0-175

RECENT DEVELOPMENTS IN THE PRODUCTION AND USE OF MONOAMMONIUM PHOSPHATE

For Presentation at Fertilizer Industry Round Table
Atlanta, Georgia
October 26 - 28, 1976

By
Hubert L. Balay
Tennessee Valley Authority
Muscle Shoals, Alabama

and
David G. Salladay
Tennessee Valley Authority
Muscle Shoals, Alabama

TENNESSEE VALLEY AUTHORITY
Muscle Shoals, Alabama

RECENT DEVELOPMENTS IN THE PRODUCTION AND USE OF MONOAMMONIUM PHOSPHATE

By

Hubert L. Balay
Tennessee Valley Authority
Muscle Shoals, Alabama

David G. Salladay
Tennessee Valley Authority
Muscle Shoals, Alabama

Introduction

The popularity of monoammonium phosphate (MAP) is growing rapidly because of its versatility. The granular product is becoming a popular bulk blend material and the powdered product is finding use as a replacement for superphosphates in granulation plants. Interest in producing suspension fertilizers from granular and powdered MAP is widespread because of its low delivered cost compared with other ammonium phosphate bases.

MAP production is also becoming popular with basic producers of ammonium phosphate products. As the BPL content of rock declines in some of the major phosphate deposits in the United States, it is becoming more difficult for diammonium phosphate producers to reach the established analysis for diammonium phosphate (18-46-0). Some diammonium phosphate producers are reaching the accepted analysis by removing solids from the phosphoric acid to increase its concentration. This presents a problem of disposal of the solids. There is no such problem in the production of monoammonium phosphate. So far, no single grade has been established for monoammonium phosphate. Several grades ranging from 10-50-0 are being produced. The grade produced depends upon the purity of the feed acid.

Processes for Production of MAP

Several processes are being used to produce MAP. Basically they are:

1. Ammoniating acid to NH_3:H_3PO_4 mole ratio of 1.3 in a preneutralizer and adding acid in a TVA ammoniator-granulator or a blunger to return the mole ratio to 1.
2. Two-step neutralization under pressure followed by flash ejection of hot concentrated slurry into a receiving tower.
3. Direct reaction of ammonia and phosphoric acid followed by flash ejection into a receiving tower.
4. Reaction of phosphoric acid and ammonia in a pipe-cross reactor in the presence of a small amount of sulfuric acid with subsequent flash ejection onto a rolling bed of solids in a TVA ammoniator-granulator.

Since all these processes were covered in previous Round Table meetings, they will not be covered in detail here.

Use of MAP in Bulk Blending

A major use of granular MAP is expected to be in bulk blending. Monoammonium phosphate has the advantage over diammonium phosphate in that all the popular ratios, even 1:4:X and 1:3:X, can be blended without the need for an additional phosphate material. If ratios below 1:2.56:X are blended from 18-46-0, granular triple or some other phosphate material must be available. More nitrogen is required with monoammonium phosphate (except in the 1:5:X ratio), but plants must usually have the nitrogen available anyway to produce higher nitrogen ratios. This eliminates the need to store and ship one more material.

All ratios, even a 1:5:X, can be blended from triple superphosphate and nitrogen; however, monoammonium phosphate has an advantage over these materials in that it contains from 60 to 66 units of plant food per ton rather than the usual 45 for triple. This results in lower freight rates and less required storage space. The higher nitrogen ratios (above 1:2.56:X) can be blended from diammonium phosphate without a second phosphate source; however, some nitrogen source other than that supplied by the DAP is required. In these grades diammonium phosphate requires less supplementary nitrogen than MAP, but nitrogen frequently can be obtained more economically from local suppliers than from either diammonium or monoammonium phosphate. If this is the case, the less nitrogen shipped with the phosphate the better. Several formulas for common grades blended from MAP and DAP are shown in table 1.

A 12-48-0 mixture of monoammonium phosphate and ammonium sulfate has been produced by the TVA pipe-cross reactor process especially for blending the popular 1:4:X ratios. This cuts down the number of materials required in these ratios and helps alleviate segregation problems that still plague blenders. A 1:4:4 ratio using this product is also shown in table 1.

MAP in Granulation

Monoammonium phosphate, especially the powdered variety, should become a popular material in granulation plants. It is expected to replace normal superphosphate and sometimes triple superphosphate in the granulation process. Because of the increasing cost of shipping phosphate rock and the pollution difficulties encountered in producing normal superphosphate, NSP is disappearing from the market. It continues to be available to producers who are basic in phosphate rock and who make their own normal super; however, it is now essentially unavailable to the independent granulator. The logical replacement for normal superphosphate is triple superphosphate; however, many granulators prefer monoammonium phosphate because of its high concentration and comparatively low storage and shipping cost. MAP is also preferred over phosphoric acid because it is more convenient to ship, especially by water. Also, it can usually be stored and used without changes in the existing equipment.

Monoammonium phosphate is especially useful in granulating high nitrogen grades. The amount of ammonia that can be used as a nitrogen source in these grades is limited because of the increased heat and liquid phase generated when the ammonia reacts with acids and superphosphate. Usually as much nitrogen as possible is obtained from ammonia and the balance is obtained from ammonium nitrate or ammonium sulfate. Both of these materials, if used in any quantity, degrade storage and handling properties of the product. Also, use of ammonium nitrate and ammonium sulfate will sometimes increase raw material cost of the product. If monoammonium phosphate is used as a phosphate source, the requirement for ammonium nitrate and ammonium sulfate is reduced because of additional nitrogen in the monoammonium phosphate.

Usually, fume evolution is decreased because there is no need to exceed the optimum amount of ammonia in a high nitrogen grade. Also, the amount of dust in the plant is reduced because there is less oversize to be crushed and, hence, less dusting.

One plant in the South has used monoammonium phosphate for about a year in its granulation process. Many of the reasons for adopting monoammonium phosphate were those given above; however, the main consideration in this case is economics. After a year's experience, the plant has had fairly good success with the monoammonium phosphate; however, all of the anticipated advantages have not developed. Specifications of the product used in this plant are listed in table 2. The general conclusion after one year's operation was that MAP handles and granulates about like triple superphosphate, although in most cases the MAP, as received, is dustier than triple and has more of a tendency to cake in storage.

When the plant began using monoammonium phosphate, it was assumed that MAP could be ammoniated from about 4.7 pounds of ammonia per unit of P_2O_5 (the amount in MAP) to 7.2 pounds of ammonia per unit of P_2O_5, or an increase of about 2.5 pounds of ammonia per unit of P_2O_5. Up to 2.4 pounds of ammonia per unit of P_2O_5 had been successfully added in the TVA pilot plant to MAP (11-55-0) made from a relatively pure wet-process acid. It was found in the plant operation that this amount of ammonia could not be added to powdered MAP made with less pure acid. Through trial and error it was found that the maximum ammoniation was 1.9 pounds of ammonia per unit of P_2O_5 and that best results were obtained if the ammoniation rate was limited to about 1.5 pounds of ammonia per unit of P_2O_5.

Difficulty was also encountered in making the pellets as large as those produced when all of the P_2O_5 was obtained from normal and triple superphosphate. In grades where all the P_2O_5 could not be obtained from MAP, triple was used as the supplementary phosphate source because it cost less than normal superphosphate. Experimentally it was found that larger granules could be produced if some normal superphosphate was used as the supplementary source.

A problem also developed with filler. Because of the high analysis of the monoammonium phosphate filler was required in established grades which had previously been formulated without filler. A suitable granular filler could not be obtained, and a fine dolomitic limestone was used as filler during the first trials with monoammonium phosphate. Later a satisfactory granular filler was obtained that appeared to improve the granulation characteristics of the mixtures. Successful formulations are shown in table 3. Eighty-three percent ammonium nitrate liquor was available and was used as supplementary nitrogen in a number of the formulations. Products containing less than 2 percent moisture stored fairly well and seemed to be similar to products produced without monoammonium phosphate. Hardness of the pellets was about the same regardless of what materials were mixed.

TVA uses granulation factors to determine how much a material will contribute to granulation. The granulation factor used for monoammonium phosphate in this plant was 0.2 as compared to 0.5 for anhydrous ammonia, 1.0 for ammonia-ammonium nitrate solutions, 0.10 for ammonium sulfate, 0.20 for normal superphosphate, and 0.2 for triple superphosphate (see first reference for explanation of granulation factors).

A Brazilian company reported results with monoammonium phosphate produced by two European companies. These results are similar to those reported above except that one of the products handled in bulk was not as dusty and did not cake as badly as the powdered material described earlier. This company also reported that granulation was similar to that obtained with well-cured and disintegrated run-of-pile triple superphosphate. Ammoniation rates were not given. However, it is believed that they were similar to those obtained in the U.S. granulation plant because the authors of that paper reported that some sulfuric acid had to be added to provide heat and to hold ammonia. It is of interest that this company added the acid at the feed end of the ammoniator-granulator so that the monoammonium phosphate was wetted with sulfuric acid before it entered the ammoniation section.

It has been reported in previous Round Table proceedings that excellent granulation has been obtained with a monoammonium phosphate produced in Europe which contains 6+ percent water. The proceedings state that further drying of the product could impair granulation properties of the product because amorphous gels formed by impurities in acids used to manufacture the MAP became dehydrated. All granulation tests reported in this paper have been made with MAP containing 3 percent or less of water. Further tests with monoammonium phosphates containing more water seem warranted.

Use of MAP in Fluid Fertilizers

As mentioned previously, there is considerable variation in impurity content of monoammonium phosphate produced in the United States. Very satisfactory 11-33-0 base suspensions have been produced from 11-55-0 grades of monoammonium phosphate which contain fairly low quantities of impurities. However, as impurity content of the monoammonium phosphate increases, the grade produced from it must be reduced because of thickening (or gelling) properties of the impurities. Grades as low as 9-27-0 must be produced from monoammonium phosphate made from sludge acid. Most of the grades produced contain about 1 percent clay. It has been found inadvisable to store any of the products except those produced from very pure monoammonium phosphate.

It is common practice to add enough ammonia to the monoammonium phosphate to bring the mixture to a mole ratio of 1.7 (about 8.1 pounds of ammonia per unit of P_2O_5 or 1:3 $N:P_2O_5$ ratio). Maximum solubility for mixtures of mono- and diammonium phosphate is obtained at mole ratio 1.45 amd more salts are in solution than at any other mole ratio, but salts that precipitate at 1.45 mole ratio are usually monoammonium phosphate.

At mole ratio 1.7, salts precipitate as diammonium phosphate. Diammonium phosphate crystals are smaller and suspend better than monoammonium phosphate crystals. The reaction between ammonia and MAP also provides heat for disintegrating granular monoammonium phosphate (when granules are used).

High intensity mixing equipment is usually required to produce suspension fertilizers from monoammonium phosphate, especially where granulated material must be disintegrated. High shear mixers driven at 1800 rpm's by 60-hp motors are common in the industry. Investment in this kind of mixing equipment is high; however, savings in using monoammonium phosphate over other phosphate sources available to the fluid fertilizer industry usually makes purchasing this equipment profitable. It is expected that more and more monoammonium phosphate will be used for this purpose because it is about the only way that fluid fertilizers can be produced at prices competitive with bulk blends.

Ammonium Polyphosphate

TVA started producing solid ammonium polyphosphate in 1966 from electric furnace phosphoric acid. In the early 1970's the cost of energy for producing electric furnace phosphoric acid rose sharply making the production of ammonium polyphosphate from this acid economically infeasible.

In 1974, TVA introduced ammonium polyphosphate (12-54-0) made from merchant grade wet-process phosphoric acid. The product is granular and contains ammonium ortho- and polyphosphates. The polyphosphate content varies from 15 to 25 percent of the total P_2O_5. The orthophosphate is mainly monoammonium phosphate.

Ammonia and wet-process orthophosphoric acid are reacted in a pipe reactor to produce an anhydrous ammonium phosphate melt. Heat of reaction converts part of the phosphate to polyphosphate. In this respect, the operation is similar to that in the production of powdered monoammonium phosphate. Gaseous ammonia is charged to the reactor. The acid usually is not heated since this will produce a product with high polyphosphate content. It is desirable to limit polyphosphate content of the product to less than 30 percent to facilitate granulation because high-polyphosphate melt will not solidify and granulate well.

TVA granular ammonium polyphosphate has excellent storage and handling characteristics. It is believed that the polyphosphate in the product contributes to these characteristics. Specifications for the product are shown in table 4.

The product has been used in bulk blending and for production of suspension fertilizers. It is especially suited to producing suspension grades since the polyphosphates are more soluble than orthophosphate and will sequester a portion of the impurities from the wet process phosphoric acid used to produce the ammonium polyphosphate. The product is ammoniated to the 1.7 mole ratio for the same reasons the monoammonium phosphate is ammoniated to that ratio. Granules tend to disintegrate rapidly in water because polyphosphate in the product goes quickly into solution helping to disintegrate the granules so that the orthophosphate portion suspends easily. An 11-33-0 base suspension that will store well for up to 60 days can be produced from this material.

Ammonium polyphosphate can be blended in the same manner as monoammonium phosphate. Its higher analysis is of some benefit in producing higher grade blends. Also, it has been reported that zinc oxide coated onto the surface of the granules reacts with the polyphosphate and is sequestered into a more available form.

Summary

Monoammonium phosphate is a versatile product which can be used in every phase of fertilizer production. Its $N:P_2O_5$ ratio is more suitable to bulk blending than that of diammonium phosphate. It serves well in granulation as a replacement for some of the more familiar phosphate forms. It is economical to ship and store because of its high analysis. It is easily made and granulated from impure phosphoric acid. This will be an important factor in future decisions to produce monoammonium phosphates rather than diammonium as the BPL content of phosphate rock decreases. Take a good look at monoammonium phosphate. We can expect to see more of it in the future.

Literature Cited

Nevins, J. L. and Achorn, F. P. "Formulation for a TVA-Type Ammoniator Granulator by Computer," Proceedings of the 19th Annual Meeting of the Fertilizer Industry Round Table, 1969, 80-89.

Young, R. D. and Hicks, G. C. "Monoammonium Phosphate in a TVA-Type Ammonium Phosphate Granulation System," Commercial Fertilizer and Plant Food Industry (Feb. 1967).

Peng, S. L. "Granulation of Compound Fertilizer Containing Nongranular Monoammonium Phosphate," Symposium on Production and Use of Nongranular Ammonium Phosphate Intermediate, Division of Fertilizer and Soil Chemistry, ACS Annual Meeting, Aug. 1973.

Balay, H. L. "Marketing Advantages of Using Solid Materials in Suspensions," Proceedings Book, 1976 NFSA Round-Up, 41-44.

Davidson, E. and Martin, I. S. E. "The 'Phosai' Form of Monoammonium Phosphate," Proceedings of the 23rd Annual Meeting, Fertilizer Industry Round Table, 1973, 88-115.

Mortenson, E. N. "Swifts Direct MAP Process," Proceedings of the 20th Annual Meeting of the Fertilizer Industry Round Table, 1970, 93-96.

Brownlie, I. A. and Graham, R. "The Use of a New Form of Monoammonium Phosphate in Place of Superphosphate as a Means of Attaining Higher Concentration in Granular NPK Fertilizer," ISMA Technical Conference Helsinki, 1963, 3-1 to 3-26.

Table 1

Bulk Blend Formula Using MAP & DAP

Grade	5-25-25	5-25-25	8-24-24	8-24-24	8-24-24
Ratio	1:5:5	1:5:5	1:3:3	1:3:3	1:3:3
Raw Material	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.
MAP (11-55-0)[a]	-	910	873	-	873
MAP (12-48-0)[b]	-	-	-	-	-
DAP (18-46-0)[c]	556	-	-	889	-
Triple super (0-46-0)	531	-	-	155	-
Urea (46-0-0)	-	-	140	-	-
Ammonium sulfate (21-0-0)	-	-	-	-	305
Potash (0-0-60)	834	834	800	800	800
Filler	79	256	187	156	22

Grade	6-24-24	6-24-24	6-24-24	6-24-24
Ratio	1:4:4	1:4:4	1:4:4	1:4:4
Raw Materials	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.
MAP (11-55-0)[a]	-	873	-	873
MAP (12-48-0)[b]	1000	-	-	-
DAP (18-46-0)[c]	-	-	667	-
Triple super (0-46-0)	-	-	377	-
Urea (46-0-0)	-	53	-	-
Ammonium sulfate (21-0-0)	-	-	-	115
Potash (0-0-60)	800	800	800	800
Filler	200	274	156	212

a Monoammonium phosphate
b Monoammonium phosphate-sulfate made by pipe-cross process
c Diammonium phosphate

Table 2

Specifications of Powdered Monoammonium Phosphate (MAP)

Moisture	2-3%
P_2O_5	50-51%
N	10%

Table 3

Granulation Formulas Using MAP

Grade	a 5-10-15	b 5-10-15	c 5-10-15	d 8-16-24	e 8-16-24	f 8-16-24
Ratio	1:2:3	1:2:3	1:2:3	1:2:3	1:2:3	1:2:3
Raw Material	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.
NH_3 (82.2-0-0)	61	49	80	80	70	80
NH_4NO_3 (liquor) (29-0-0)	104	104	87	135	182	135
Ammonium sulfate (21-0-0)	-	-	-	-	-	-
Normal super (0-18-0)	534	245	823	267	397	190
Triple super (0-46-0)	-	-	-	-	-	-
Monoammonium phosphate (10-52-0)	200	312	100	544	497	590
Sulfate of potash-magnesia	-	-	-	100	-	-
Potash (0-0-60)	492	492	492	751	787	787
H_2SO_4 (93%)	100	145	125	120	134	125
Filler	614	694	370	-	-	153
Micronutrient mix	-	-	-	50	-	-
Steam	116	100	68	37	-	-
Ammoniation rate of MAP (No. NH_3/unit P_2O_5)	0.2	0	0	1.9	0.5	1.9

a Granulated well with granular filler; recycle build up with fine filler
b Amount of NH_3 increased over original amount formulated; granulated well with granular filler
c Granulated well with granular filler
d Granulated well; some trouble holding ammonia
e Granulated well
f Granulated well; some trouble holding ammonia

Table 3
(Continued)

Grade	g 5-15-30	h 5-15-30	i 8-24-24	j 8-24-24	k 14-14-14
Ratio	1:3:6	1:3:6	1:3:3	1:3:3	1:1:1
Raw Material	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.	No./Ton Prod.
NH_3 (82.2-0-0)	60	70	70	89	63
NH_4NO_3 (liquor) (29-0-0)	55	-	75	-	166
Ammonium sulfate (21-0-0)	-	-	-	-	591
Normal super (0-18-0)	-	412	-	150	-
Triple super (0-46-0)	275	-	169	-	-
Monoammonium phosphate (10-52-0)	350	448	809	871	560
Sulfate of potash-magnesia	-	-	-	-	-
Potash (0-0-60)	984	484	787	787	460
H_2SO_4 (93%)	100	111	125	130	130
Filler	207	-	-	-	65
Micronutrient mix	-	-	-	-	-
Steam	-	95	-	-	-
Ammoniation rate of MAP (No. NH_3/unit P_2O_5)	0.4	1.1	0.7	1.7	1.8

g Granulated well with granular filler
h Did not granulate well
i Some over granulation
j Would not hold ammonia
k Granulated well; some oversize; product hygroscopic; MAP only source of P_2O_5

Table 4

Specifications of Granular Ammonium Polyphosphate (APP)

Moisture	2.0%
P_2O_5	54%
Polyphosphate, % of total P_2O_5	15-25%
N	12%