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AMMONIATION OF SUPERPHOSPHATE

by

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This paper, which was read for the first time at a meeting of The Fertiliser Society in York on 23rd April, 1953, will be presented at the Technical Meetings in Cambridge on 15th and 17th September, 1953.

THE INTERNATIONAL SUPERPHOSPHATE
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AMMONIATION OF SUPERPHOSPHATE AND COMPOUND FERTILISERS BASED ON SUPERPHOSPHATE

This paper reviews briefly the history of ammoniation, it records the reasons for my Company's interest in the ammoniation of superphosphate and compound fertilisers based on superphosphate, it deals with the chemistry of ammoniation, touches on the agronomic results obtained by the use of ammoniated products in Scotland and finally it outlines the technique of ammoniation as practised in America and in our own factories.

History of Ammoniation of Superphosphate

Although in 1873 McDougal proposed the use of superphosphate for absorbing ammonia from coal gas, his process does not appear to have been adopted. Patents relating to somewhat similar processes followed in Europe and America but, so far as we can trace, none came into commercial operation and it was not until the early nineteen-twenties when the development of the synthetic ammonia process made anhydrous or aqueous ammonia freely and cheaply available that fertiliser manufacturers in the U.S.A. began to make use of ammonia as a source of nitrogen in their compound fertilisers. In 1928, some 5,000 short tons of free ammonia was used to ammoniate superphosphate in the U.S.A. and in the following year, ammonia and ammonium nitrate were used for the first time. Consumption expanded rapidly and by 1951 the use of ammonia in the form of aqueous and anhydrous ammonia, ammoniating solutions etc. had so increased as to provide over 50% of the 545,000 short tons of nitrogen used in compound fertilisers (Jacob, 1952).

In Europe, at least one French manufacturer had carried out laboratory and semi-scale work on the ammoniation of superphosphate after the 1914-18 war but for commercial reasons, production on an industrial scale did not immediately follow (Matignon, 1923). There appears to have been little or no ammoniated superphosphate made in Belgium or Germany before the last war, as it was not commercially attractive, but there may have been production in Russia, judging from Russian publications on the subject (Berlin, 1933). In more recent years, French and German superphosphate producers have been marketing ammoniated material and we believe this is finding acceptance.

Unless the Parrish process (1936) is regarded as being an ammoniation process, there does not appear to have been any substantial manufacture of ammoniated superphosphate in the U.K.

until last year when ammoniation was practised on quite a large scale by my Company in Scotland, where by the end of the current fertiliser year, we expect to have produced approximately 90,000 tons of ammoniated granular fertiliser. It is interesting to speculate as to whether the spectacular increase in consumption of ammonia achieved in the U.S.A. will be repeated here.

Reasons for Interest in Ammoniation

The following are the main reasons why interest has been shown in the production of ammoniated superphosphate or ammoniated compound fertilisers based on superphosphate :—

- (a) Ammoniation provides a means of reducing costs ;
- (b) It helps to effect a higher degree of concentration in compounds ;
- (c) It can improve the physical character of powder compounds and in the case of granular compounds, it prevents bag rot ;
- (d) It permits the incorporation of nitrates in granular compound fertilisers ;
- (e) It makes possible the use of an indigenous material presently going to waste and incidentally prevents associated nuisance.

(a) COST

Let us deal first with the question of cost. Before examining the comparative cost of nitrogen in different materials in this country, it is useful to consider the prices of various nitrogenous fertilisers in the U.S.A., where ammoniation has made such great headway. Table I shows such comparative prices for a range of fertiliser materials in the year 1949. The prices are national average wholesale prices.

Table I

Average wholesale f.o.b. prices per unit of nitrogen in various fertiliser materials in bulk car lots			
Material	% Nitrogen	Unit price \$	Ratio
Sulphate of ammonia ..	21	2.29	1.00
Calcium Cyanamide ..	22	2.82	1.23
Sodium Nitrate ..	15	3.15	1.38
Urea	42	2.01	0.88
Ammonium Nitrate ..	35	1.73	0.76
Ammoniating Solutions	37-45.5	1.23	0.54
Anhydrous Ammonia ..	82.4	0.94	0.41

(Mehring & Bennett, 1951).

Examination of these figures shows the considerable price advantage to anhydrous ammonia or ammoniating solutions. It is obvious that a fertiliser manufacturer in the U.S.A. will prefer to use as much of these materials as is technically possible in preference to sulphate of ammonia or ammonium nitrate.

We could not find a national average f.o.b. price for aqueous ammonia but from several figures we did obtain, it appears that this lies between the price for anhydrous ammonia and that of ammoniating solutions. All three are substantially cheaper than the solid forms of nitrogenous fertiliser.

Fertiliser manufacturers in the U.K. do not use the same range of nitrogenous fertiliser ingredients in their compounds as do the Americans so it is not possible to produce the same comparison of prices in the U.K. as we have shown in Table I. However, if we make use of prices paid by industrial users for certain materials, it is possible to give some indication of comparative unit prices. Table II gives these U.K. prices on a delivered basis. The sulphate of ammonia figure shown is the 1953 March/June price paid by merchants.

Table II

Average Wholesale Prices of Nitrogen in Various Fertiliser Materials in the U.K.			
Material	% Nitrogen	Unit Price Shillings per unit N ₂	Ratio
Sulphate of Ammonia ..	20.6	15.3	1.00
Nitrate of Soda (Chilean)	16	36.3	2.37
Urea (Tech. Pure) ..	46	17.3	1.13
Ammonium Nitrate ..	35	18.3	1.20
Aqueous Ammonia (30% NH ₃)	24.7	10.3	0.67

It is obvious that when the price of a unit of nitrogen in aqueous ammonia is compared with the price of a unit of nitrogen in sulphate of ammonia — the usual source of nitrogen in U.K. compound fertilisers — there is a substantial advantage in favour of aqueous ammonia.

In addition to the price advantage in favour of aqueous ammonia, there is a probability of substantial savings in handling charges at the receiving works. It is usually cheaper to receive and handle liquids than solids, especially if the latter are received in bags.

In Table II the price of aqueous ammonia shown is that of 30%

synthetic ammonia liquor at the national delivered price. For fertilisers, however, there is no need to have ammonia of this purity and as will be seen later, depending on the location of a fertiliser works, by-product liquor might be obtained at a lower price than synthetic liquor.

When dealing with the chemistry of ammoniation, it will be shown that the quantity of free ammonia which can be added to superphosphate is limited, but enough has probably been said to indicate that there are real cost advantages to be had, even by this limited use, always providing that water solubility alone is not accepted as the criterion of agronomic availability of P_2O_5 in a fertiliser.

(b) CONCENTRATION

With regard to the use of ammonia to increase the concentration of compound fertilisers, anhydrous ammonia which contains 82.4% nitrogen is four times more concentrated than sulphate of ammonia, while the ammoniating solutions contain as much as twice the nitrogen content of sulphate of ammonia and even 30% aqueous ammonia is 1.2 times as concentrated in respect of nitrogen as is sulphate of ammonia.

Let us consider an N.P.K. compound containing 25 plant food units and incorporating 50% of superphosphate. If this is ammoniated to the extent of 3% NH_3 on the weight of superphosphate, the increase in plant food unit content, if the N.P.K. ratio is maintained, is 1.13 when anhydrous ammonia replaces part of the sulphate of ammonia, 1.90 when ammonia/urea solution is used and 1.43 when ammonia/ammonium nitrate is used. In the case of ammoniation with 30% aqueous ammonia, the increase in concentration is only fractional unless the product is dried when an increase in concentration approaching that obtainable by use of anhydrous ammonia is possible. Drying the product of ammoniation from nitrogen solutions effects some increase in concentration but as these solutions usually contain less than 20% water, the effect is not so marked.

At a time when high transportation and package charges and high labour costs for distribution on the farm have excited keen interest in methods of obtaining concentration in fertilisers, often at higher production cost per plant food unit, we feel that attention should be given to ammoniation as a means of effecting even a limited increase in concentration, while at the same time lowering costs.

(c) PHYSICAL CONDITION AND BAG ROT

Ammoniation of superphosphate or powder compounds based on superphosphate improves the physical condition and reduces the

maturing time necessary to obtain good handling properties. This probably results from the neutralising of the free acid.

Granular superphosphate and granular compound fertilisers are prone to cause bag rot if packed in hessian bags. This is caused by the release of volatile fluorides from the superphosphate and by evolution of hydrogen chloride from granular compounds containing chlorides. Hessian bags are so liable to rot, and in recent years have proved so expensive that most fertiliser manufacturers in the U.K. have been forced to pack their fertilisers in multi-ply paper bags incorporating a bitumen union kraft layer as a barrier against rot.

We have found that ammoniation of superphosphate or of granular compound fertilisers based on superphosphate removes all tendency of these fertilisers to cause bag rot. So effective is ammoniation that we have stored ammoniated granular fertilisers for years in hessian bags without the bags showing the slightest sign of bag rot.

This improvement may not be of great importance at the moment when paper bags are cheaper than hessian, but the price advantage to paper is not great nor necessarily permanent, and ammoniation affords a free choice of package without fear of rot.

(d) INCORPORATION OF NITRATES

By neutralising the free acid in superphosphate, ammoniation permits the incorporation of nitrates in granular compound fertilisers. Though it is possible to mix nitrates with superphosphate in powder form with limited loss of nitrate nitrogen, it is quite impossible to use nitrates in granular compounds, as the reaction between the nitrates and free phosphoric acid in the superphosphate, followed by the raising of the temperature of the material in the dryer, results in very substantial volatilisation of oxides of nitrogen. From a limited number of tests on a make of some hundreds of tons of compound, it would appear that ammoniation permits the use of nitrates in granular compounds. This opens up the possibility of using ammonia/ammonium nitrate solutions in U.K. granular compounds with resulting advantage in cost and concentration.

(e) USE OF WASTE LIQUORS

Not all the ammonia produced as a result of the carbonisation of coal in the U.K. is recovered, and not only is this indigenous material lost but much of it finds its way into sewers or into rivers, where pollution can be costly to local authorities, destructive of amenity, or indeed constitute a legal offence; alternatively it is released into the sea in proximity to harbours or beaches, where also it is liable to create offence.

It is not easy to get any exact measure of the extent to which

ammonia is lost in this way but the following figures give some guide as to what was happening in 1951. All figures for NH_3 are expressed as 100% NH_3 .

Total coal carbonised was approximately 49 million tons, of which 26 million tons was carbonised in gas works and 23 million tons in coke ovens. With a yield of 5 lbs. NH_3 per ton of coal carbonised in gas works and 5.5 lbs. NH_3 per ton of coal carbonised in coke ovens, this represents a potential production of 115,000 tons NH_3 . Sulphate of ammonia production accounted for 77,600 tons and other uses (pure ammonia, ammonium salts other than sulphate, the ammonia soda process etc.) absorbed 18,500 tons. There is thus an apparent loss of 19,000 tons.

Let us consider this loss in further detail. Wastage of gas liquor is known to be occurring at about 700 works in the U.K. On the basis of coal carbonised, it is estimated that the potential from these works is about 11,000 tons NH_3 , but the great majority are so small that installation of recovery plants, though maybe highly desirable on the score of amenity, is likely to prove uneconomic.

Ammonia was reported to have been recovered from gas works carbonising about 20 million tons of coal, and at about 5 lbs. NH_3 per ton this would give 44,500 tons NH_3 , whereas the actual recovery was only 24,500 tons as sulphate and 12,000 tons as liquor, a discrepancy of 8,000 tons NH_3 .

It would appear, therefore, that of the total waste in 1951 of 19,000 tons NH_3 , some 8,000 tons was lost through inefficient running of existing recovery plants and 11,000 tons was run to waste.

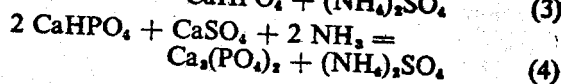
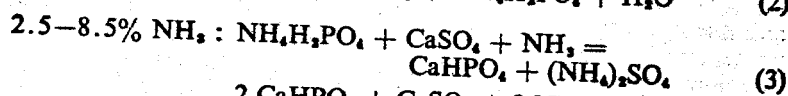
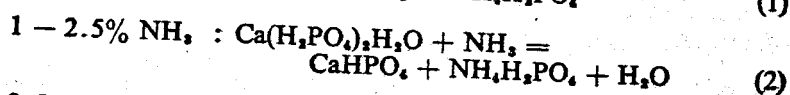
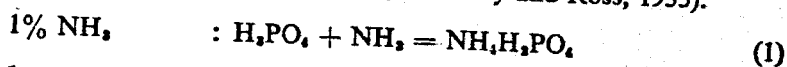
In addition to the above potential supply of ammonia which is being lost, there is the possibility that some of the ammonia presently being recovered uneconomically as sulphate of ammonia could profitably be recovered as concentrated ammonia liquor. This would result in a U.K. saving in sulphuric acid.

J. Bell (1950) describes types of plant suitable for the recovery of ammonia as ammonia liquor and estimates the cost of such recovery as being between 2/3d. and 3/5d. per unit, depending on the strength of the gas liquor. If we increase these prices by 20% to bring them more in line with present-day costs, we get figures of 2/8d. and 4/1d. per unit. These figures, though they are for liquor concentrated perhaps to 18-22% NH_3 , compare favourably with the figures for synthetic ammonia and, of course, the cost of nitrogen is very much lower than that of nitrogen in sulphate of ammonia.

Chemistry of Ammoniation

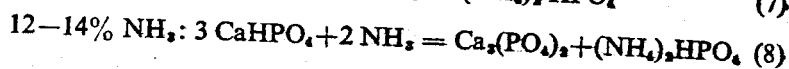
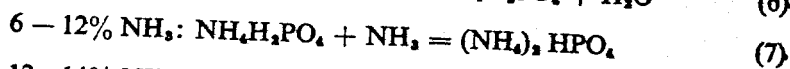
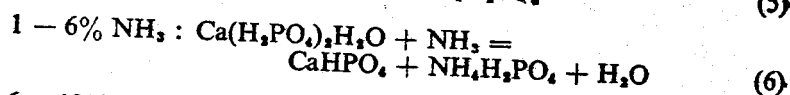
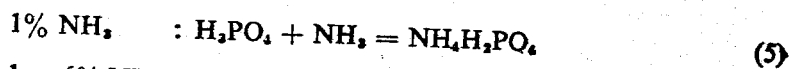
Since the chemistry of the fixation of free ammonia by reaction with the constituents of superphosphate or of triple superphosphate has been described by many writers in considerable detail, and as

we have no contribution to offer to the fundamental chemistry, it will suffice to list only a few of the main reactions to serve as a reminder of what happens when ammonia in increasing quantity is added to superphosphate (White, Hardesty and Ross, 1935).



Equations (1) and (2) show that addition of up to 2.5% NH₃ to superphosphate under normal conditions of temperature and pressure results in the formation of water soluble mon-ammonium phosphate and citrate or citric soluble dicalcium phosphate. According to equations (3) and (4), if there is further addition of ammonia, reactions with the calcium sulphate present in superphosphate take place with resulting formation of additional dicalcium phosphate. The latter in its turn is converted into more basic calcium phosphate which is water insoluble and only partially citrate or citric soluble. Though the formula for tricalcium phosphate has been used in the equations, this is merely for convenience in presentation to represent basic phosphates lying between dicalcium phosphate and hydroxyapatite in composition, such formation being responsible for reduction in the agronomic availability of the superphosphate.

Triple superphosphate has generally a low content of calcium sulphate so the reactions resulting from the addition of gradually increasing percentages of ammonia differ in part from the reactions resulting from the addition of ammonia to normal superphosphate. They may be represented as follows :-



Reactions (5) and (6) take place at much the same level of

ammonia addition in relation to P_2O_5 content as do reactions (1) and (2) in the case of normal supers, and formation of tricalcium or basic phosphates does not really occur unless triples are ammoniated at high temperatures under pressure. As there is generally a little calcium sulphate present, reactions (3) and (4) take place but to a limited extent.

The reactions in highly ammoniated superphosphate depend largely on the moisture content and the temperature of the mixture, and dicalcium phosphate, more basic phosphates such as hydroxyapatite, fluorapatite, syngenites like $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$ or combinations of sulphate and phosphate such as ardealite, $CaSO_4 \cdot CaHPO_4 \cdot 4H_2O$, are all possible (Marshall, Hendricks and Hill, 1940).

As most of the published work showing distribution of P_2O_5 between water soluble, citrate soluble, total P_2O_5 with varying ammonia addition is in respect of American superphosphates made from native rock, it may be interesting to see the results of tests we made in the laboratory on a superphosphate made from Morocco phosphate.

These results, shown graphically in Fig. I, are for samples prepared by adding varying quantities of strong aqueous ammonia to 200 grammes of superphosphate. The samples were tested the day after ammonia addition, having been allowed to cool to room temperature.

It will be observed that the water soluble phosphate content drops rapidly with increasing degree of ammoniation, while the phosphate soluble in 2% citric acid or in neutral ammonium citrate remains relatively constant throughout. The reason why there is so little reversion of citrate soluble P_2O_5 , compared with what is experienced in American practice may well result from fairly rapid cooling after ammoniation. In large-scale American ammoniation, where there is often no subsequent cooling, the reversion of citrate soluble phosphate can be appreciable after the addition of about 3% NH_3 (Hardesty, Ross and Adams, 1943). In an earlier unduplicated series of tests similar to these, we found citric acid solubility remaining constant with increasing ammonia addition, whereas citrate solubility fell after 3.5% N_2 had been added. We have not been able to replicate the results obtained in this test and it may be that different superphosphates react differently.

The experiments were repeated for triple superphosphate and are shown in graph form in Fig. 2.

From this, it is seen that water soluble P_2O_5 falls until 6 or 7% N_2 has been added, thereafter remaining fairly constant as might be expected from equations (5) and (6).

Both citric and citrate soluble P_2O_5 remain steady even at high levels of ammoniation — this also is as expected.

Considerable attention has been given in America to means of preventing reversion when superphosphate is ammoniated with high NH_3 percentages — controlled cooling or more especially removal of moisture being the most promising. At moisture contents of 2%, or less, reversion is small even at high temperatures. Ammoniation with anhydrous ammonia is attractive on this score.

Recent work in France (Andres, 1952) suggests that in the manufacture of ammoniated superphosphate the addition of metallic compounds before ammoniation has facilitated the fixing of twice the normal quantity of ammonia without increasing consumption of sulphuric acid or reversion of available P_2O_5 .

We believe that considerable attention is being given to means of increasing ammoniation without increasing reversion and that the work presently being carried out will prove successful.

Agronomic Results achieved with Ammoniated Superphosphate or Compounds based on Superphosphate

The continuing development of the ammoniation of superphosphate in the U.S.A. from 1928 to the present time might have been assumed as evidence that save on markedly calcareous soils ammoniated superphosphate is as good a source of P_2O_5 as non-ammoniated supers. Though there is a history of years of successful manufacture and use with many evaluations by agronomists, we felt it necessary to make some of our own material and try it out under Scottish conditions, first in pot tests and later in full-scale trials carried out by ourselves and under the auspices of the agricultural colleges.

To this end we made first of all some ammoniated superphosphate and then later some ammoniated granular compound fertilisers.

Pot and field trials were carried out over the years 1947/51 by S.A.I., the East of Scotland College of Agriculture, the Macaulay Institute and Jealott's Hill Research Station. Field trials sites were selected, where possible, on land which had low phosphate status in order that the maximum response to phosphate treatments might be obtained. The object of these trials was to determine the extent to which the availability of phosphate to the plant is affected by levels of ammoniation not in excess of 4.5% nitrogen on the superphosphate.

The analyses of the phosphate materials used in the trials are given in the following table.

Table III
Analyses of Phosphate Fertilisers used in Pot and Field Trials

Fertiliser	Code No.	% N ₂	% Sol. P ₂ O ₅	% Cit. Sol. P ₂ O ₅	% Cit. Acid Sol. P ₂ O ₅	% Total P ₂ O ₅	% K ₂ O
Superphosphate	S1	—	18.0	18.6	18.5	19.5	—
Ammoniated Super	U.S.1	4.1	10.0	13.0	—	19.0	—
„ „	49/L/1	4.5	3.8	11.9	15.7	17.2	—
„ „	49/L/2	2.4	11.1	15.1	16.9	18.3	—
„ „	50/L/1	3.7	7.4	—	16.5	18.1	—
„ „	50/L/2	4.4	5.3	—	16.3	17.7	—
Superphosphate Compound (Non-ammoniated)	S2	—	18.1	—	18.7	20.0	—
Compound (Ammoniated with straight ammonia)*	C2	8.0	6.9	7.6	7.7	7.8	13.9
Compound (Ammoniated with ammonia/ammonium nitrate)*	A2	8.3	5.0	7.6	7.4	7.9	14.3
Compound (Ammoniated with ammonia/ammonium nitrate)*	AN	8.5	5.6	8.0	8.2	8.4	14.6

* These two compounds were ammoniated to the extent of 3% NH₃ on the superphosphate content.

In passing, it is of interest to note that the analyses of the three compounds given in this table illustrate the degree of concentration of plant food units which can be achieved by ammoniation.

In all the field trials conducted on ammoniated superphosphate, the levels of nitrogen application were balanced throughout by the applications of appropriate amounts of sulphate of ammonia. A basal dressing of sulphate of ammonia and muriate of potash was applied to all plots.

In trials on ammoniated compounds, the levels of nitrogen and potash application were similarly balanced.

The results have not been published so it is not yet possible to refer to them, save to say that there was little significant difference between ammoniated material and superphosphate, provided the level of ammoniation is below 3% NH₃.

It may be of interest to report the results obtained in our own trials in 1951. These were as follows:—

FIELD TRIALS CONDUCTED BY S.A.I. IN 1951

Crop : Potatoes.

Layout : 4 x 4 Latin Squares.

Treatment : *Per Acre*

Plot A : 718 lb. Compound Fertiliser C2+121.7 lb. S/A+113.3 lb. 60% M/Pot.

„ B : 709 lb. Compound Fertiliser A2+112 lb. S/A+111 lb. 60% M/Pot.

„ C : 667 lb. Compound Fertiliser AN+121.7 lb. S/A+118.3 lb. 60% M/Pot.

„ D : 392 lb. S/A+280 lb. 60% M/Pot.

The above treatments provide :—

A. B. & C. —56 lb. P_2O_5 : 82 lb. N: 168 lb. K_2O per acre.
 D. —Nil : 82 lb. N: 168 lb. K_2O per acre.

Results :

Yield in Tons per acre

	A	B	C	D	S.E	Sig. Diff.	
Mountskip, Gorebridge	8.99	8.92	8.92	7.77	.09	.32	A>D. B>D. C>D. All others non-significant
Lanfine Mains, Newmilns	10.5	10.7	11.1	8.3	.425	1.47	A>D. B>D. C>D. All others non-significant
Dumfries House Mains	10.6	12	11.2	6.7	.66	2.2	A>D. B>D. C>D. All others non-significant
Bannockburn	8.73	8.47	8.76	7.97	.46		Trial non-significant
Lawers School	15.6	15.1	15.8	11.6	.23	.8	A>D. B>D. C>D. All others non-significant
St. Leonards, Lanark	12.1	12.8	11.3	11.3	.57		Trial non-significant
Smithfield, Aberdeen	10.8	11.6	9.9	8.4	.64	2.2	A>D. B>D. All others non-significant
Aitkenhead, Blairgowrie	10.4	9.6	10.8	9.6	.67		Trial non-significant
Hetton, Northumberland	14.7	13.3	14.6	12.3	.47	1.62	A>D. C>D. All others non-significant
Beauly, Inverness	11.7	11	11	5.5	.36	1.24	A>D. B>D. C>D. All others non-significant
Dykebar, Paisley	13.8	12.8	13.5	11.6	.36	1.23	A>D. C>D. All others non-significant
Mungoswalls, Berwick	7.38	7.17	7.74	6.37	.24	.82	A>D. C>D. (B barely >D). All others non-significant
Balquharran	8.45	9.36	8.8	8.11	.83		Trial non-significant

Conclusion : In no case was a significant difference established between treatments A, B and C, even on sites where the low yield obtained with treatment D (lacking phosphate) indicated that a substantial P_2O_5 deficiency is being met by the phosphate applied in treatments A, B and C.

Most of these trials were conducted on neutral or slightly acid soil types such as are common in Scotland. It would appear desirable to extend these trials to sandy or calcareous soil types on which the higher levels of ammoniation might possibly show to greater disadvantage.

Technique of Ammoniation

American Practice. In the U.S.A. a large number of different types of ammoniating solutions are available. Table No. IV gives the compositions and physical properties of a selection of these solutions. Also included for comparison are anhydrous ammonia and aqueous ammonia.

Among the factors which decide the type of solution to be used are total nitrogen content, ratio of nitrogen in the form of free NH_3 to total nitrogen, density, vapour pressure and crystallisation temperature. The total nitrogen content and density are important from the point of view of transport and storage, whereas the free NH_3 determines the quantity of liquor which can be used for ammoniation. The vapour pressure and crystallisation temperatures are obviously of importance with regard to the type of handling equipment available or to be installed.

In the U.S.A. the standard equipment used consists of batch-mixing equipment of the type outlined in Fig. 3. The materials of construction vary with the type of ammoniating solution, mild steel being used for straight ammonia solutions and stainless steel or aluminium being used for solutions containing ammonium nitrate. Compressed air or pumps or occasionally its own pressure is used to handle the liquor from tank car to storage and from storage to mixing. Both storage tanks and pipelines are often lagged to reduce the liability to crystallisation and the pipelines are usually laid out in such a way as to facilitate easy drainage. Fig. 3 is self-explanatory and probably all we need add is that the mixer is often operated to give an absorption rate of 16-17 lbs. of NH_3 per cubic foot per hour.

In some of the more recent plants, pug mill or blunger type mixers are used to give continuous ammoniation and in these absorption rates as high as 66 lbs. of NH_3 per cubic foot per hour have been achieved.

After mixing, the ammoniated superphosphate is conveyed to storage or, occasionally, to be dried and then cooled. Normally, the ammoniated superphosphate will leave the mixer at from 115 to 150°F. and it is preferable that this should be cooled quickly if rapid dispatch is required, and if a tendency to reversion is to be avoided.

Until very recent times practically all the ammoniated superphosphate or compound fertilisers based on superphosphate produced in the U.S.A. were made in powder form but, within the last

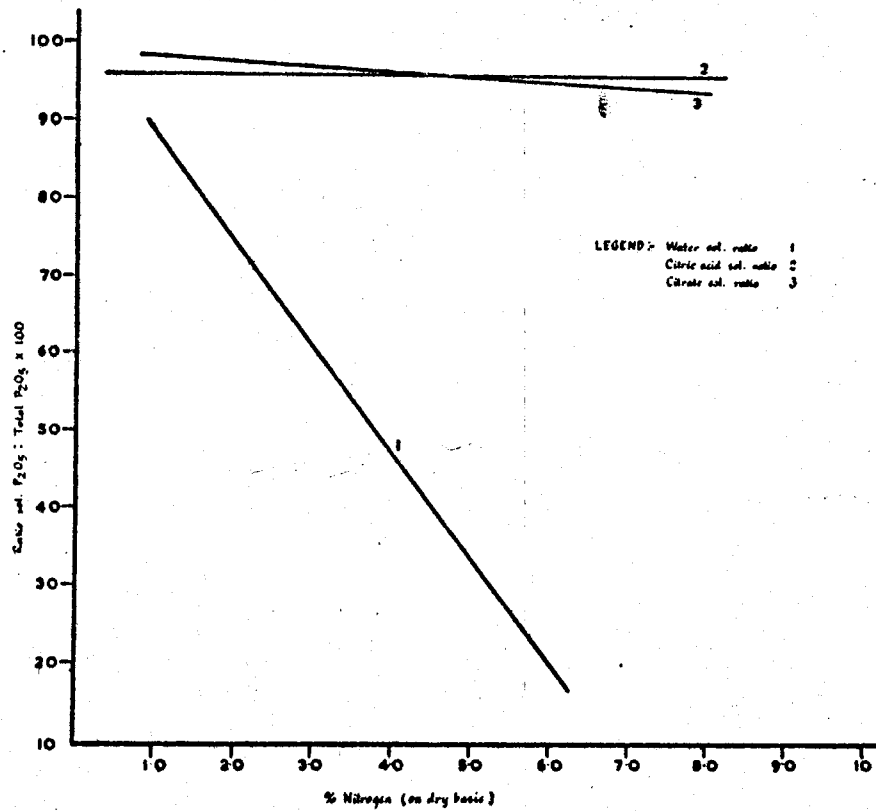


FIG. 1
AMMONIATION OF SUPERPHOSPHATE

few years, at least three plants have started to produce ammoniated granular compound fertilisers.

S.A.I. Experience

When first we started to make ammoniated superphosphate, we made our mixes in a small pan-type concrete mixer, weighing superphosphate into the mixer and adding ammonia from a carboy mounted on a scale, by means of a small hand pump. At first the ammonia was poured on to the supers while the mixer was running but this gave rise to considerable loss of ammonia. It was soon found that the most satisfactory technique was to lead the ammonia under the surface of the superphosphate. Absorption was rapid and surrounding atmospheric conditions not too intolerable. After addition of the requisite quantity of ammonia, the mixture was discharged to the floor, turned over several times by spade and left to cool. This method sufficed to provide the ammoniated superphosphate used in the pot trials previously reported, but when quantities of several hundred tons were required, and when we wanted to make granular compounds, we had to make use of a full-scale granulation plant. Fig. 4 shows the arrangement used. This was a 5 ton/hr. pan-mixer type of granulation plant of conventional design.

Aqueous ammonia, run by gravity from an overhead storage tank was measured in a measuring tank and run by pipe to discharge in the pan at points immediately behind the ploughs. By this means rapid absorption of ammonia was obtained and shrouding of the pan was hardly necessary. However, as we wished to be able to ammoniate with by-product ammonia liquor containing H_2S , we later provided a shroud round the pan and exhausted this to the primary air inlet of the granulation plant furnace.

We found it desirable to add approximately three quarters of the granulation water before adding the ammonia as not only did this procedure give better absorption but also it helped to facilitate granulation which was found to be more difficult after adding the ammonia.

We had little difficulty in producing several hundred tons of granular ammoniated compounds which were used in field trials on a variety of soils and crops and which we subjected to storage trials in the works.

Most of the material we produced was ammoniated to the extent of 3% NH_3 on the supers content of the compound, since this is the level commonly used in the U.S.A. We carried out nitrogen balances and apart from confirming an expectation that no nitrogen loss should result, these exercises showed us just how difficult it is to produce an exact materials balance on a plant of the granulation plant type.

We next tried the ammoniation of our granular compounds with ammoniating solutions containing ammonium nitrate or urea. The ammonium nitrate solution was approximately comparable to a standard solution available in the U.S.A. and had the following composition : 55% NH_4NO_3 , 22.5% free NH_3 , 37.7% total N. The urea solution was not comparable to any used in the U.S.A. as it contained no free carbon dioxide. It was also diluted to lower the vapour pressure to permit of handling in our equipment. The analysis was 31.8% urea, 23.3% free NH_3 , 33.8% total N.

We used these solutions in sufficient quantity to add 3% NH_3 on the superphosphate content of the compounds and we found no difficulty whatsoever in control of the plant or in producing an attractive product. Carefully controlled N.P.K. balances showed no significant loss of nitrogen when using the ammonium nitrate solution, though there was a slightly higher acidity than is normal in the exhaust gases from the granulation plant dryer. There was no sign of nitrogen oxides and we feel it not unreasonable to say that use of ammoniating solutions containing ammonium nitrate permits the incorporation of nitrates in granular compounds. We have a very vivid memory of what happened some years ago when we incorporated ammonium nitrate in a granular compound — even though this contained substantial quantities of limestone — the brown fumes from the dryer were picturesque but expensive.

In the case of the ammonia/urea solution, we appeared to have a slight nitrogen loss. A determination of urea in the finished product showed that nearly half of the urea added had been decomposed. There was also a greater reversion of water soluble P_2O_5 than had been experienced previously. Calculation showed that if we took into account the free ammonia from the decomposition of urea, the ammoniation was actually at the level of 4% NH_3 on the supers and not 3%. This higher level of ammoniation gave us the greater reversion. There was no sign of production of insoluble nitrogen compounds, such as we had been led to expect from some American work.

In addition to testing the materials we produced agronomically, we examined them for storage properties in paper bags and in hessian bags. Though at times it appeared that ammoniated material had slightly less tendency to set than non-ammoniated compounds of the same analyses, we very much doubt that any observed difference was significant. A really significant difference was that in no case did ammoniated material show the slightest tendency to rot bags. Freedom from bag rot remained even after material had been stored between two and three years and this was as true for material ammoniated with ammoniating solutions as it was for material ammoniated with aqueous ammonia. As bag rot can be extremely expensive, the advantage resulting from ammoniation is substantial.

Thus we had found it practicable on the full plant scale to ammoniate using aqueous ammonia, ammonia/ammonium nitrate solution, ammonia/urea solution and to produce a good product free from any tendency to bag rot. We would have liked to make use of ammoniating solutions as permanent practice but, unfortunately, these are not commercially available in this country, so we next investigated the possibility of ammoniating using by-product ammonia liquor. The solutions we used tested 14% NH_3 , 15-16% CO_2 and 3-4% H_2S .

Since H_2S is liberated when by-product ammonia liquor is added to superphosphate, we arranged to shroud the open pan mixer in which granulation is effected and to exhaust this to the primary air supply to the coal-fired furnace heating the dryer. This had the effect not only of putting the pan mixer under a slight suction and so preventing offence but also of affording a means of burning the H_2S .

In the result we found that despite their low nitrogen content and high H_2S , CO_2 and H_2O contents, it was possible to make use of these by-product liquors. At this point, however, it is relevant to consider the safety precautions necessary to allow of the use of ammonia solutions in plant practice.

Safety

It is essential to protect workmen from contact not only with ammoniating solutions but also from the fumes resulting from their use. While working on ammonia lines and containers, the worker should use tight safety goggles and protective clothing and should be equipped with a gas mask. The canister-type mask is one claimed to be suitable for concentrations below 3% NH_3 but suffers from the disadvantage that it is not easy to tell its progress towards exhaustion. For high concentrations, the supplied-air type of equipment should be used and, indeed, it might be preferable to standardise on this type. A safety observer is a wise precaution while connecting and disconnecting ammonia tank cars.

As air containing 15-25% of ammonia is explosive, all electrical equipment should be spark-proof and well-earthed. No open flame should be allowed near pipes, valves, tanks or any other equipment that has contained ammonia solution, until it is certain that they are thoroughly clean and contain no scale, liquid or gas. At least one fatal accident is known to have occurred recently when a welder ignited an ammonia/air atmosphere above ammonia liquor in a stock tank which had not been properly emptied.

The following table shows the physiological effect of different concentrations of ammonia.

	Parts NH ₃ per million of atmosphere
Least detectable odour	53
Maximum allowable concentration for exposure for 8 hours or for repeated exposure	85
Maximum allowable concentration for single exposure, say 4 hours. Slight throat and eye irritation may occur	100
Considerable throat irritation	400
Eye irritation with usually no serious after-effect, provided exposure is very short ..	700
<i>With slightly higher concentration exposure is unbearable</i>	
Fatal concentration	5,000-10,000

In the case of by-product liquor containing hydrogen sulphide, precautions must also be observed to keep the concentration of this gas very low. The physiological effect of this gas is shown in the following table.

	Parts H ₂ S per million of atmosphere
Symptoms of local irritation of eyes and respiratory tract after one hour's exposure	100
Dangerous if inhaled for one hour. Causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6-8 minutes	200
Very dangerous if inhaled for 15-30 min. Causes severe irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs which may readily prove fatal	500
Immediate unconsciousness resulting in death unless artificial respiration applied at once	1,000

Hydrogen sulphide can also cause explosion; air containing 5-28% H₂S is explosive.

Having established that we could successfully ammoniate our

compound fertilisers on a pan mixer type of granulation plant, we next tried out the process on a rotating tube-type of plant. We found it more difficult to form good granules and there were rather more fines formed than is normal in this particular plant. It was established that while in this case rather more difficulty emerged, ammoniation was practicable in either pan-type or tube-type plants.

During the trials on the tube-type plant, it was observed that some of the product prepared from by-product ammonia liquor and stored in bulk in a warehouse near to the sea was very damp on the surface. It appeared that the material had absorbed much more moisture than was usual with either non-ammoniated granular compounds or granular compounds ammoniated with synthetic ammonia. In order to ascertain whether any of the constituents of by-product ammonia could be responsible for increased hygroscopicity, we felt it desirable to put some tests in hand to check this point.

A number of different types of ammoniated fertilisers were exposed in a humidity cabinet to varying conditions of temperature and humidity. The samples were allowed to come to equilibrium moisture content and the results of these moisture absorption tests are shown in Table V. Sample I was a potato fertiliser ($N_f : P_2O_5 : K_2O = 8 : 7 : 14$ approx.) and II, III and IV were comparable ammoniated products; sample V, the control for Nos. VI and VII, had $N_f : P_2O_5 : K_2O = 8 : 8 : 6$, the P_2O_5 figures being in terms of water soluble phosphate.

The conclusions drawn from this work were that there was no evidence that the use of by-product ammonia liquor gave a product which was less satisfactory than material ammoniated with synthetic ammonia. Furthermore, the moisture uptake of these products as compared with that of the control samples was such that no change in behaviour of the fertiliser on ammoniation was expected. On the other hand, the fertilisers containing ammonium nitrate or urea were much more hygroscopic than the other samples. It is of interest that the extent of this effect appears to be out of all proportion to the amount of ammonium nitrate or urea present. For example, sample III was ammoniated with a solution containing 22.5% free ammonia and 55% ammonium nitrate and the degree of ammoniation was equivalent to 3% NH_3 on the superphosphate used. Therefore, the ammonium nitrate added was approximately only 3% of the fertiliser. This compares with a difference of 14% moisture content between this sample and the control III at 73% RH, 20°C. Similarly, a calculated 1.9% urea in sample IV is associated with an increase of 8% moisture content as compared with the control sample II at 73% RH, 20°C. However, these products are less hygroscopic than "Nitro-Chalk" so that, provided appropriate precautions are taken, it should be possible to manufacture fertilisers

Table V
Equilibrium moisture contents 1% of dry matter

Sample No.	I	II	III	IV	V	VI	VII
Ammoniating liquor	None	Synthetic ammonia	Ammonia + NH ₄ NO ₃	Ammonia + urea	None	By-product ammonia	Synthetic ammonia
Initial moisture content	8.0	3.0	1.5	2.4	1.6	0.7	1.1
Water content at 55% RH, 20°C. ..	1.1	0.9	1.4	2.2	1.2	1.8	1.8
Water content at 73% RH, 20°C. ..	4.8	2.2	16.3	10.3	4.3	5.0	5.7
Water content at 73% RH, 20°C. after prelim. exposure at 90% RH	5.7	6.1	16.4	14.0	7.9	8.1	9.4
Water content at 71% RH, 25°C. ..	4.6	2.1	17.1	11.2	4.4	5.1	4.7
Water content at 73% RH, 30°C. ..	3.7	2.3	18.9	10.6	3.8	4.6	4.8
Water content at 90% RH, 20°C.* ..	41.9 45.2	45.0 46.6	51.0 57.9	58.9 60.3	34.9 55.5	41.8 42.1	43.2 43.7

* Note. At 90% RH, the increases in weight were so rapid and so large that the test was stopped after 9 days before the samples had attained equilibrium. All except samples V and VI were then surrounded by drops of solutions.

containing ammonium nitrate or urea without undue storage difficulties being experienced.

We then decided that as our preliminary agronomic evaluation had suggested that, provided ammoniation was limited to 3% NH_3 on the superphosphate content of the compound, ammoniated compounds were as effective as non-ammoniated compounds of the same analyses; as ammoniation appeared to offer a prospect of lower costs; as ammoniation was technically feasible and as the real test of a product is its commercial acceptability, we should endeavour to produce all our make of compounds in ammoniated form. For domestic reasons, it was decided to apply this conclusion at only three of our works. We decided to limit the extent of ammoniation to 2% NH_3 on the superphosphate content of the compound, partly because we wanted to be conservative, partly because the quantity of ammonia available is rather limited at the moment and partly because ammoniation on the plant scale involves the fines in at least two journeys through the granulator, with a consequent possibility of over-ammoniation of a portion of the product.

We used a by-product liquor testing 25-28% NH_3 , 0.3% CO_2 and 0.01% H_2S at two of our plants, a pan-type plant and a tube-type plant, while at the other plant, a tube-type plant, we used a by-product liquor testing 14-16% NH_3 , 16% CO_2 and 1.1% H_2S .

We have had very little trouble with the pan-type plant and have produced quite a good product. The method of operation developed at this works is roughly as follows :—

Ammonia, stored in two old Lancashire boilers, is run by gravity to an 800 gallon header tank over the granulation plant. This feeds a vented tank fitted with a sight glass and calibrated from 0 to 15 gallons. Normal usage is from 7-10 gallons per batch depending on the superphosphate content of the compound being made. Water is sprayed into the mixer at the same time as the 16 cwt. batch is being brought up the skip hoist. This gives a wet surface to the pan receiving the dry ingredients. As soon as the batch has been tipped into the mixer, the ammonia is run in through an open-ended pipe which discharges under the level of the mixture and immediately behind a plough so that it is very quickly mixed through the batch. The whole of the ammonia is added without interruption. While ammonia is being added, water is sprayed on and, of course, stirring allowed to continue. Heat is evolved during the mixing, the temperature rise being 10 to 12°F. The time of granulation in the pan is about 3.5 to 4 minutes.

From the mixer, the granules pass to the rotary dryer where they are dried to a moisture content of 2.5-3%, rising to a temperature of 200°F. in the dryer and thereafter being cooled to 80-90°F. before passing to storage. This plant had no real difficulty in

producing a good granular product. The product is rather smoother than it was last year and the throughput rate up a little but we doubt whether this is attributable to ammoniation.

The following are some of the analyses obtained on this plant:—

Table VI
Analyses of Ammoniated and Non-ammoniated Compound Fertilisers

Compound	% W. Sol. P_2O_5			% Cit. Sol. P_2O_5		% total P_2O_5	% Free Acid as P_2O_5	% K_2O
	% N ₂	% P_2O_5	=% of total P_2O_5	% P_2O_5	=% of total P_2O_5			
Grain Non-ammon.	5.1	9.5	64	12.8	87	14.7	0.56	6.1
„ Ammoniated	5.1	8.0	53	12.4	82	15.2	0.01	6.1
Potato Non-ammon.	5.9	8.9	80	10.2	92	11.1	1.44	12.0
„ Ammoniated	6.1	7.8	69	10.0	89	11.3	0.04	12.0
Turnip Non-ammon.	5.0	9.0	65	—	—	13.9	0.32	6.1
„ Ammoniated	5.2	7.7	54	12.2	86	14.3	nil	6.2

All the fertilisers contained some finely ground Gafsa phosphate and this accounts for the apparent low conversion of water soluble phosphate. In each case the water soluble phosphate of the ammoniated compounds has dropped by 12-15% of the quantity of water soluble phosphate in the non-ammoniated compounds.

At the second plant, a tube-type plant, using this high quality by-product liquor, we had more trouble in obtaining good granulation efficiency, there being a tendency to form an excessive proportion of fines. It was found preferable to add the ammonia at a point one-third of the way along the tube from the feed end and finally it was decided to add all the ammonia in one of the tubes and to have no ammonia addition to the tube which receives the recycled fines. This permitted granulation to be continued without excessive formation of fines. The addition of ammonia was by means of a coarse spray and quantity control was affected by a rotameter. At first, the ammonia was added before the water but this was found to give rise to considerable difficulties in granulating. Later, when the arrangement was changed to add the ammonia after the water, the control was not much more difficult than with non-ammoniated compounds. Any difficulties then experienced were due to a slightly heavier fines recycle. Temperature rise across the granulating tube was found to be 10-15°F. We are not quoting analytical results as we have no comparable non-ammoniated product analyses.

At our third plant, where we used a low strength by-product

liquor with a high carbon dioxide content, we have had a great deal of trouble, nearly all the difficulties being associated with an excessive production of fines. This is our oldest granulation plant and one which has always shown a tendency to have difficulty with recycled fines but these difficulties were greatly exaggerated when using this by-product liquor for ammoniation. The temperature rise on ammoniation was also found to be much lower than on the comparable tube-type plant using the relatively pure by-product ammonia containing practically no acid gases.

It was then observed at one point when the granulator was stationary that large gas bubbles were rising from a pool of liquor which had leaked into the tube. Subsequent tests showed that when the liquor was mixed with compound fertiliser powder, bubbles of carbon dioxide and hydrogen sulphide were evolved. Microscopic examination of the mixture showed that twelve minutes after an addition, when observation ceased, bubbles were still being slowly evolved and causing the wet lumps to disintegrate. Pure aqueous ammonia and the by-product ammonia liquor containing practically no acid gases did not give this effect. It was also found that the lower temperature of reaction of ammoniation could be quantitatively explained by the evolution of these acid gases. This work suggested that the granulation difficulties being experienced and the excessive production of fines were due to the disruption of the granules by the liberation of the carbon dioxide and hydrogen sulphide.

It was then decided to attempt ammoniation at this plant using synthetic ammonia liquor containing no acid gases. It is extremely difficult to judge changes in granulation efficiency by visual observation of the product from the granulator or dryer and it was decided to base comparisons on sieve analysis of materials from the dryer. This material did not, of course, provide an accurate estimate of granulation efficiency as it contained recycled material from the oversize breakers but care was taken to standardise conditions so that, as far as possible, the results were comparable. Granulation efficiency was defined as the percentage of product ex dryer lying in the size range 5-16 B.S.S. The results showed that at normal production rates the ratios of granulation efficiency were :—

	Granulation Efficiency Ratios
Non-ammoniated	100
Ammoniated with ammonia containing no acid gases	73
Ammoniated with ammonia containing 16% CO ₂ , 1% H ₂ S	54

If it is assumed that the screens were working perfectly to give

a product containing only material within the size range 5-16 B.S.S., then calculations show that the production of 100 tons product would be associated with the following recycles.

	Recycles	
	Tons Fines	Tons Oversize
Non-ammoniated	34	110
Ammoniated with ammonia containing no acid gases	100	133
Ammoniated with ammonia containing 16% CO ₂ , 1% H ₂ S	195	159

The fines would go back to the granulator to be rewetted and the cracked oversize straight to the dryer. It will be seen that this would lead to a considerable increase in water consumption and to a heavy overload on the dryer. In practice, the screens do not work perfectly, particularly the fines screen which becomes very heavily overloaded. The result is that the product contains a very large proportion of undersize material. This has the effect of reducing the above potential water consumption and dryer overload. The fines recycle, however, was still increased to such an extent that the water consumption (including the water in the ammonia liquor) rose from 20-25 gallons/ton to 42-52 gallons/ton. In the case of the comparable tube-type plant which was using the fully decarbonated ammonia, the water consumption only rose from 20 to 30 gallons/ton, whereas with the pan-type plant there was no rise in water usage.

This work has shown that ammoniation with pure ammonia solutions is relatively simple but that ammoniation with liquors containing a high proportion of acid gases can, particularly in the tube-type of plant, give rise to considerable difficulties with the granulation process. We are continuing our investigations to determine the maximum permissible limit of acid gases which can be tolerated and it may well prove to be desirable to define different levels of acid gases for different types of granulation plant.

Marketing

In marketing ammoniated products, regard must be had to the fact that though P₂O₅ available to the plant is substantially unchanged, the content of water soluble P₂O₅ is reduced. After consultation with agricultural authorities, we chose to give a water soluble guarantee and, in addition, to declare the figure of citric acid soluble P₂O₅. Under the Fertiliser and Feeding Stuffs Act, this additional declaration operates as an implied warranty. As has been shown previously in this paper, the proportion of the total P₂O₅ which is water soluble is fairly high, and we felt that, such being the case, the effective soluble phosphoric acid content of our

compounds was more accurately described by the citric acid than by the water soluble test.

The citric acid test was chosen for three reasons :—

- (1) On all the evidence available, it gives an accurate description of fertiliser value ;
- (2) The method of analysis is simple and direct, and the results are reproducible ;
- (3) The analytical procedure is laid down in the Regulations under the Act and consequently a warranty given is capable of being checked in accordance with the provisions of the Act and of the Regulations.

The ammonium citrate test (A.O.A.C. method) is of course used by the Americans for ammoniated compounds. On the first of the above three counts, it is probably as good as the citric acid test, but it is inferior on both the second and the third counts, and so the citric acid test has been used to describe our compounds.

Finally, my thanks are due to all my colleagues, whose work I have reported, and to the Directors of Scottish Agricultural Industries Ltd. for permission to publish this paper.

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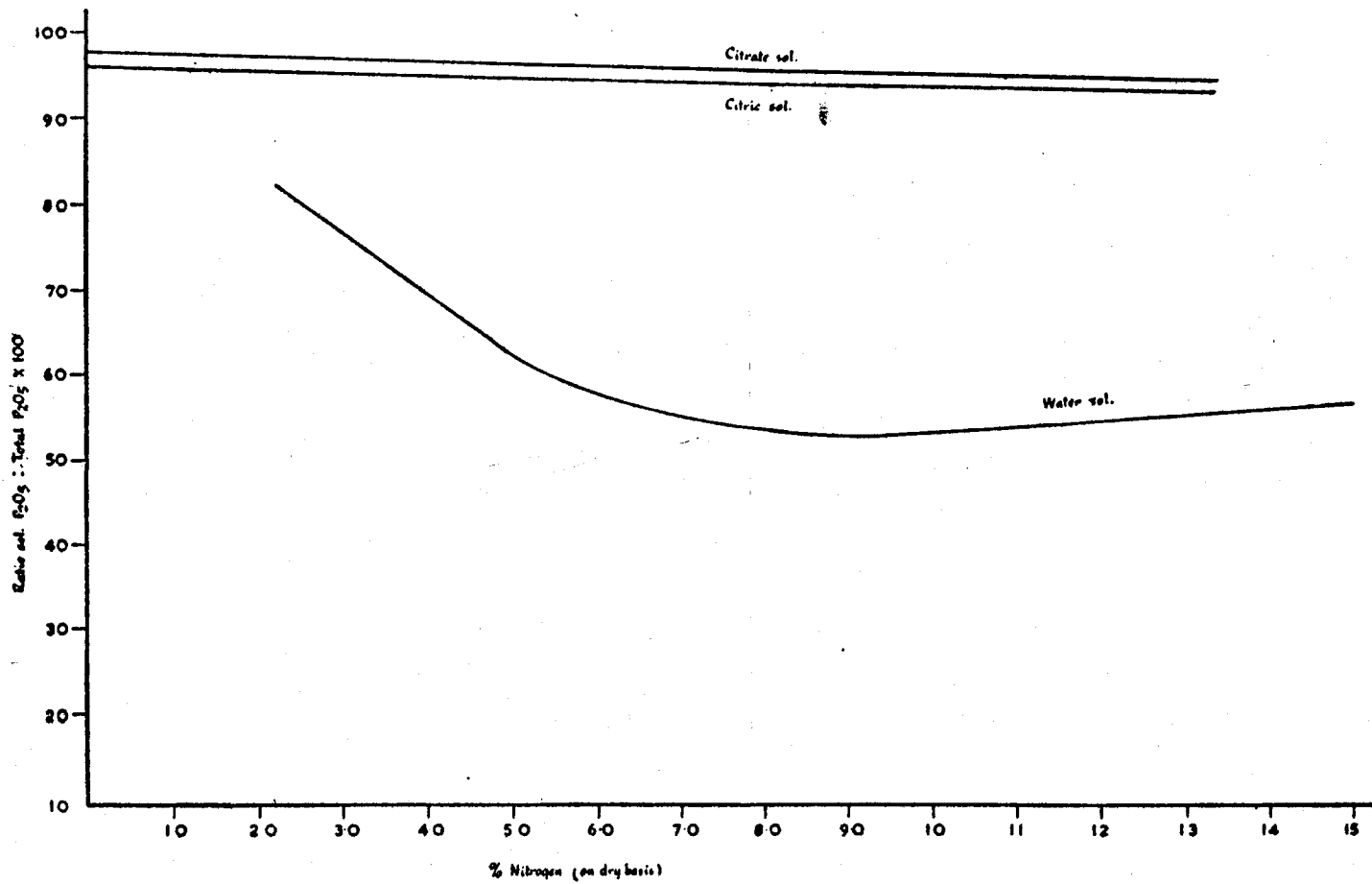


FIG. 2
AMMONIATION OF TRIPLE SUPERS

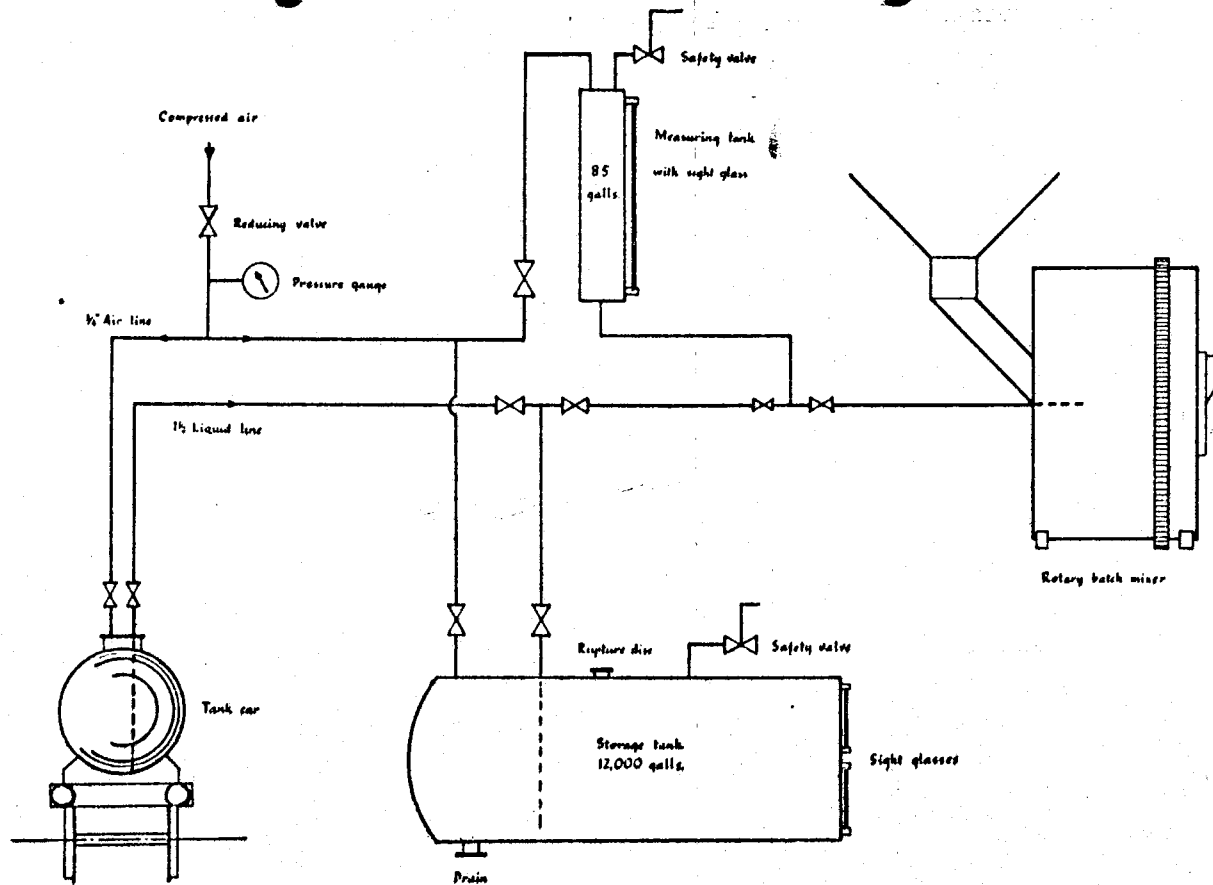


FIG. 3
 AMMONIATION EQUIPMENT LAYOUT AS USED IN U.S.A.

Table IV

	% NH ₄ NO ₃	% Urea	% Free NH ₃	% Ammonium Carbonate	% H ₂ O	% Total N ₂	Approx. Specific Gravity at 60°F.	Approx. Vapour Pressure p. s.i.g. at 104°F.	Approx. Temp. at which salt begins to crystallise— °F.
Anhydrous Ammonia	—	—	99.9	—	—	82.2	0.618	211	—
Aqueous Ammonia	—	—	30.0	—	70.0	24.6	0.895	11	—
Nitrogen Sol. A	65.0	—	21.7	—	13.3	40.6	1.142	10	23
" " B	55.5	—	26.0	—	18.5	40.8	1.079	15	-13
" " C	66.8	—	16.6	—	16.6	37.0	1.182	3	48
" " D	60.0	—	34.0	—	6.0	49.0	1.045	50	-49
UAL—A	—	32.5	28.9	18.1	20.5	45.5	0.895	66	5
UAL—B	—	43.1	23.5	16.4	17.0	45.3	1.046	55	30

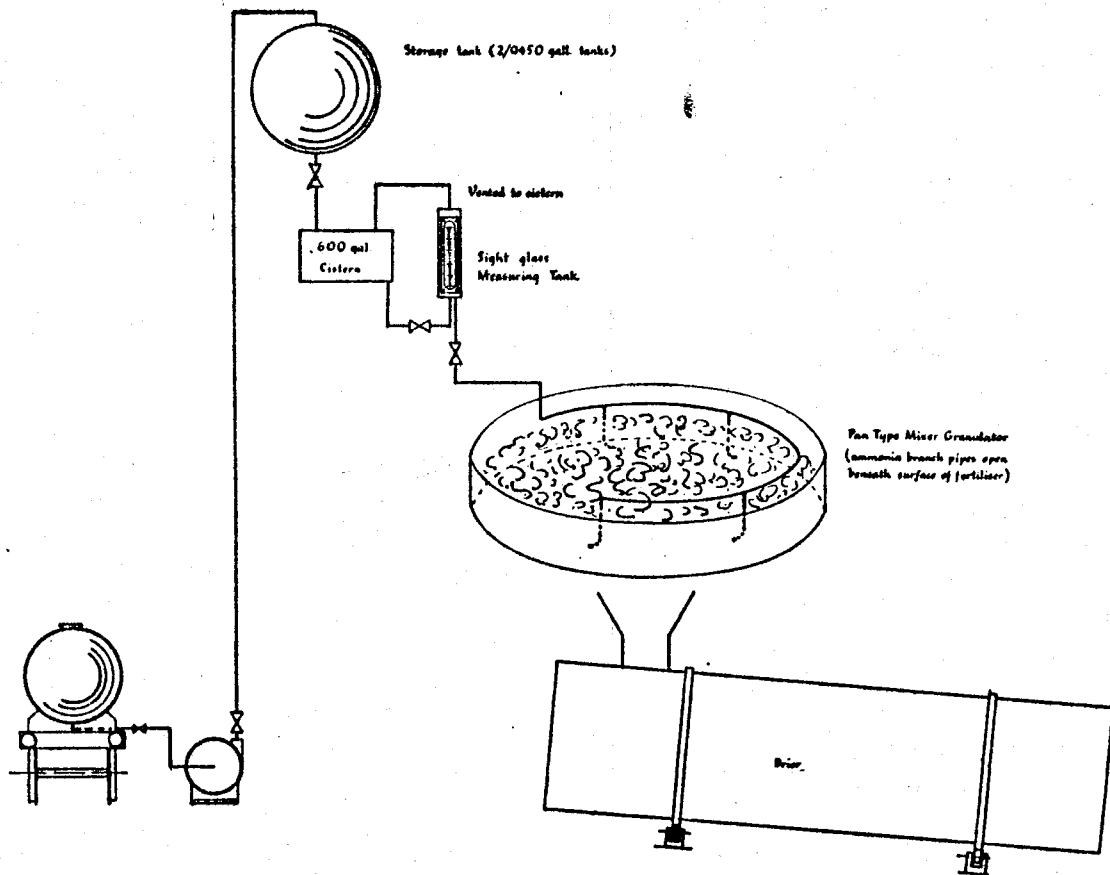


FIG. 4
 AMMONIATION EQUIPMENT LAYOUT AS USED BY S.A.I. ON PAN TYPE GRANULATION PLANT