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ALTERNATIVES TO SUPERPHOSPHATE.

EXPERIMENTAL WORK.

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AMMONIATION OF SUPERPHOSPHATE.

The ammoniation of superphosphate is now an established procedure in Canada and the U.S.A., where phosphate fertilizers are sold on the basis of citrate-soluble P_2O_5 . In Britain however the process has only recently begun to be developed. We ourselves have investigated various aspects of ammoniation in the laboratory, and the following is a condensed account of the experiments and of their results.

Ammoniation with aqueous ammonia.

Matured superphosphate was treated with ammonia solution of S.G. 0.88 in various ratios within a range from 1 to 4 mols NH_3 per mol of water-soluble P_2O_5 in the superphosphate. This was carried out both with the superphosphate alone, and in the presence of sufficient ammonium nitrate and muriate of potash to give a mixture with an N : P_2O_5 : K_2O weight ratio of 2 : 3 : 2.

Citrate-soluble* water-insoluble P_2O_5 was formed at the expense of water-soluble P_2O_5 , the amounts of each varying in a linear manner with the degree of ammoniation up to a value of 3 mols NH_3 per mol water-soluble P_2O_5 . At the lower ammoniation ratios, the citrate-soluble, water-insoluble P_2O_5 was probably present as dicalcium phosphate, but at the highest ratios investigated it is believed that citrate-soluble tricalcium phosphate was present. A study of the reaction temperatures indicated that the superphosphate had the greatest affinity towards the first 3 mols NH_3 added per mol water-soluble P_2O_5 . This was confirmed by the results for the losses of ammonia when samples were exposed to air of 75% relative humidity; for ratios up to 3 mols NH_3 per mol water-soluble P_2O_5 , nitrogen losses were small, but they increased rapidly with increasing degree of ammoniation in excess of the above figure. Ammonia losses during reaction also increased appreciably when the degree of ammoniation rose above 3 mols NH_3 .

When portions of the products were stored without drying at laboratory temperature for 3 months, no decrease in the citrate solubility of the P_2O_5 took place either in samples of ammoniated superphosphate or in those samples in which ammonium nitrate and muriate of potash were also present. A disadvantage of using aqueous ammonia is that ratios of more than 1 mol NH_3 per mol water-soluble P_2O_5 lead to wet and sticky products, which would be difficult to handle, and which would need drying, with considerable addition to the cost of manufacture. For this reason, the use of solutions containing ammonium nitrate or urea as well as ammonia, or of gaseous ammonia, is to be preferred. Solutions of the above type were first used in the U.S.A., where their use is now widespread; they have surprisingly low vapour pressures considering the small proportions in which water is present.

* A.O.A.C. test.

Ammoniation with an ammonia/ammonium nitrate solution.

The solution employed had an analysis : free NH_3 16.7%, H_2O 20.8%, NH_4NO_3 62.4%. In general, results were obtained similar to those reported for aqueous ammoniation. Considerably higher ammoniation ratios were however possible without producing a wet and sticky material. Nitrogen losses during ammoniation were greater than with aqueous ammonia, due partly to the higher temperatures reached, but mainly to the difficulty of mixing in the solution rapidly by hand. With these solutions, efficient and rapid mixing is essential to minimise losses, as the vapour pressure of ammonia increase sharply with increasing temperature.

The products were submitted to more drastic storage conditions than those described in the previous section, being heated for 30 days at 70°C in containers fitted with valves, so that pressure could not develop but air could not enter to cause drying of the material. Even under these conditions the citrate solubility did not fall below 83 - 85%, these worst values being obtained with the most highly ammoniated samples, to which about 4 mols of NH_3 had been added per mol of water-soluble P_2O_5 . There was some indication that the presence of potassium chloride helped to reduce the reversion of P_2O_5 to citrate-insoluble forms. In spite of the severity of the above conditions ammonia losses were small, and where the ammoniation rate was not above 3 mols NH_3 the loss was only 3 - 4%. In practice, conditions would generally be much less drastic than the above, as the product should be cooled before storage or bagging.

Ammoniation with gaseous NH_3 .

When ammonia under a pressure of a few inches of water was passed over the surface of matured superphosphate which was kept in motion, reaction proceeded smoothly, and up to 3.3 mols NH_3 per mol of water-soluble P_2O_5 was absorbed rapidly. Little or no reversion of citrate-soluble P_2O_5 to unavailable forms occurred, and the products were much superior to superphosphate in physical condition. The rate of absorption of ammonia was increased when the superphosphate was mixed with ammonium sulphate and muriate of potash before ammoniation, and again little reversion of citrate-soluble P_2O_5 to unavailable forms occurred. During subsequent granulation and drying, some loss of ammonia occurred; it seemed that, with anhydrous NH_3 , only about 2.5 mols became firmly fixed per mol of initially water-soluble P_2O_5 .

A mixture with an N : P_2O_5 : K_2O weight ratio of 1 : 1 : 1.5 was ammoniated and granulated, but the quantity of water required to give a high proportion of granules in the range between 5 and 18 mesh B.S.S. sieves was critical, and more water was required than with normal mixtures based on superphosphate. The granules were rather soft, and further batches made with 25% of the total nitrogen as ammonium nitrate showed improvement neither in ease of granulation nor in granule strength.

THE PRODUCTION OF NEUTRAL NITROPHOSPHATE.

The present paper is limited to work carried out in our research laboratories on a process involving the following steps:

1. Attack on phosphate rock with nitric acid, mixed with either sulphuric acid or ammonium sulphate.
2. Ammoniation of the resulting slurry, followed by granulation, with or without the addition of muriate of potash, and drying.

These stages will be dealt with in turn.

The nitric acid - phosphate rock reaction stage.

Attack on the rock with nitric acid alone or mixed with sulphuric acid.

Moroccan phosphate rock, ground to give 62% passing a 100 mesh B.S.S. sieve, was treated with nitric acid of 65% w/w HNO_3 , or mixtures of this with sulphuric acid of 77% w/w H_2SO_4 , in proportions sufficient theoretically to convert the whole of the P_2O_5 in rock to phosphoric acid. The maximum temperature reached varied from 70 to 90°C., depending on the ratio $\text{HNO}_3/\text{H}_2\text{SO}_4$. In the range 1 to 4 mols HNO_3 per mol H_2SO_4 , the ratio did not affect the reaction rate appreciably, but the rate tended to be slightly higher with the larger $\text{HNO}_3/\text{H}_2\text{SO}_4$ ratios and with nitric acid alone. In the $\text{HNO}_3/\text{H}_2\text{SO}_4$ range investigated, attack on the rock was more rapid than when sulphuric acid of 70% H_2SO_4 is used alone, and the reaction time of 1 hr. at 80°C was sufficient to convert 90 to 95% of the rock P_2O_5 to water-soluble forms.

When either the nitric acid alone, or the mixed nitric and sulphuric acids, were reacted with Moroccan rock, losses occurred amounting to about 1.3 lbs N per 100 lbs rock (130 lbs 100% HNO_3 per ton of rock). This could be reduced to about 0.4 lb N per 100 lbs of rock, by adding the sulphuric acid to the rock 15 minutes before adding the nitric acid. Calcining the rock before reaction also reduced the nitrogen loss appreciably, and here prior addition of sulphuric acid did not reduce the loss further, this being of the order of 0.2 lb N per 100 lbs of rock when the rock was calcined at 500°C. The nitrogen loss for a given weight of rock was practically independent of the $\text{HNO}_3/\text{H}_2\text{SO}_4$ ratio in the range 1 to 4 mols HNO_3 per mol H_2SO_4 . Investigation showed that the greater part of this nitrogen loss was due to evaporation of nitric acid with the gas driven off from the rock; only a fraction of the gas consisted of oxides of nitrogen formed by reduction of the nitric acid by the organic matter in the rock.

Attack on the rock by nitric acid in the presence of ammonium sulphate.

The presence of ammonium sulphate, in proportions up to 1.9 mols per mol of P_2O_5 , was found to have a negligible effect on the velocity of the reaction between nitric acid of 65% w/w HNO_3 and Moroccan phosphate rock ground to the same degree of fineness as before, the acid to rock ratio being 6 mols HNO_3 per mol of rock P_2O_5 . Prior solution of the ammonium sulphate in the acid resulted in a slightly more complete attack on the rock P_2O_5 , had a greater effect in reducing foaming, and gave a more homogeneous slurry than did mixture of the ammonium sulphate with the rock before reaction with the acid. In either case, a reaction time of 1 hr. at 70 to 80°C was more than sufficient for the conversion of 95% of the rock P_2O_5 to forms soluble in ammonium citrate solution.

Attack on the rock by nitric acid containing ammonium sulphate in solution, with lower acid/rock ratios than that used above, is dealt with at the end of Section B below.

Ammoniation of the reacted phosphate rock/nitric acid mixtures.

A. With aqueous ammonia.

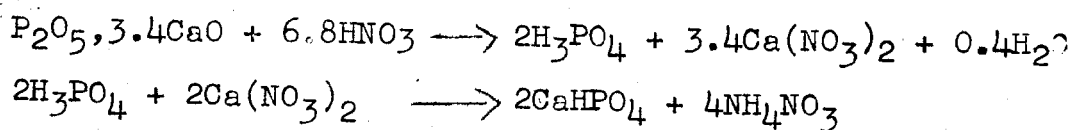
Slurries were prepared as above, by reacting Moroccan phosphate rock for 1 hr. at 80°C, either with nitric acid of 65% w/w HNO_3 , or with mixtures of this with sulphuric acid of 77% w/w H_2SO_4 , the acid/rock ratio being sufficient theoretically to bring about complete conversion of the rock phosphate to phosphoric acid; the ratio of the two acids varied from 1 to 4 mols HNO_3 per mol H_2SO_4 . To these slurries was added ammonia solution of S.G. 0.896 in proportions varying from 3 to 5.75 mols NH_3 per mol P_2O_5 . In every case more than 90% of the P_2O_5 in the product was obtained in a form soluble in neutral ammonium citrate solution. Within the range studied, the ratio HNO_3/H_2SO_4 in the mixed acids had only a slight effect on the proportion of the P_2O_5 in the ammoniated product which was citrate-soluble. The maximum neutralisation temperature varied from 50 to 80°C, depending on the degree of ammoniation.

When aqueous ammonia is used in the above proportions, the products are very wet. They would be difficult to dry, and the fuel cost would be considerable. In the experiments, in which mixing took place in a beaker, losses of ammonia were high, amounting to 20 to 30% when no cooling was attempted, and to 5 to 16% when the ammoniation temperature was kept below 50°C.

B. With gaseous ammonia under pressure.

For these experiments, a closed heavy metal vessel fitted with a gate stirrer was employed, and the slurry was agitated continuously during ammoniation. Preliminary work showed that ammoniation of the reacted acid nitrophosphate slurries was rapid when the mixture was at about 40°C; when starting with a cold slurry however, the temperature had to reach 40 to 50°C before ammonia was absorbed rapidly. The concentrations and ratios of the acids used in preparing the slurries were as before. Working on quantities of about 1 lb., 20 minutes ammoniation at a pressure of 15 to 30 lb. per sq. in. was sufficient to give products containing some free ammonia and having a pH value of 8.5 or above. The consistency of the final slurry depended on the $\text{H}_2\text{SO}_4/\text{HNO}_3$ ratio; slurries obtained with ratios below 0.9 mol H_2SO_4 per mol of P_2O_5 being very thin. Granulation was made possible by partly drying the slurries with hot air; after drying at 70°C however the granules were rather softer than those normally made from superphosphate. It was also noticed that the larger granules, although dry on the outside, were still damp in the centre; when broken down, the resulting material clogged an 18 mesh B.S.S. screen. The presence of muriate of potash did not appear to affect the ease of granulation. During an experimental ammoniation, the temperature did not rise above 90°C, the heat being conducted away rapidly by the massive mixing pot; on a large scale however, especially since the acid slurry would be hot in the first place, efficient cooling would be required, as it is believed that high temperature during ammoniation leads to the formation of unavailable forms of P_2O_5 .

Further experiments were carried out with nitric acid alone, and mixed with sulphuric acid in ratios up to 0.85 mols H_2SO_4 per mol HNO_3 . The acid to rock ratio was also varied, upwards from that theoretically necessary to convert the whole of the rock P_2O_5 to phosphoric acid. The slurries were ammoniated under pressure as before, and were then granulated at 50°C and dried at 70°C. The granular material had 95 to 98% of its P_2O_5 in forms soluble in ammonium citrate solution. Where only the theoretical proportion of acid was present, about 4 mols NH_3 could be introduced per mol of P_2O_5 , the main reactions in the absence of sulphuric acid being as follows:



leaving about 1.4 mols calcium nitrate in the product.

A small quantity of water-soluble P_2O_5 , representing up to 15% of the total P_2O_5 , was present in some products after ammoniation, probably as ammonium phosphate. In the $\text{HNO}_3/\text{H}_2\text{SO}_4$ range investigated, a large proportion of the sulphate appeared in the product as ammonium sulphate, little calcium sulphate being present.

It was at first assumed that any water-soluble CaO present in the product was in the form of calcium nitrate, which it was desired to eliminate because of its hygroscopic nature. In order to minimise the proportion of water-soluble CaO, it was found necessary to use at least 1.4 mols H_2SO_4 per mol of P_2O_5 . Although it was afterwards found that no calcium nitrate was present in products where 24% of the total CaO was water-soluble, it was nevertheless noted that a product containing only 0.9 mols H_2SO_4 per mol of P_2O_5 was more hygroscopic than one containing 1.4 mols H_2SO_4 .

A number of granular products with desired NPK ratios were prepared by adding triple superphosphate and muriate of potash to ammoniated slurries prepared as above (except that acid of 60% HNO_3 was used in these and subsequent experiments) drying these partially by means of hot air, then granulating and drying in a small rotary drum in the laboratory. The products had the following analyses:

No.	%N.	%Total P_2O_5 .	% K_2O .
1	10.6	10.8	16.9
2 *	14.5	12.2	7.0
3	11.6	24.0	nil
4	7.4	18.6	13.9
5	9.5	19.5	9.8

* No triple superphosphate added.

All of the above products had about 98% of their total P_2O_5 contained in forms soluble in ammonium citrate solution.

Acid nitrophosphate slurries prepared by reacting phosphate rock with nitric acid in the presence of ammonium sulphate were also ammoniated under pressure, and similar results to the above were obtained. Since in this case some of the ammonia was added in the ammonium sulphate, less was necessary in the later stage, with the consequence that the reaction temperature was lower, so that there was less tendency for reversion of P_2O_5 to citrate-insoluble forms.

The use of solutions of ammonium sulphate in nitric acid was investigated further, the HNO_3/P_2O_5 molecular ratio being varied in the range 3.5 to 5.7/1 and the $HNO_3/(NH_4)_2SO_4$ molecular ratio kept steady at 4.3/1. It was found that, after ammoniation, a 95% conversion of rock P_2O_5 to citrate-soluble P_2O_5 could be obtained with an acid/rock ratio of 5.1 mols HNO_3 per mol of P_2O_5 , and a 90% conversion with an acid/rock ratio as low as 4.2 mols HNO_3 per mol of P_2O_5 . Further reduction in the acid/rock ratio however caused a more rapid decrease in available P_2O_5 , so that at 3.5 mols HNO_3 per mol of P_2O_5 the conversion had fallen to 76%.

C. With gaseous ammonia at atmospheric pressure.

A solution of ammonium sulphate in acid of 60% HNO_3 was prepared, and was used for the treatment of Moroccan rock, the proportions being 5.8 mols HNO_3 and 1.4 mols $(\text{NH}_4)_2\text{SO}_4$ per mol of P_2O_5 . With continuous agitation of the slurry, ammonia was absorbed rapidly to the same degree as under pressure, whether the ammonia was bubbled through the slurry or circulated over the surface.

Another slurry was prepared in which the proportions were 4.8 mols HNO_3 and 1.1 mols $(\text{NH}_4)_2\text{SO}_4$ per mol of P_2O_5 . In this case the slurry was too viscous for ammonia to be bubbled through it, but circulation over the surface resulted in rapid absorption.

Hygroscopicity of granular nitrophosphate.

A rough test for comparing the hygroscopicities of granular materials was developed. Granules between 5 and 18 mesh B.S.S. were sieved out of the products, and for each test 50 gms were placed in a 1" tube giving a column of height between 3 and 4". Air at 25°C and of 80% relative humidity was passed through the tube for 2 hours, during which time 560 litres were passed. The total quantity of water passed through the column in this way, would, if it had all been absorbed, have raised the moisture content of the granules by about 20%.

The nitrophosphates, with their considerable proportions of ammonium nitrate, were expected to be more hygroscopic than granular materials prepared from superphosphate and ammonium sulphate, and this proved to be the case. The material picked up moisture and caked as a result. However, the materials which had been prepared by the use of about 6 mols HNO_3 per mol of P_2O_5 , and contained at least 1.4 mols SO_3 per mol of P_2O_5 , proved superior to Nitro-Chalk, which was taken as a standard for comparison because its behaviour in the field was well known. Actually the Nitro-Chalk absorbed less water (1.9% against 3% and over), but the water remained at the granule surface, causing severe caking and eventually separation of liquid phase. With the more porous nitrophosphate granules, the moisture soaked in, so that there was less caking and no separation of the liquid phase. The presence of muriate of potash in some of the nitrophosphates did not appear to affect the hygroscopicity to a great extent.

THE PRODUCTION OF SILICOPHOSPHATE FERTILIZERS FROM
WASTE GYPSUM.

The process by which cement and sulphuric acid are produced from naturally-occurring calcium sulphate (anhydrite or gypsum) is well known, and has been operated on a very large scale both in this country and in Europe. There are two major difficulties in the way of using waste gypsum in this process, these relating to the fluorine and P_2O_5 contained in this material. Fluorine is a poison for the catalyst used in the contact process in making sulphuric acid, while P_2O_5 contained in cement results in an increase in the setting time. The second difficulty is evidently overcome if a similar process can be used, still producing sulphuric acid but making a silicophosphate fertilizer instead of the cement. Production of calcium silicophosphate was investigated during the work carried out at the Building Research Station for the Ministry of Supply during the war ((1) pages 10 and 85), mixes of phosphate rock with sand and calcium carbonate being heated both on a laboratory scale and in small rotary kilns to temperatures ranging from 1450 to 1600°C. It was only necessary for us to substitute the waste gypsum for the calcium carbonate used in this process. There still remains the necessity to remove fluorine from the exit gases before the SO_2 can be used for the production of sulphuric acid by the contact process.

Fertilizers, of which the P_2O_5 content is soluble in ammonium citrate solution, have been produced by the Tennessee Valley Authority by heating mixtures of phosphate rock and silica in an oil-fired shaft furnace (2). In this country, sodium silicophosphate was produced experimentally on a large scale during the war (1). Similar products have been produced for some time in Germany under the names of Rhenania phosphate and Röchling phosphate. Considerable information on calcium silicophosphate and the system $CaO-P_2O_5-SiO_2$ is given by Eisenberger, Lehrman, and Turner (3) and by Klement and Schleede (4). From the German work it appeared that, to obtain a product of high citrate-solubility, it would be advisable to operate in that portion of the $CaO-P_2O_5-SiO_2$ diagram bordered by $Ca_3P_2O_8$ and Ca_2SiO_4 . An Austrian patent (5) recommends ratios of $9CaO, P_2O_5, 3SiO_2$ or $8CaO, P_2O_5, 2.5SiO_2$, both of which lie in the above mentioned region of the system.

Experiments were carried out by the speaker with two different phosphate rock-gypsum-silica mixtures, corresponding in composition to $8CaO, P_2O_5, 2.5SiO_2$ and $6CaO, P_2O_5, 2SiO_2$, the former lying in the above-mentioned region and the latter outside it.

The gypsum used originated from phosphoric acid manufactured by the wet process, and contained 84% $CaSO_4$, 0.7% F, and 1.2% P_2O_5 ; Moroccan rock was used together with ordinary brown sand. The muffle furnace, through which steam could be passed, was heated electrically by silicon-carbide rods, and could be operated up to a temperature of 1450°C. Temperatures were measured with a thermocouple and millivoltmeter which could be read to 0.1, i.e. within 5 to 10°C at the higher temperatures. The reactants were all ground to pass a 100 mesh B.S.S. sieve, and were well mixed before heating. After heating, the products were cooled rapidly by withdrawing from the furnace and allowing the containing vessel to stand in the air. The maximum temperature to which the mixtures were subjected varied between 1300 and 1440°C, and in some cases steam was passed through the furnace. At the higher temperatures the containing vessels had to be of platinum, but silica was employed where possible, although devitrification was rapid.

To obtain high conversion of the P_2O_5 to citrate-soluble forms, the presence of steam during heating was necessary. The composition $6CaO, P_2O_5, 2SiO_2$ in no case gave a conversion over 32.6%.

The highest conversions were achieved with the composition $8CaO, P_2O_5, 2.5SiO_2$, but to obtain a conversion of 90% a temperature of 1430 to 1440°C was necessary, and the presence of steam. Reduction of the temperature to 1390°C resulted in a drop in the conversion to 60%. With the above lime- P_2O_5 -silica ratio the high temperature mentioned above seemed necessary also to remove about 100% of the sulphur present. A considerable proportion of the SO_2 was evolved after fusion, and it appeared that loss of the SO_2 raised the fusion temperature, so that the mass solidified with a honeycomb structure.

With mixtures of the composition $6CaO, P_2O_5, 2SiO_2$ the removal of sulphur took place at a lower temperature, and most of the SO_2 seemed to be evolved before fusion occurred. The passing of steam was a definite advantage, as the following table shows:

Temperature (°C.)	Percentage removal of sulphur	
	Without steam	With steam
1300	80	-
1350	-	97
1400	88	-

1350°C was the sintering temperature of this particular mixture, lying very close to the fusion temperature of about 1380°C.

With mixtures of the composition $8CaO, P_2O_5, 2.5SiO_2$ there was a removal of only 90% of the sulphur at 1390°C in the presence of steam, even though fusion had occurred.

In order to obtain a product with about 90% of its total P_2O_5 contained in forms soluble in ammonium citrate solution, it was necessary to remove 70 to 75% of the fluorine originally present. In the presence of steam this was possible with the composition $8CaO, P_2O_5, 2.5SiO_2$ at 1430 to 1440°C; the composition $6CaO, P_2O_5, 2SiO_2$ only gave off 50 to 55% of its fluorine under these conditions. Total P_2O_5 contents were about 18% with the $8CaO$ mixtures, 20.5% with the $6CaO$ mixtures.

Conclusions are then as follows:

1. Sulphur removal is easier with the composition $6CaO, P_2O_5, 2SiO_2$; fluorine removal and the obtaining of a high conversion to citrate-soluble P_2O_5 is simpler with the composition $8CaO, P_2O_5, 2.5SiO_2$.
2. To facilitate fluorine removal and obtain a product containing round about 90% of its total P_2O_5 in a citrate-soluble form, heat treatment in an atmosphere of steam at a temperature approaching 1450°C is required. Under these conditions sulphur removal is complete but a fused product will result.
3. A 90% conversion to citrate-soluble P_2O_5 requires the removal of at least 70 - 75% of the fluorine, so that the fluorine content of the product does not exceed 0.7%.

INTERIM CONCLUSIONS.

Taking the American chemical test for available P_2O_5 as the criterion, our results show that ammoniation of superphosphate by means of ammonia-ammonium nitrate solutions can proceed up to 3 mols free NH_3 per mol of initially water-soluble P_2O_5 with only small losses of available P_2O_5 , assuming that mixing of superphosphate and solution is rapid and thorough, and cooling arrangements are adequate. This is a much higher degree of ammoniation than earlier American publications had shown to be possible, but a recent paper by T.C. Rogers (6) confirms our findings. The work has been stopped for the present, but doubts are felt on two points:

1. Can firm granules be produced from highly-ammoniated superphosphate and salts such as ammonium sulphate and potassium chloride?
2. Is the American chemical test a good criterion of the availability to the plant of P_2O_5 in highly-ammoniated superphosphate?

The field of nitrophosphate production is a very wide one, in which a number of materials can be used in different combinations and proportions. A number of different products are being made on the large scale by different manufacturers, while other possibilities have been investigated by ourselves and others. Granular products with satisfactory properties can readily be produced with almost any ratios of N, P, and K, these products being more concentrated than mixtures made with superphosphate and ammonium sulphate. Agronomically these materials are of enhanced value because of their contents of nitrate; doubt is felt as to the value of their P_2O_5 contents for calcareous soils, but for use on slightly acid soils they are believed to be of high value.

Our calcination experiments were in the nature of a preliminary investigation. We expect to pursue the matter further, but the high temperature required suggests high costs for fuel and for maintenance of kiln linings.

The thanks of the speaker are due to the Directors of Fisons Ltd. for permission to give this paper and to make known the results obtained in the experiments, and to colleagues who have assisted in the work.

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