

Thermal Decomposition of High Analysis Fertilizers

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High analysis fertilizers offer advantages to the manufacturer and the user, and each year many thousands of tons are made, shipped, and used, mostly without incident. There are occasional reports of fires, however, which show that these mixtures of chemicals must be handled properly. This paper shows some of the conditions that lead to fires, and how the products can be handled safely.

THIS STUDY of the thermal decomposition of high analysis fertilizers concerns only those that have been completely processed or have at least reached the drying stage. It does not deal with flash fires in ammoniators or fires due mainly to the action of nitric acid upon organic matter.

The type of decomposition dealt with here is due to inorganic reactions, though limited amounts of urea or other organic compounds do not necessarily prevent it. It may occur even in fertilizers that are well ammoniated. The reaction requires a high temperature for starting, but it is self-sustaining when once initiated, and will spread throughout the available mass of fertilizer. The heat of reaction may raise the temperature in the active zone to 732° F. (400° C.) or higher, and there is plentiful emission of fumes that smell strongly of chlorine. In this paper the onset of this sort of self-sustained decomposition is called "ignition."

Such decomposition destroys the fertilizer itself, and the heat is likely to damage buildings and equipment. Still more serious is the danger of toxic fumes, and protection of personnel should be the first consideration in any fire control effort. As the reaction does not require air, the liberal use of water is the only generally practical way of stopping it.

This type of decomposition was discussed by Drobot before the Division of Fertilizer and Soil Chemistry of the American Chemical Society in September 1957 (7).

The higher the temperature, the sooner ignition occurs. Considering the six fertilizers of principal interest here, spontaneous ignition occurred promptly (within about an hour) at temperatures from 410° to 482° F. (210° to 250° C.). At 338° F. (170° C.), ignition times of 96 to 600 hours were observed. At 302° F. (150° C.), only three of the six fertilizers ignited spontaneously, requiring 675 to 1700 hours. None ignited at 266° F. (130° C.), though ignition at this temperature has been observed occasionally in other fertilizers. Spontaneous

ignition at 212° F. (100° C.) would not be expected, and it did not occur during this investigation.

Tests included analyses of the gases evolved before and during self-sustaining decomposition, a few analyses of the residual solids, and measurements of the rate at which gas was evolved. In most of the latter tests that were run at 302° F. (150° C.) or higher, heating was continued until self-sustaining decomposition set in. Other tests to show the conditions required for ignition were also made.

Although most of the work was done on fertilizers made in the pilot plant or produced commercially, other materials were tested, including mixtures of ammoniated superphosphate with fertilizer salts, and fertilizers with organic admixtures. The data on blends with ammoniated superphosphate showed that although both chloride and nitrate are needed for the type of decomposition under consideration, the concentration of one or the other can be rather low without preventing the reaction. The organic materials tend to inhibit the reaction.

Materials Tested

The most complete series of tests was run on a set of six fertilizers, each made on a pilot plant or commercial scale. Table I gives information about these products, including the process and the principal ingredients, the analyses, and the calculated compositions in terms of single compounds.

Three of the six were 12-12-12 fertilizers, made by different processes and differing widely in nitrate content. Two were of 16-8-8 grade, and differed mainly in that one contained urea, supplied as an ingredient of the ammoniating solution, while the other did not. The last fertilizer of the set was a 15-0-14, distinguished by its high dolomite content as well as its lack of phosphate.

The calculated compositions (Table I) are based upon the formulations, and

are not entirely consistent with the analyses, though the differences are considered insignificant in the present connection. Reasonable assumptions were made concerning the compositions of the superphosphates and the reactions occurring during ammoniation. It was also assumed that enough liquid phase was present to permit interactions among the salts, and that solid salts would be formed in inverse order of solubility. The small amounts of sodium salts that are indicated would come from sodium chloride, assumed to be the principal impurity in the potassium chloride.

The dominant potassium salt appears to be the sulfate, except in the 12-12-12 nitrates, which contains a large proportion of potassium nitrate. In all the other five cases the principal nitrate is the ammonium salt, and calculations indicate that in every case the chloride is present as ammonium chloride.

Other materials on which special tests were made are described in connection with the tests.

Test Procedures and Results

Large samples, 15 to 20 pounds, were held at elevated temperatures for a number of days or weeks, with periodic sampling of the gases evolved. The container that was used is a 19-inch length of 6-inch stainless steel pipe with ends welded on. A 1-inch connector holds a union that serves as a charging port and also holds a rupture disk and vent. There are a thermocouple well and another nipple that serves as a sampling tube and also provides a connection for a pressure gage. The sample container is submerged in an electrically heated, thermostatically controlled fused salt bath.

The valve of the sampling tube is normally left open so that the evolved gas can escape. When the first gas sample is to be taken from a fresh charge in the container, the gas is pumped from the container, and the valve is closed. The pressure gradually increases, and a

Table I. Ingredients, Analyses, and Compositions of Test Fertilizers

Grade	12-12-12 ^a	12-12-12 ^a	12-12-12 ^b	16-8-8 ^c	16-8-8 ^a	15-0-14 ^a
Process	Batch ammoniation	Prereactor	Nitrphosphate	Prereactor	Prereactor	Prereactor
Ammoniating agent	Nitrana ^{e,d}	Nitrana ^c	NH ₃	Nitrana ^c	Urana ^e	Nitrana ^c
Acid in prereactor	...	H ₂ SO ₄	...	H ₂ SO ₄	H ₂ SO ₄ and H ₃ PO ₄	H ₂ SO ₄
Principal sources of P ₂ O ₅	Normal and concd. superphosphate	Normal and concd. superphosphate	Phosphate rock	Normal and concd. superphosphate	Normal superphosphate	...
Dolomite, lb. per ton	None	20	None	20	20	490
Analysis, wt. %						
Ammoniacal N	11.30	8.60	7.02	11.74	11.10	10.52
Nitrate N	1.45	3.90	5.32	4.26	4.42	4.61
Urea N	0	0	0	0	1.13	0
Total N	12.75	12.50	12.34	16.00	16.65	15.13
Water-soluble P ₂ O ₅	7.47	5.59	2.23	4.35	2.98	0
Citrate-insoluble P ₂ O ₅	0.17	0.12	0.0	0.35	0.05	0
Total P ₂ O ₅	12.15	12.28	12.14	8.30	8.43	0
Water-soluble K ₂ O ^f	12.74	12.04	Not detd.	8.04	8.29	14.3
H ₂ O	2.4	0.9	1.1	0.4	0.8	1.0
Organic C	0.15	0.13	0.07	0.05	Not detd.	Not detd.
Cl	10.1	9.32	9.37	6.30	6.64	10.7
pH in water	5.0	5.1	Not detd.	5.4	5.5	6.1
Compn. calcd. from formulation, wt. %						
NH ₄ Cl	14.8	15.1	14.9	9.8	9.9	17.2
NH ₄ NO ₃	7.9	19.2	11.1	29.0	27.5	25.1
(NH ₄) ₂ SO ₄	22.2	14.1	12.4	4.3
NH ₄ H ₂ PO ₄	9.3	9.3	6.3	5.8	5.2	...
KNO ₃	...	3.0	26.8
NaNO ₃	1.2
Urea	2.5	...
K ₂ SO ₄	22.8	20.5	...	15.2	15.0	26.3
Na ₂ SO ₄	1.1	1.1	...	0.6	1.0	1.4
CaHPO ₄	5.2	...	15.5
Ca ₃ (PO ₄) ₂	6.5	12.3	...	8.7	9.7	...
(Fe and Al)PO ₄	1.7	1.8	1.6	1.3	1.2	...
CaSO ₄ and MgSO ₄	2.0	11.3	16.5	9.9	11.1	0.2
Dolomite or calcite	...	0.9	...	0.9	1.0	24.4
H ₂ O	2.4	0.9	1.1	0.4	0.8	1.0
Other (CaF ₂ , SiO ₂ , etc.)	4.1	4.6	5.0	4.3	2.2	0.1

^a Pilot plant product.

^b Commercial product.

^c Nitrana. 19.0% NH₃; 72.5% NH₄NO₃; 8.5% H₂O.

^d Urana. 19.5% NH₃; 66.3% NH₄NO₃; 6.0% urea; 8.2% H₂O.

^e Sample also contained 766 pounds (NH₄)₂SO₄ per ton.

^f In all six fertilizers, K₂O supplied as fertilizer grade KCl.

Table II. Analysis of Gases Evolved by Fertilizers Held at 338° F. (170° C.) Prior to Ignition of Fertilizer

Product	Time of Sampling from Start of Test, Hours	Weight %						
		H ₂ O	CO ₂	NH ₃	N ₂ O	N ₂	NO ^a	Cl ₂ ^b
12-12-12								
By batch ammoniation	43	16.9	76.7	0	1.83	3.04	0.99	0.54
	67	17.8	11.8	0	4.87	64.6	0	0.92
By prereactor	99	14.44	13.98	0	4.27	66.93	0	0.38
Nitrphosphate	24	80.3	5.5	1.0	0.12	13.1	<0.1	0
	48	74.4	7.7	0.9	0.06	17.0	0	0
	72	71.5	7.8	0.7	0.06	20.0	0	0
	96	61.2	7.3	0.6	0.09	30.8	0	0
	168	65.2	2.3	0.2	1.5	30.8	0	0
16-8-8								
By prereactor (Nitrana)	8	3.84	44.56	0.05	0.22	51.33	0	0
	73	0.52	26.58	None	1.93	70.97	0	0
	174	4.48	3.69	0.16	5.00	86.67	0	0
By prereactor (Urana)	6	1.43	83.45	5.85	0.04	9.20	0.03	^c
	124	0.91	37.19	1.34	0.37	60.19	0	^c
	197	0.26	38.62	0.89	0.31	59.92	0	^c
	289	17.94	42.47	0.29	0.17	39.09	0.04	^c
	363	0.72	56.70	0.37	0.21	42.00	0	^c
15-0-14 by prereactor	23	3.36	76.25	20.4	0	0	0	0
	66	5.68	67.00	27.48	0	0	0	0
	142	5.67	63.18	30.69	0	0	0	0

^a May include NO, NO₂(N₂O₄), NOCl, and HNO₃.

^b May also include some NOCl and HCl.

^c No analysis made for this component.

gas sample is taken when it reaches a convenient value, 10 p.s.i. or more. The valve is then left open until sampling is to be repeated.

Table II shows analyses of gases evolved by the six fertilizers at 338° F. (170° C.) at various times prior to ignition. Table III shows analyses of samples of 12-12-12 nitrphosphate held at 338° F. for two different periods short of ignition, and also shows very limited data on a 16-8-8 before and after heating.

Even larger samples of fertilizer are used when the gas evolved during self-sustained decomposition is to be analyzed. The container is a steel box, approximately a 1-foot cube with a vent, and an electrically heated sampling tube. The box is covered with magnesia insulation. The fertilizer is ignited by playing an oxyacetylene flame on the outside of the box, blocks of insulation being temporarily removed to permit this. During the active combustion a portion of the gas is run through an absorption train, or into a number of gas-sampling balloons. Table IV shows analyses of both gas samples and solid residues.

Because this work extended over more than a year, there was some variation in methods of analysis, which were adaptations of well known procedures. In brief, the procedures were as follows:

Water. When balloon samples were used, pyridine was admitted to one balloon, and the water in the pyridine was determined by a Karl Fischer titration. In an absorption train, the bulk of the water was caught in an ice-cooled trap, and the remainder was taken up by Dehydrite, which was weighed. In one run water was determined by difference.

Carbon Dioxide. The details depended upon the sampling procedure used, but in any event the carbon dioxide was finally weighed after absorption on Ascarite.

Chlorine. An aqueous solution obtained from the absorption train, or a sample from a balloon, was treated with 3% hydrogen peroxide, which reduced chlorine to chloride, and this was determined by a modified Volhard procedure. Though the results were calculated to elemental chlorine, it is likely that small amounts of nitrosyl chloride and hydrochloric acid were included.

Ammonia (Free or in Sublimed Salts). This was determined by Kjeldahl distillation of an aqueous solution obtained from the absorption train or a balloon sample.

Nitric Oxide and Nitrogen Dioxide. An aqueous solution of these acid-forming oxides of nitrogen was treated with hydrogen peroxide, and the nitrogen was determined by the Devarda procedure. Any nitric acid—from sublimed ammonium nitrate, for example—would be included, and so would any nitrogen evolved as nitrosyl chloride.

Nitrous Oxide. This was determined

Table III. Changes in Fertilizers Prior to Ignition When Held at Elevated Temperatures

	12-12-12 Nitrphosphate		16-8-8 by Prereactor (Nitrana)	
	45	87	0	672
Hours in test	45	87	0	672
Temp., ° F. (° C.)	338 (170)	338 (170)	302 (150)	302 (150)
Total N, %	11.73	11.23	16.00	12.85
Ammoniacal N, %	6.63	6.29
Water-soluble P ₂ O ₅ , %	1.17	1.54
Citrate-insoluble P ₂ O ₅ , %	0.08	0.05
Total P ₂ O ₅ , %	13.02	13.18
Cl, %	9.82	9.94
H ₂ O, %	0.43	0.38
pH	4.05	3.85	5.4	3.4

Table IV. Products of Self-Sustained Decomposition

	12-12-12		16-8-8 by Prereactor	
	By prereactor	Nitrphosphate	Nitrana	Urana
Residue analysis, wt. %				
Initial sample	67.5	60.1	55.0	59.0
Ammoniacal N	2.59	0.01	4.57	2.70
Nitrate N	0.05	0.06	0.03	^a
Urea N	0	0	0	^a
Total N	2.64	0.07	4.60	3.13
Total P ₂ O ₅	17.8	20.6	12.80	14.7
Water-soluble P ₂ O ₅	1.53	0.29	6.95	3.58
Citrate-insoluble P ₂ O ₅	2.22	10.4	1.88	1.82
K ₂ O	18.86	^a	12.27	13.6
Cl	9.7	8.67	1.3	2.6
H ₂ O	0.22	0.12	0.27	0.25
pH	3.3	^a	2.2	2.8
Analysis of gas during decomposition, wt. %				
H ₂ O	62.0	56.0	30.3	68.4
CO ₂	3.82	0.10	6.52	1.64
NH ₃	2.57	0	3.02	3.82
N ₂ O	10.01	12.0	12.23	6.64
N ₂	16.07	22.7	39.02	17.46
NO ^b	0.0	2.58	0.97	0.0
Cl ₂ ^c	5.56	6.63	7.94	2.08

^a Not determined.

^b Includes nitrogen of NO, NO₂, HNO₃, and NOCl, all calculated as NO.

^c May also include some chlorine combined as NOCl and HCl.

by infrared spectrophotometry, using either a balloon sample or the non-condensable gases from the absorption train.

Nitrogen was determined by difference.

Rate of Gas Evolution

The rates at which gas was evolved by the different fertilizers at elevated temperatures were measured. The procedure is simple, repeated measurements can be made on the same sample, and the rate gives a general idea of the activity of the decomposition. When the main gas-producing reaction is known to be exothermic, the results give a relative idea of the rate at which heat is being generated. Changes in the rate of gas evolution suggest changes in the nature or relative extents of the reactions.

Figure 1 is a schematic view of the apparatus.

The sample containers are 200-ml. round-bottomed flasks, with the single neck ending in the socket of a ball joint. Except during actual measurements, the flasks containing samples are kept immersed to their necks in an oil bath at

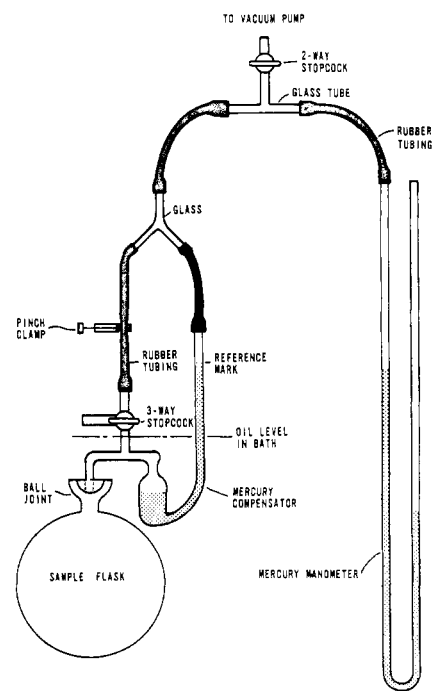


Figure 1. Apparatus for measuring rate of gas evolution

Table V. Gas Evolution and Spontaneous Ignition

Time Held at 338° F., Hr.	12-12-12			16-8-8 by Prereactor		15-0-14
	By batch	By pre-	Nitra-	Nitrana		by Pre-
	ammoniation	reactor	phosphate	Urana		reactor
Gas Evolution Rates, at 338° F., Mmoles/(Hr.)(100 G. Sample)						
25	1040	580	100	480	40	1330
50	1150	620	85	650	75	1210
75	1180	690	82	920	110	830
100	...	810	88	1430	155	560
150	...	1210	133	3330	250	300
200	268	...	375	220
250	510	160
300	675	130
350	860	...
400	1070	...
450	1300	...
500	1540	...
550	1810	...
Total gas evolved prior to ignition, g.-mole/100 g.	0.102	0.179	0.044	0.253	0.484	0.163
Time for spontaneous ignition at stated temp., hr.						
302° F. (150° C.)	800 ^a	850	1700	675	2000 ^a	2500 ^a
338° F. (170° C.)	96	192	240	152	600	324
374° F. (190° C.)	22	15	25	20	57	134
Temp. for sponta- neous ignition in 1 hr., ° F. (° C.)	437 (225)	437 (225)	410 (210)	450 (232)	457 (236)	482 (250)

^a Failed to ignite in this period.

Table VI. Fertilizer Temperatures for Self-Sustained Decomposition

Grade	Nitrate N, %	Cl, %	Self-Sustained Decompn. after Ignition with Fertilizer	
			95° F.	176° F.
12-12-12				
Batch ammoniation	1.45	10.1	No	No
Prereactor	3.90	9.32	Yes	Yes
Nitrphosphate	5.32	9.37	Yes	Yes
16-8-8				
Prereactor (Nitrana)	4.26	6.30	Yes	Yes
Prereactor (Urana)	4.42	6.64	Yes	Yes
15-0-14, prereactor	4.61	10.7	No	Yes
18-9-9 with K ₂ SO ₄	9.98	0.48	No	No
10-10-10 with N from urea and NH ₃	0	7.8	No	No
16-8-8, commercial	1.77	6.58	No	No

the test temperature, completely unstoppered. The volume of each flask is determined, as is the volume of the compensator assembly up to the three-way stopcock on one side and the reference mark on the other. The working volume comprises the sum of the volumes of the flask and compensator, diminished by the volume of the mercury and the sample. The true density of the fertilizer, needed for computing the volume, is determined by displacement of acetone in a graduated cylinder. With the stopcocks and pinchclamp closed, the pressure of the gas can be computed from the barometric pressure, the manometer reading, and the previously determined pressure required to force the mercury in the compensator up to the reference mark.

At the start of a measurement, the absolute pressure in the sample container is reduced to about 50 mm. of mercury below atmospheric pressure, and it is usually allowed to rise to about 50 mm. above atmospheric pressure. Each measurement is made with the mercury adjusted to the reference mark,

and the elapsed time is recorded. Results are expressed as micromoles of gas per hour per 100 grams of fertilizer.

Measurements on separate samples were made at 374° F. (190° C.), 338° F. (170° C.), 302° F. (150° C.), 226° F. (130° C.), and 212° F. (100° C.). When practical, they were continued until the samples had ignited. Ignition that happened to occur during a measurement was obvious, for the rapid flow of gas forced the mercury out the tubes. In the intervals between measurements, the temperatures of the samples were monitored with thermocouples connected to a recorder, and ignition of a sample appeared as a sudden rise in temperature. The occurrence of ignition could also be told by a change in the appearance of the sample, and in doubtful cases a portion was analyzed to show whether a large loss of nitrogen had occurred.

The gas evolution data from tests at 338° F. (170° C.) are representative, and are shown in Table V, the rates at

round numbers of hours having been taken from plots of the rates of gas evolution against time. In these plots, the areas under the curves, up to the times of ignition, represent the total numbers of moles of gas evolved in the preignition periods, as given in the table.

The effect of temperature upon the rate of gas evolution is of great interest, but it is clear from inspection of Table V that no single rate of gas evolution can be stated for a given fertilizer at a given temperature. However, the effect of temperature is shown well by special calculations based on data for one of the fertilizers, the 16-8-8 by prereactor, made with Nitrana solution. For this fertilizer, the numbers of hours required for evolution of 10,000 micromoles of gas were calculated to be:

Temp., ° F.	Temp., ° C.	Hours
374	190	2
338	170	21
302	150	68
266	130	812
212	100	Over 2400

In fact, the total evolution of gas in 2400 hours (100 days) at 212° F. was calculated to be only 2800 μmoles.

Table V also gives the ignition times of the six fertilizers at various test temperatures. The temperatures for short-time ignition, approximately 1 hour, were determined by heating samples of the fertilizers in test tubes immersed in an oil bath, the temperature of which was raised at about 3° to 5° F. per minute. Ignition was shown by a sudden rise in the temperature of the sample, so that it was higher than the bath temperature, and by fuming.

Minimum Pile Temperature for Self-Sustained Decomposition. When the reaction provides ample heat for its own propagation, the initial temperature of the fertilizer makes little difference, but if the reaction generates barely enough heat, self-sustained combustion will occur only if the pile of fertilizer is somewhat hot to begin with. Just how hot it must be will depend upon a number of things, including the quantity of fertilizer, the nature of the container, the rate at which heat is applied, and the intensity and size of the source of heat. Under fixed test conditions, the required pile temperature should be fairly reproducible.

Figure 2 shows the apparatus used for the measurements reported here. The pipe is filled with the fertilizer, and three thermocouples are placed with their junctions 3, 9, and 15 inches, respectively, from the metal plate. The pipe was kept horizontal for the measurements shown here.

At the beginning of a test, the charge is brought to the desired temperature,

and an oxyacetylene flame is played upon the steel plate until its center is red hot, 5 minutes or less if ignition is evident sooner. If self-sustaining decomposition occurs, the progress of the reaction is shown by successive large increases in temperature at the three thermocouples. There is also heavy fuming.

Table VI shows the results of tests at two initial temperatures, 176° F. (80° C.) and 95° F. (35° C.). In a rough way, these represent the material entering the pile and the final pile temperature in summer storage. Four of the six fertilizers continued to burn when ignited by the hot metal, even with the initial temperature as low as 95° F., the 15-0-14 ignited only with the mass temperature 176° F., and the 12-12-12 made by batch ammoniation would not ignite with the mass at either temperature. No heat source of relatively short life, such as a burning brand or fertilizer bag, would be likely to ignite a pile of this 12-12-12.

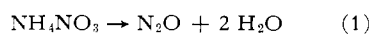
Table VI shows results of tests on three other fertilizers as well, a low-chloride 18-9-9, a 10-10-10 with all nitrogen supplied as either ammonia or urea, and a commercial 16-8-8 of moderate nitrate content. None of these three could be ignited with the mass at either temperature.

Additional tests, not reported in detail here, showed that the range of pile temperatures needed to permit ignition by a flame extends at least from 40° F. (5° C.) to 284° F. (140° C.). Presumably there is no real upper limit, as some fertilizers should not undergo self-sustaining decomposition at any temperature.

Discussion

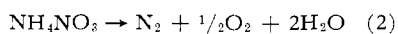
There is a tendency to treat the reactions of high analysis fertilizers such as these as being due solely to the ammonium nitrate that they contain, but the facts do not bear this out. The presence of chloride is evidently important.

Two important decomposition reactions of ammonium nitrate are:



$$\Delta H_{410^\circ \text{F.}} = -51,900 \text{ B.t.u.}$$

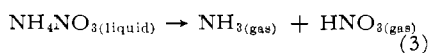
$$\Delta H_{662^\circ \text{F.}} = -62,100 \text{ B.t.u.}$$



$$\Delta H_{410^\circ \text{F.}} = -86,900 \text{ B.t.u.}$$

$$\Delta H_{662^\circ \text{F.}} = -96,900 \text{ B.t.u.}$$

These reactions are highly exothermic, but there is one that absorbs heat:



$$\Delta H_{410^\circ \text{F.}} = +39,900 \text{ B.t.u.}$$

The rate of this reaction is such that when ammonium nitrate is freely exposed,

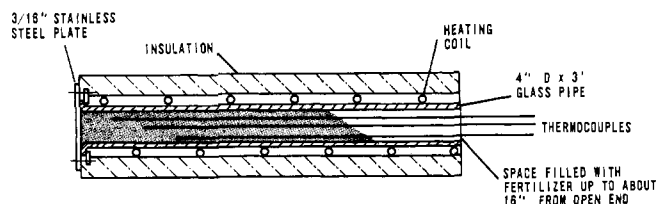
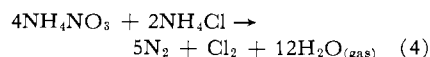


Figure 2. Apparatus for determining fertilizer temperature necessary for self-sustained combustion

so that the gases can escape, its decomposition is not self-sustaining, but ceases when the external supply of heat is cut off.

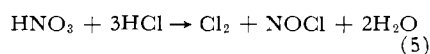
A mixture of ammonium nitrate and ammonium chloride can react as follows:



$$\Delta H_{410^\circ \text{F.}} = -508,000 \text{ B.t.u.}$$

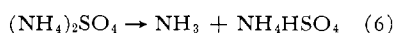
$$\Delta H_{662^\circ \text{F.}} = -554,000 \text{ B.t.u.}$$

The chloride ion has an additional effect, in that it is known to catalyze the decomposition of ammonium nitrate according to Equation 2, without accelerating the dissociation into ammonia and nitric acid. As most fertilizer mixtures are distinctly acidic, there is also a chance that the following reaction will take place:



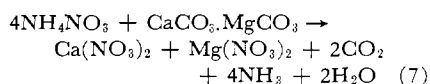
In at least one case the presence of nitrosyl chloride was shown by its infrared absorption spectrum, but it is believed that Reaction 4 is generally of greater importance in the decomposition of fertilizers such as these.

There may be some loss of ammonia from ammonium sulfate:



However, the data in Table II indicate that this reaction is unimportant, at least before ignition.

The following reaction no doubt occurs in all of the fertilizers containing both ammonium nitrate and dolomite, especially the 15-0-14:



Part of the ammonia may be oxidized before it escapes. This reaction removes ammonium nitrate from the mixture, thus hindering Reactions 1 to 4. It also tends to make the mixture somewhat less acidic, by replacing part of the acid-reacting ammonium nitrate with calcium and magnesium nitrates. Because dolomite reacts so readily with acidic materials, no fertilizer mixture that contains a substantial proportion of dolomite can remain more than mildly acidic.

The only one of these fertilizers that contained urea was the 16-8-8 made with Urana, and this contained only 2.5%. No definite equation can be written to show the fate of urea in such a mixture, but it is assumed that the carbon finally appears as carbon dioxide and the nitrogen as ammonia or its oxidation products.

Some carbon dioxide was evolved by each of the fertilizers, even the 12-12-12 made by batch ammoniation and the 12-12-12 nitraphosphate, though these fertilizers were made without urea or added dolomite. It is assumed that this came partly from calcium carbonate originally in the rock and not completely destroyed during acidulation, and partly from the oxidation of the small quantity of organic compounds originally in the phosphate rock and only partly oxidized during processing.

There are other possible reactions, such as those of the phosphates and fluorides with other constituents of the fertilizers. Some of these may be important—for example, in causing the reversion of phosphates to citrate-insoluble forms. Some of the reversion reactions probably involve disproportionation into a more basic, and hence more insoluble, residue, and a more acidic soluble portion. These will increase the apparent acidity of the mass.

In light of the discussion above, the following additional comments may be made.

None of the fertilizers gave important amounts of chlorine or of acid-forming nitrogen oxides in the preignition gases.

Relatively little gas was evolved by the 12-12-12 nitraphosphate, and this was especially low in carbon dioxide. This is presumably because conditions in the nitraphosphate process are especially favorable for decomposing carbonates and oxidizing organic matter.

The 16-8-8 that contained urea was slower to ignite than the one without urea. Carbon dioxide was a particularly prominent ingredient of the preignition gas from the fertilizer containing urea.

The high dolomite content of the 15-0-14 is presumably the cause of the difficulty in igniting this fertilizer, and of the high percentages of carbon dioxide and ammonia in the preignition gas.

Table VII. Effect of Nitrate and Chloride on Ignition Characteristics

Sample ^a No.	Cl Added as KCl, %	NO ₃ N Added, %		Temp., ° F., When Sample Removed from Bath		Max. Sample Temp., ° F., after Removal	Decomn. Self- Sustaining after Removal from Bath	Rate of Burning after Removal from Bath
		As NH ₄ NO ₃	As KNO ₃	Bath	Sample			
1	10	0.68	0	464	446	514	Yes	Very slow
2	10	1.13	0	464	419	536	Yes	Slow
3	10	2.26	0	451	426	545	Yes	Very vigorous
4	10	3.39	0	446	401	635	Yes	Very vigorous
5	10	0	0.68	509	477	531	No	...
6	10	0	1.13	491	471	513	No	...
7	10	0	2.26	478	448	622	Yes	Slow
8	10	0	3.39	482	442	608	Yes	Slow
9	0	2.26	0	486	430	493	No	...
10	1	2.26	0	469	410	554	Yes	Very vigorous
11	3	2.26	0	428	392	545	Yes	Very vigorous
12	5	2.26	0	455	392	541	Yes	Moderately fast
13	10	2.26	0	464	444	554	Yes	Vigorous

^a Ammoniated superphosphate mixed with indicated quantities of KCl, NH₄NO₃, and KNO₃.

Table VIII. Ignition of Fertilizers with a Concentrated Source of Heat^a

Grade	10-10-10	10-10-10	8-16-16	12-12-12
Method of preparation	Batch ammoniation	Batch ammoniation	Batch ammoniation	Nitrphosphate process
Source of nitrogen	Nitrana 2	Urana 15	Nitrana 2	NH ₃ and HNO ₃
Nitrate N, %	2.85	1.7	2.3	5.3
Cl, %	7.8	7.8	12.3	9.4
Heat input				
15 watts	N.T. ^b	N.T.	N.T.	No ignition up to 240 hr.
20 watts	N.T.	N.T.	N.T.	Ignited after 36 hr.
25 watts	Ignited after 2.6 hr.	No ignition up to 94 hr.	No ignition up to 94 hr.	N.T.
35 watts	N.T.	No ignition up to 94 hr.	No ignition up to 94 hr.	N.T.

^a Source of heat was 100-watt bulb with voltage adjusted to produce desired watts.

^b Not tried.

Mixtures of Ammoniated Superphosphate with Salts

Tests were made on mixtures of ammoniated superphosphate containing different percentages of potassium chloride and potassium or ammonium nitrate. One-hundred-gram samples in 125-ml. Florence flasks were heated in a salt bath, with results shown in Table VII.

The first eight samples all contained 10% chlorine added as potassium chloride, together with varying amounts and kinds of nitrate. Samples 1 to 4 contained from 0.68 to 3.39% nitrate nitrogen added as ammonium nitrate. Samples 5 to 8 contained the same respective percentages of nitrate nitrogen as 1 to 4, but supplied as potassium nitrate. These samples required higher temperatures for spontaneous ignition than the ones with ammonium nitrate.

The last five samples all contained 2.26% nitrate nitrogen added as ammonium nitrate, but had different percentages of chlorine, added as potassium chloride. In sample 9 there was no chlorine, and this sample showed no reaction. One per cent chlorine gave a vigorous reaction and a substantial temperature rise. In this group, the mixture with 3% chlorine was most active, those with 5 and 10% chlorine showing smaller temperature rises and

less vigorous reaction. Equation 4 calls for 2 equivalents of chloride to 4 equivalents of nitrate, or 2.8 parts of chlorine by weight to 2.26 parts of nitrate nitrogen.

Ignition by a Submerged Heater

The possibility of igniting a large mass of fertilizer by a submerged heater must be considered, a possible heater being an electric light bulb inadvertently covered by the fertilizer, and not turned off.

A heater submerged in a very large mass of fertilizer will attain a certain maximum temperature, after which heat will flow away as fast as it is supplied. The maximum temperature attained depends directly upon the power input and inversely upon the diameter of the heat source, assumed to be a sphere. For example, a 25-watt input in a sphere of 20-cm. (about 8 inches) diameter could raise the temperature at its center by about 180° F. (100° C.), not enough to cause spontaneous ignition, except in very exceptional circumstances. The same 25-watt input in a sphere of 10-cm. diameter could raise the temperature by about 360° F. (200° C.), which would frequently be sufficient for ignition.

Table VIII shows the results of some experiments in which samples of ferti-

lizer contained in a metal box, the same 1-foot cube described previously, were heated by means of an electric light bulb at the center of the box. This was a 100-watt bulb intended to operate at 115 volts; the applied voltage was controlled with a variable transformer to give the desired power input, 15 to 35 watts. The data show that two of the fertilizers in Table VIII (only the 12-12-12 nitrphosphate is one of the six described in Table I) were ignited with heat inputs of 20 to 25 watts, and that three failed to ignite with even 35 watts.

Spontaneous Heating

None of the six fertilizers of Table I ignited spontaneously at 266° F. (130° C.), but all showed appreciable rates of gas evolution at this temperature. In these tests the temperature was held at 266° F. by the controlled oil bath, but in a pile of fertilizer the temperature would rise if the rate of liberation of heat exceeded the rate of loss.

To consider a specific case, the rate of gas evolution by the 16-8-8 pre-reactor (Nitrana) was 8.6 μmoles per hour per 100 grams at 266° F. The corresponding rate of heat evolution depends upon the relative quantities of material entering into the different reactions, and these are not known

definitely. However, by making reasonable assumptions, one can calculate that the heat would be enough to raise the temperature on the order of 0.5° F. per day if there were no loss. If heat could not be dissipated so quickly from the interior of the pile, the temperature would rise and the reaction would be accelerated. Because of uncertainties of the calculation and the variations in heat transfer conditions possible, an exact point at which rising temperature of the pile would be encountered cannot be determined. For this fertilizer in a large pile, 266° F. (130° C.) would be in the uncertain range. It would consequently be safer to make a practice of cooling it below 212° F. (100° C.) before storing.

Effect of Organic Matter

A set of three fertilizers was made on a laboratory scale. These were basically 8-7-4's, with such additional plant food as the filler contained. The

filler amounted to 580 pounds per ton of a fertilizer. In one it was inorganic, a mixture of sand and expanded vermiculite, in another it was cottonseed meal, and in the third it was activated sewage sludge. The fertilizers with the organic fillers consistently evolved more gas than the straight inorganic one. Nevertheless, the inorganic one gave prompt spontaneous ignition when heated to 468° F. (242° C.), while neither of those with organic filler ignited spontaneously even when heated to 545° F. (285° C.), the highest convenient temperature.

These tests were made on well ammoniated fertilizers. The work of Hardesty and Davis (2, 3) has shown that underammoniated fertilizers containing organic material can heat spontaneously, even starting at room temperature, to such a degree that they ignite. Moreover, the test conditions were unsuitable for showing the spontaneous heating due to oxidation of organic matter. Thus, even though

these fertilizers did not show a sudden, sharp ignition like the inorganic ones, they would be subject to spontaneous heating and possible destruction if placed in pile storage while hot.

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PLANT ANALYSES

Rapid Determination of Nitrate and Nitrite in Plant Material

Because of its rapidity and simplicity, this modification of the Nelson, Kurtz, and Bray method is well adapted for measuring day-to-day changes in nitrate or nitrite or for other applications in which the basic plant material remains essentially constant. Modifications suggested are use of copper and slightly more reagent powder, and allowance of more latitude in the time schedule of operations.

A MODIFICATION of the Nelson, Kurtz, and Bray (2) method for the determination of nitrate and nitrite determines nitrite by diazotization of sulfanilic acid and coupling with 1-naphthylamine to form a red dye. Nitrate must be reduced to nitrite for this analysis. The modifications suggested are the use of copper, the use of slightly more reagent powder, and the allowance of more latitude in the time schedule of operations than was proposed by the original authors.

Procedure

For determination of nitrate in the absence of nitrite, an aqueous extract of plant material is made, usually at the ratio of 1 gram of fresh or 0.1 gram of dried plant material to 20 ml. of water. To 1 ml. of this extract are added 9 ml. of 20% acetic acid solution containing

0.2 p.p.m. of copper as copper sulfate. By the use of a measuring scoop, 0.8 gram (between 0.6 and 1.0 gram) of the powder described by Nelson, Kurtz, and Bray (2) is added. This powder is an intimate mixture of 100 grams of barium sulfate, 75 grams of citric acid, 10 grams of manganous sulfate dihydrate, 4 grams of sulfanilic acid, 2 grams of powdered zinc, and 2 grams of 1-naphthylamine. The sample is then shaken for about 15 seconds, and is similarly shaken 3 minutes later. After 3 minutes more the sample is shaken for the third time and is centrifuged for 3 minutes at 1000 × G. The supernatant solution is poured through a small loose plug of borosilicate glass wool, the light absorbance is measured at a wave length of 520 mμ, and the amount of nitrate is calculated from a standard curve. The time between shakings is relatively unimportant; it can be halved or doubled with little

change in results. Usually the powder is added to eight sample tubes in succession, the tubes are shaken successively by hand at 3-minute intervals, and all eight tubes are centrifuged simultaneously.

The same procedure may be used for the determination of nitrite in the absence of nitrate, but if nitrite is to be determined in the presence of nitrate, the zinc, manganese sulfate, and cupric sulfate should be omitted.

The determination of nitrate in the presence of nitrite requires two runs, one with the zinc, manganese sulfate, and cupric sulfate and the other without these substances. Different standard curves must be made for nitrate and nitrite, as not all of the nitrate originally present appears as nitrite after the reduction (Figure 1).

The water should be as free from copper as is possible, because the final

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