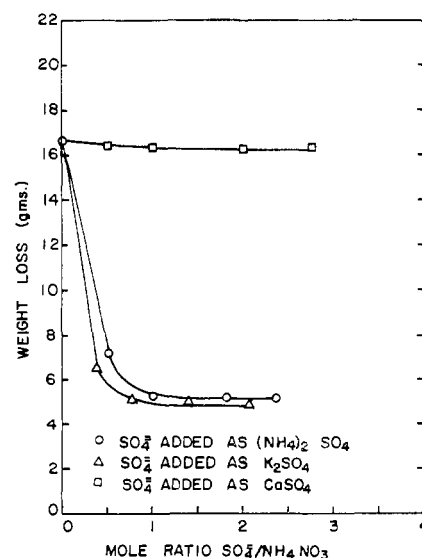

Figure 4. Effect of sulfate ion on stability of 100-gram samples of mixture G, heated 16 hours at 130° C.

Table IV. Effect of Sulfate Ion on Reversion of Water-Soluble P_2O_5 in 100-Gram Samples of Mixture G, Heated 16 Hours at 130° C.

Sulfate Salt Added	% SO_4^{-2}	Water-Soluble P_2O_5, G. Before	Water-Soluble P_2O_5, G. After	Citrate-Soluble P_2O_5 after Heating, G.
	0.00	11.92	7.24	4.68
$(NH_4)_2SO_4$	7.21	11.98	8.67	2.31
	14.58	12.02	11.89	0.13
	26.76	12.16	12.07	0.09
	34.98	12.07	11.96	0.11
K_2SO_4	5.52	11.87	9.04	2.83
	11.02	11.97	11.80	0.17
	20.28	12.04	11.94	0.10
	28.43	12.01	11.87	0.14

Table V. Nitrogen and Chloride Losses from 100-Gram Samples of Mixture G, Heated 16 Hours at 130° C.

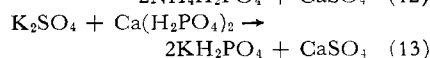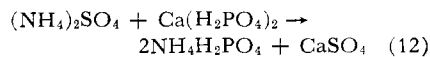| Sulfate Salt Added	% SO_4^{-2}	Total N Lost, G.	Cl^- Lost, G.
	0.00	4.24	3.97
	0.00	4.11	3.84
$(NH_4)_2SO_4$	7.21	1.13	0.92
	14.58	0.47	0.33
	26.76	0.44	0.39
	34.98	0.43	0.31
K_2SO_4	5.52	1.85	1.78
	11.02	0.67	0.39
	20.28	0.46	0.32
	28.43	0.40	0.29

5.0 grams at a sulfate content of 11%. Whether the sulfate was supplied by the ammonium salt or the potassium salt, the 5.0-gram level was approached as the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. As can be seen from Figure 4, the addition of sulfate as $CaSO_4$ did not have the same stabilizing effect.

Results of the P_2O_5 analyses in Table IV show that the reversion of water-soluble P_2O_5 to citrate-soluble P_2O_5 is reduced by the addition of sulfate as $(NH_4)_2SO_4$ or K_2SO_4. At a sulfate concentration of 11% almost all of the P_2O_5 remained in the water-soluble form. Nitrogen and chloride losses were also reduced considerably as the sulfate concentration increased (Table V).

X-ray diffraction studies were made on two of the heated samples: in one the sulfate was supplied by the ammonium salt and in the other, by the potassium salt. Because of the complexity of the mixtures, it was difficult to identify the compounds. In the mixture where the

sulfate was added as ammonium sulfate, $NH_4H_2PO_4$, NH_4Cl, $CaSO_4$, and $(NH_4)_2SO_4$ were identified. Compounds identified from the mixture in which the sulfate was added as potassium sulfate were KH_2PO_4, NH_4Cl, $CaSO_4$, and K_2SO_4.

The results of the P_2O_5 analyses and the x-ray diffraction studies indicate that the following reactions probably occur:

$$(NH_4)_2SO_4 + Ca(H_2PO_4)_2 \rightarrow 2NH_4H_2PO_4 + CaSO_4 \quad (12)$$
$$K_2SO_4 + Ca(H_2PO_4)_2 \rightarrow 2KH_2PO_4 + CaSO_4 \quad (13)$$

These reactions explain why the P_2O_5 remains water-soluble if sufficient ammonium sulfate or potassium sulfate is present in the mixture. Reactions 12 and 13 are also important in inhibiting the decomposition of the fertilizer because with the removal of calcium as insoluble, thermostable calcium sulfate, the reversion of the phosphate to citrate-soluble dicalcium phosphate cannot occur. This prevents the formation of free phosphoric acid according to Equa-

tion 3. With the control of the free acid in the mixture Reactions 4, 5, and 7 cannot proceed and the decomposition is effectively stopped. It is evident from Equations 12 and 13 that addition of the sulfate to the fertilizer as calcium sulfate would not stabilize the mixture. This was confirmed experimentally.

The maximum stability of the fertilizer was obtained as the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. However, considering Reactions 12 and 13, it would appear that the maximum stability should be obtained when the mole ratio of sulfate ion to monocalcium phosphate approaches 1 to 1. In Figure 5, the weight loss from mixture G has been plotted against the $SO_4^{-2}/Ca(H_2PO_4)_2$ mole ratio. Maximum stability was obtained when the ratio was slightly more than 1 to 1, and to confirm the significance of this ratio, mixture H was prepared in which the ammonium nitrate concentration was
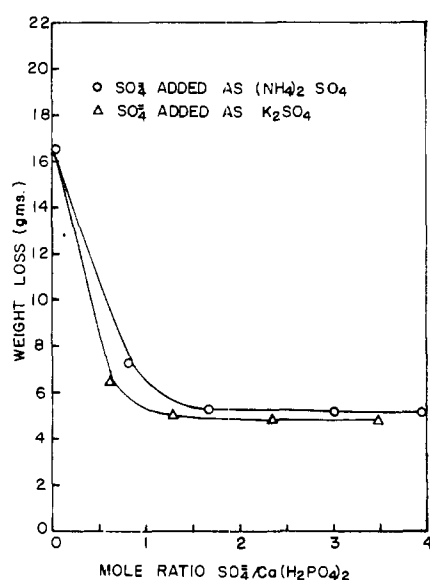

Figure 5. Effect of sulfate ion on stability of 100-gram samples of mixture G, heated 16 hours at 130° C.
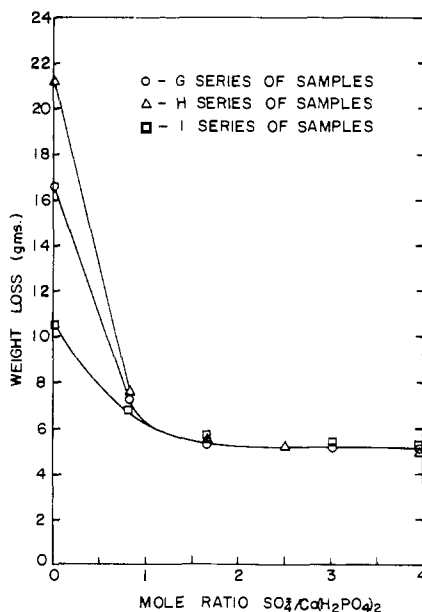

Figure 6. Weight loss data for G, H, and I series of mixtures, plotted against $SO_4^{-2}/Ca(H_2PO_4)_2$ mole ratio
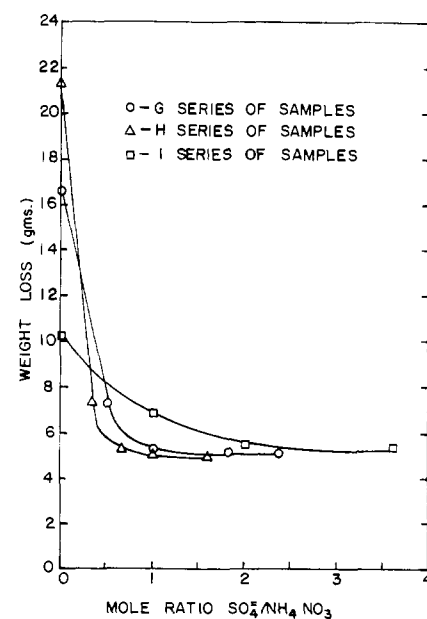

Figure 7. Weight loss data for G, H, and I series of mixtures, plotted against SO_4^{-2}/NH_4NO_3 mole ratio

50% greater than in mixture G. The sulfate concentration was varied in the same manner as with mixture G. Weight loss was greater in mixture H than in mixture G, but dropped sharply as the sulfate concentration increased and approached a minimum of 5.0 grams as the mole ratio approached 1 to 1.

Mixture I, which contained 50% less ammonium nitrate than mixture G, did not lose so much weight as mixture G, as was expected. The losses again reached a minimum at about the same mole ratio of sulfate ion to monocalcium phosphate as in mixture G and H. For comparison of the results of the runs made with the G, H, and I series of samples, the weight loss data for all runs were plotted against the $SO_4^{-2}/Ca(H_2PO_4)_2$ mole ratio in Figure 6 and the SO_4^{-2}/NH_4NO_3 mole ratio in Figure 7. Maximum stability is obtained in all three mixtures as the $SO_4^{-2}/Ca(H_2PO_4)_2$ mole ratio reaches 1 to 1. This is not true as the SO_4^{-2}/NH_4NO_3 mole ratio approaches 1 to 1 in the fertilizer mixtures. In mixture H, maximum stability is reached at a SO_4^{-2}/NH_4NO_3 mole ratio of 0.5 to 1, and in mixture I, at a 2 to 1 mole ratio.

These results indicate that an important factor in inhibiting the decomposition is to prevent the formation of free acid in the mixture. This can be accomplished by adding either ammonium sulfate or potassium sulfate to the fertilizer.

Conclusions

The stability of laboratory fertilizer mixtures was found to be dependent upon temperature, acidity, concentration of chloride and sulfates, and the presence of both ammonium and nitrate ions. Under certain conditions decomposition of the samples was initiated at temperatures as low as 100° C. and the rate of decomposition increased rapidly with temperature. Nitrogen, nitrous oxide, and chlorine were identified as the principal gaseous reaction products.

A key reaction in decomposition was the hydrolysis of monocalcium phosphate, which resulted in the formation of dicalcium phosphate and phosphoric acid. Reaction of the acid, ammonium nitrate, and ammonium chloride caused substantial losses of nitrogen and chloride from the fertilizer mixtures. The effects obtained in these tests are those which would be observed during the commercial manufacture of fertilizer blends where unammoniated superphosphate is used. The stabilizing effect of ammonium sulfate or potassium sulfate in the fertilizer blends was conclusively demonstrated.

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FERTILIZER MATERIALS

Characterization of Some Ammonium Polyphosphates

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Methods of preparation and crystallographic properties are described for six ammonium pyrophosphates, six ammonium tripolyphosphates, an ammonium nitrate pyrophosphate, and a long-chain ammonium polyphosphate. The information will be useful in identification of these compounds in ammonium polyphosphate fertilizers.

AMMONIUM polyphosphate fertilizers, products of the reaction of ammonia with superphosphoric acid (10), are mixtures of the ammonium salts of ortho-, pyro-, and more highly condensed phosphoric acids. As these materials are finding increasing use as fertilizers, the properties of their individual components are being studied. Fourteen of these components are described here—six pyrophosphates, six tripolyphosphates, a long-chain polyphosphate, and an ammonium nitrate pyrophosphate.

The sodium and potassium salts of condensed phosphoric acids have been studied extensively (12), but the ammonium salts have been neglected because they have been thought to be unstable and difficult to prepare as pure compounds. Studies of the solubilities of the ammonium pyro- (5) and tri-polyphosphates, however, showed these salts to be easily prepared and moderately stable.

Ammonium salts of condensed phosphoric acids are reported in the literature (3, 4, 7, 8, 11, 12), but their crystallographic descriptions are incomplete, and some of the reported compositions are in error.

Preparation and Characterization

All the salts were either prepared from recrystallized reagents or obtained as solid phases in solubility determinations (5). Characterizations were made only on preparations that were shown by petrographic examination to be homogeneous and well crystallized, gave consistent x-ray powder diffraction spectra, and had the same chemical composition from preparation to preparation.

Chemical analyses were made on air-dried preparations to prevent dehydration or other alteration which might occur above room temperature. The hydrate water contents of some of the preparations, which were determined by difference, are slightly high. All the preparations were examined by paper chromatography to verify the phosphate species. Phosphorus was determined photometrically (6) and ammonia was determined by distillation with sodium hydroxide.

Morphological and optical properties were determined with a polarizing microscope. Densities of all the salts were calculated from their chemical compositions and refractive indices by the Gladstone-Dale relationship (9); densities of coarsely crystalline materials were determined also from single-crystal x-ray data.

X-ray diffraction spectra were obtained with a Norelco high-angle goniometer and CuKα radiation ($\lambda = 1.5405$ A.). Lattice constants and space-group