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HIGH QUALITY GRANULAR AMMONIUM SULPHATE PRODUCTION

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SUMMARY

In 1986 Esso Chemical's market research group identified a need for a form of sulphur which was to have the following characteristics:

a) The sulphur had to be in the sulphate form so that it would be readily available to the crops as a nutrient.

b) It had to have physical characteristics that would make it easy to handle and apply with conventional farming equipment.

c) It had to be size compatible and readily blendable with existing products such as MAP and Urea, and could not segregate during shipping and handling.

It was felt that the only product which would have all of these characteristics was a granular form of ammonium sulphate.

A world wide search was carried out by Esso Chemical Canada's Agricultural Chemicals Technology Division New Products Group, to determine if such a product was being commercially produced. Incitec, an Australian company, was the only commercial producer identified.

In the summer of 1986, Esso purchased Incitec's technology and in December of 1986, nine months after the initial "New Product" suggestion was brought forth, Esso was commercially producing a high quality granular ammonium sulphate. The product has been in commercial production ever since.

HISTORY

Ammonium sulphate was originally produced as a by-product from the coking of coal, the refining of nickel, and also from the production of caprolactum. The synthetic production of ammonium sulphate became popular just before World War I when ammonia became commercially available in large quantities.(1) Currently about 47% of the world's ammonium sulphate is synthetically produced, the rest is produced as a by-product.(1)

By-product crystalline ammonium sulphate was initially used as an inexpensive source of nitrogen. As more concentrated forms of nitrogen, such as urea with 46% nitrogen and ammonium nitrate with 34% nitrogen became available, ammonium sulphate became less popular as a nitrogen source. Currently, ammonium sulphate is becoming popular as a source of "plant available" soluble sulphur. It has found particularly strong acceptance in Western Canada, as a sulphate source for canola crops.

In North America, virtually all tonnage quantities of ammonium sulphate are produced as by-product. The largest producer is Allied-Signal, who manufactures about 1,200,000 metric tonnes per year, or 36% of the 3,350,000(1) tonnes produced annually in North America.

In Western Canada there are three producers of ammonium sulphate: Sherritt Gordon Mines, which has a capacity of 200,000 tonnes of by-product crystalline ammonium sulphate per year; Cominco, with an annual capacity of 125,000 tonnes of by-product crystalline ammonium sulphate; and Esso Chemical with an annual capacity of about 225,000 tonnes of synthetic granular ammonium sulphate.

Esso Chemical Alberta Limited is the only commercial producer of synthetic granular ammonium sulphate in North America. All other North American producers manufacture by-product ammonium sulphate in the crystalline form.

Granular products have a distinct advantage over crystalline products because of their superior blending and handling characteristics.

Over the last three decades there have been numerous attempts at producing a high quality granular ammonium sulphate. In 1964, Burns patented a process for granulating synthetic ammonium sulphate in a drum granulation plant where fresh ammonia and sulphuric acid were fed to, and reacted in, a conventional granulator.(2) TVA patented a process in 1969 which was analogous to the pre-neutralizer process currently used to manufacture DAP.(3) Sulphuric acid and ammonia were reacted in a pre-neutralizer to a mole ratio of 1.1 to 1, N to S. This highly corrosive mixture was then pumped up to the granulator where further neutralization was carried out.(4) Due to a variety of problems including high corrosion rates and unstable granulation, neither of these processes is in commercial use today.

As the abundance of small sized by-product crystalline ammonium sulphate increased, attempts were made to co-granulate these crystals into granules to improve their quality and make them more saleable. TVA has recently developed a process in which crystalline ammonium sulphate is co-granulated with fresh sulphuric acid and ammonia. This final product contains about 80% by-product crystals and the other 20% is made up of fresh reactants.(5) This process was recently commercialized in the United States, but has been experiencing some start up problems.(9)

In 1977, Incitec, an Australian company, developed a pipe reactor process for producing a high quality granular ammonium sulphate in a conventional drum granulation plant. They have been using this process commercially for over ten years at two Australian granulation plants, and currently produce over 100,000 tonnes per year.

In 1986, Esso Chemical licensed ammonium sulphate technology from Incitec. The plant was started up in December of 1986, and Esso has been producing granular ammonium sulphate ever since. Esso and Incitec have made a number of improvements to the original process and as a result have jointly filed patent applications on both the improved process and the improved product.

PROCESS DESCRIPTION

Incitec's process was retrofitted into Esso's conventional drum type granulation plant which, at that time, was only producing MAP. The retrofit was designed such that both ammonium sulphate and MAP can be made on the same granulation train, with very little downtime required to switch product grades.

The process as described below is typical of the one used at Esso's plant in Redwater and both Incitec plants in Australia.

The process is shown in Figure #1. The conventional pre-neutralizer has been replaced by a pipe reactor with a mixing tee. Scrubber liquor and ammonia are combined in the first stage of the mixing tee. This mixture is then further combined with sulphuric acid in the second stage of the mixing tee, and is fed to the pipe reactor where the reaction runs almost to completion. The resulting ammonium sulphate/bisulphate slurry then discharges onto the granulation bed which contains recycled fines and crushed oversized particles. Ammonia is fed into the granulation bed via a sparger, to bring the bed up to the final mole ratio of 2:1, N:S. The product then exits the granulator and is fed to conventional drying, screening, recycle, and cooling equipment.

Flashing steam and ammonia slip are exhausted to the scrubbers, which are maintained slightly acidic by the addition of sulphuric acid to the scrubber liquor circulation tank. The scrubber liquor is then recycled back to the pipe reactor mixing tee. An additive is introduced into the granulator to promote good granulation.

The process was designed to produce 30 tonnes per hour. This rate has been commercially demonstrated and uprates of up to 50 tonnes per hour are feasible with some equipment modifications. Both of the Australian plants were originally designed to operate at 15 tonnes per hour but they have since been uprated. The Gibson Island Plant produces 35 tonnes per hour, and the Greenleaf Plant produces 20 tonnes per hour. Further uprates are planned as needed to meet market requirements.

PROCESS CONTROL

The granulation of ammonium sulphate is a docile, easily controlled operation. Control of the granulator is obtained by adjusting liquid feeds to the mixing tee and not by control of the solids recycle ratio. The solids recycle ratio is typically in the range of 3:1 to 10:1. The recycle ratio is generally determined by granulation efficiency and size requirements, and not by moisture limitations in the granulator.

While control of the process is relatively simple, straying outside of the specified control range can result in one of the following two conditions:

a) Product size in the granulator is lost, and the plant begins to fill up with fine sulphate dust which can slip through the scrubbing system. In this situation, it is often necessary to dump the contents of the solids system and reseed the plant to start up again.

b) A hard, good-looking product will be produced, but after a few days it will set up solidly in the storage building and require extreme measures to break it up.

UTILIZATION OF WASTE STREAMS

The process chemistry is simple and well documented in the literature.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \qquad - 499.63 \text{ Kcal/Kg}$$

The highly exothermic nature of this process yields some interesting advantages. The reaction liberates enough heat to evaporate about 0.7 tonne of water for every tonne of product produced. The plant can, therefore, consume significant quantities of dilute aqueous streams such as waste sulphuric acid, aqueous ammonia, or ammonium sulphate liquor. In fact, one of Incitec's plants was successfully retrofitted to consume aqueous ammonia from an adjacent urea plant. This resulted in a considerable amount of energy savings, as steam was no longer required to strip the ammonia from this solution.

A computer model, developed by Incitec, has shown that a 30 tonne per hour ammonium sulphate plant can consume approximately 20,000 kilograms per hour of 20% aqueous ammonia from a urea plant, or about 18,000 kilograms per hour of ammonium sulphate liquor from a by-product plant. Incitec's simulation can be utilized to determine the effects of introducing other aqueous streams into the pipe reactor.

PRODUCT QUALITY

The granular ammonium sulphate produced by this process is hard, low in dust levels, consistent in size, free flowing, and non-caking. Esso's major objective in producing a high quality granular ammonium sulphate was to produce a granule which would be completely blend compatible with Esso's other granular products. The problem with local crystalline ammonium sulphate is that it tends to be small and irregularly shaped and will not blend uniformly with other products such as urea and ammonium phosphate. Once blended, crystalline ammonium sulphate will segregate during handling. This results in unpredictable, non-homogeneous blends being applied to the fields, causing non-uniform distribution of nutrients to crops. Esso's granular ammonium sulphate does not segregate from blends during handling and, therefore, always results in consistent uniform distribution of nutrients to crops.

Table #1 shows the size distribution range and size guide numbers (SGN) of various North American ammonium sulphates versus granular urea. Products whose SGN vary more than 10% will tend not to blend together well.(7) Therefore, in order to form a non-segregating blend with urea, a fertilizer must have a size guide number of about 230-280. Esso's granular ammonium sulphate has a SGN of 253 and, therefore, will blend very well with urea and other quality granular products, while domestic ammonium sulphates have SGN ranging from 123 to 213 and will segregate during handling.

Figure #2 is a representation of what happens to a typical 50/50 blend of crystalline ammonium sulphate and MAP after some handling. The blend has segregated badly. The blend in Figure #3 is 50/50 granular ammonium sulphate and MAP. This blend did not segregate during handling.

Esso's granular ammonium sulphate has a crush strength two times as high as any other granular ammonium sulphate reported in literature. In addition, it is low in dust levels, it is free flowing, consistent in size, and does not cake in storage.

In Australia, Incitec's granular ammonium sulphate is sold at a premium price over crystalline sulphate and has virtually displaced the traditional crystalline sulphate market. Because of its unique non-caking characteristics, it is blended with super phosphates and used as an alternative to DAP, especially where sulphur deficiency occurs. Table #2 shows a comparison of Incitec's granular ammonium sulphate size versus other Australian products. Note that the typical Australian product is smaller than typical North American product.

Demand for Esso's product has increased steadily since initial start-up 22 months ago.

This strong market demand demonstrates the farmers desire for a high quality, free flowing, non-caking, blend-compatible source of ammonium sulphate.

PRODUCT AND PROCESS IMPROVEMENT

Esso has worked to dramatically improve the quality of their granular ammonium sulphate. As shown in Table #2, Australian product size requirements are smaller than in North America. Therefore, Incitec had no need to produce larger product, because there was no market demand for it. When Esso approached Incitec, to purchase their technology, it was recognized that the product size would be an issue. To resolve this concern, Esso worked improve the process and thus the quality of the product. The result of this effort was a larger, harder, rounder granular ammonium sulphate than ever before produced, which was still free flowing and non-caking. This is shown in Table #3 which compares Esso ammonium sulphate to original Incitec ammonium sulphate.

Esso and Incitec have jointly filed patents on the improved product and on the process improvements which have been made to Incitec technology.

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8. Allied Chemical, Product Guide, SULF-N45

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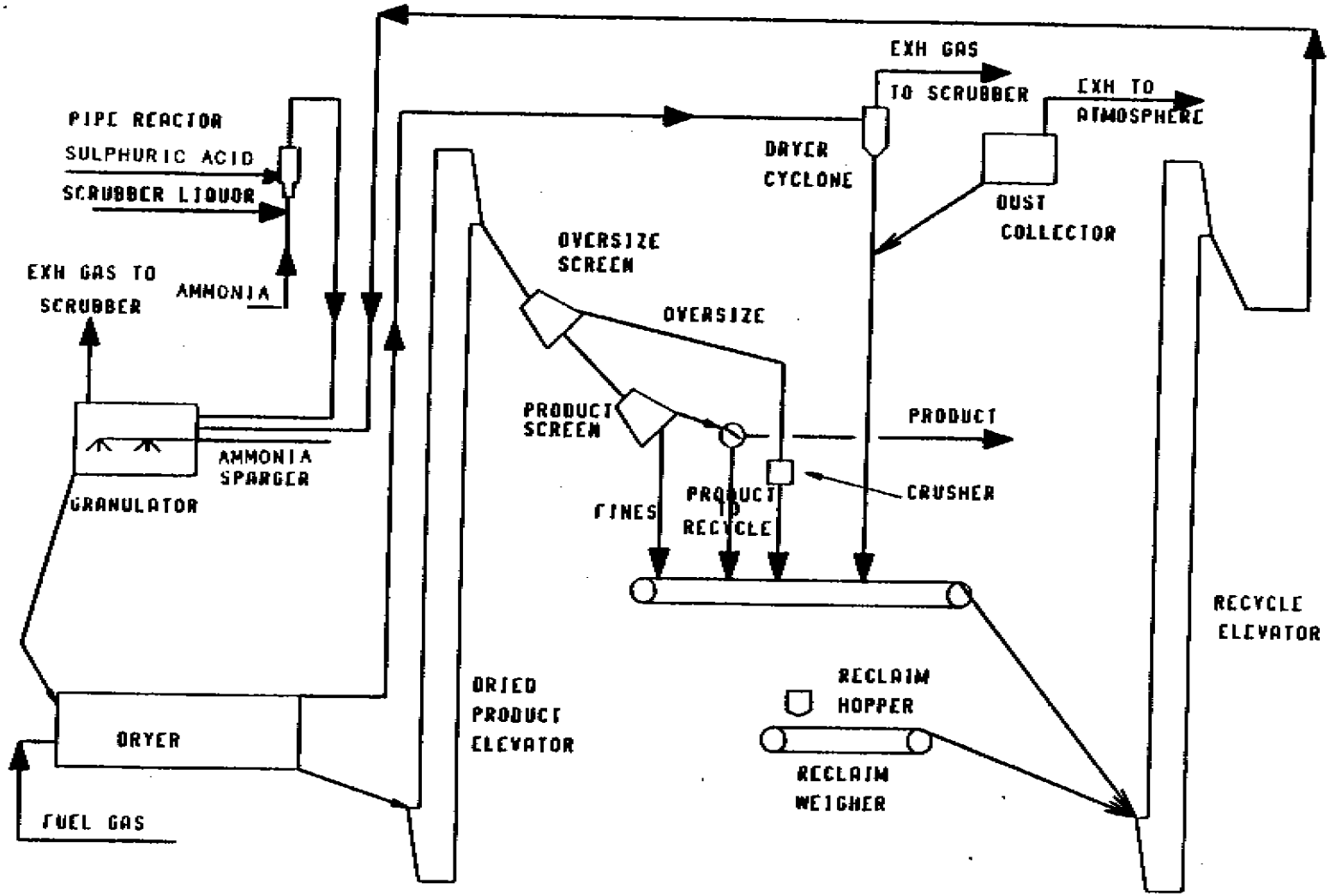

PROCESS FLOWSHEET

FIGURE 1

FIGURE 2 Here's a typical blend with regular 21-0-0-24 crystalline ammonium sulphate. Segregation is evident.

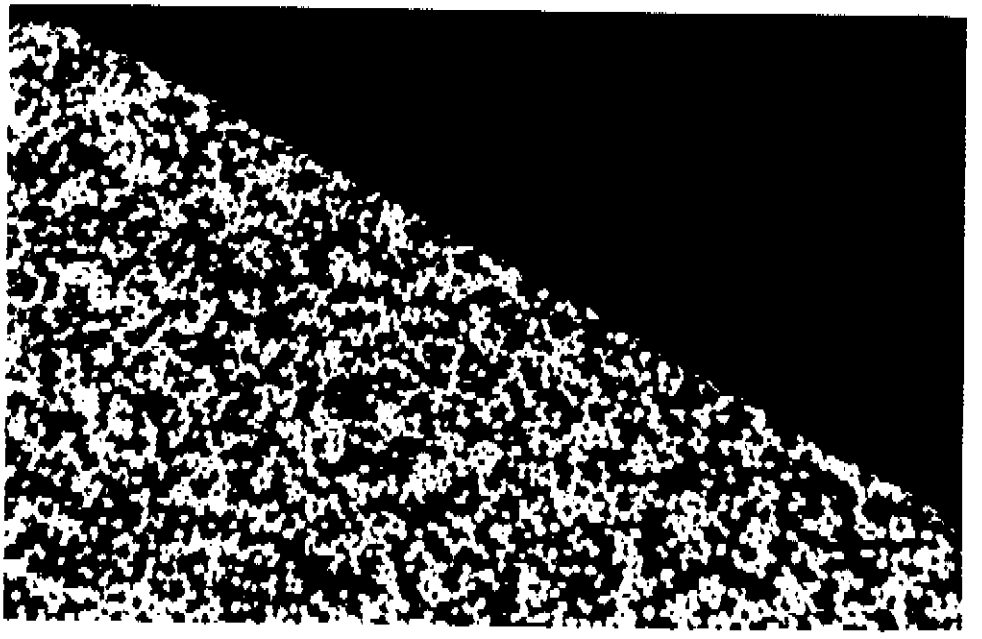

FIGURE 3 Minimal segregation of 20-0-0-24 ENGRO granular ammonium sulphate blend due to similar granule size.

Table #1 **AMMONIUM SULPHATE PRODUCT QUALITY COMPARISION**

Cumulative Particle Size Distribution MM	Tyler Mesh	Esso Granular Urea	Esso Granular Ammonium Sulphate	Domestic Crystalline Ammonium Sulphate	Imported Screened Crystalline Ammonium Sulphate(8)	TVA Granular Ammonium Sulphate
+3.4	(+6)	1	4	0	4-10	-
+2.4	(+8)	60	61	8	15-40	-
+1.7	(+10)	98	97	-	40-70	-
+1.4	(+12)	100	100	55	80-90	-
+1.0	(+16)	Tr	Tr	85	95-99	95(10)
+0.6	(+28)	-	-	98	-	-
Size Guide Number		255	253	123	155-213	220(10)
Crush Strength (Kg) Pfizer Hardness -2.4MM +2.8MM		-	4.5-5.7	-	-	2.3(6)

TABLES:1
August 1988

Table #2

AUSTRALIAN PRODUCT SIZE COMPARISON

Cumulative Particle Size Distribution		Incitec Prilled Urea	Incitec Granular Ammonium Sulphate	Australian Crystalline Ammonium Sulphate
MM	Tyler Mesh			
+3.4	+6	-	3.5	0
+2.8	+7	1.5	10	0
+2.0	+9	39	45-75	0
+1.7	+10	67	80	1.0
+1.4	+12	89	90	-
+1.18	+14	95	95	10
+0.85	+20	99	99	19
+0.5	+32	100	100	50
+0.25	+60	-	-	90
SGN		187	196	50

TABLES:2
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Table #3

COMPARISON OF ESSO'S GRANULAR AMMONIUM SULPHATE TO INCITEC'S GRANULAR AMMONIUM SULPHATE

Cumulative Particle Size Distribution MM	Tyler Mesh	Esso (Improved Grade) Granular Ammonium Sulphate	Incitec (Regular Grade) Granular Ammonium Sulphate
+3.4	+6	4	3.5 maximum
+2.4	+8	61	10
+2.0	+9	-	45-75
+1.7	+10	97	80
+1.4	+12	100	90
+0.85	+20	-	99
SGN		253	196
Pfizer Hardness (Kg) -2.4 +2.8		4.5-5.7	1.6-3.1
% Water		0.1	0.1-0.2

TA/88/6 High quality granular ammonium sulphate production by M. Fischbein, Esso Chemical, Alberta, Canada and A.M. Brown, Incitec Ltd., Brisbane, Australia.

DISCUSSION (Rapporteur Mr. P. STOKKA, Norsk Hydro, Norway)

Q - Mr. H. ALLYOT, Technip, France

1/ What is the N to S molar ratio of the slurry out of the pipe reactor ?

A - Unfortunately, because we are patenting the process and patents are pending, there are lots of questions that I will not be able to answer, and that happens to be one of them.

Q - 2/ Will you give more information on your gas cleaning system ? For example, what type of scrubbers you are using, the number, are there any tail gas scrubbers with water wash ?

A - Yes, we have two scrubber systems. They are the same scrubber systems that we were using previously on our MAP plant. There is a wet venturi scrubber system on the dryer. And on the granulator it is also a wet venturi system, and there is a tail gas scrubber. But the tail gas scrubber really is not required for ammonium sulphate. I does not really do anything.

Q - 3/ This question is related to the characteristics of the scrubbing liquor. Can you tell us the N/S ratio, density, the pH and especially in the case where you are using aqueous ammonia or aqueous ammonium sulphate as raw materials ?

A - Again I can't give you too many details about the scrubber liquor. I can say that we control the pH by adding sulphuric acid. That is the pH control. We do not add sulphate liquor or anything like that to it, just 93% or 98% sulphuric acid and the process reactants.

Q - 4/ In your paper, you said that sometimes you use some solution of ammonium sulphates from other plants.

A - We have not done that ourselves. Incitec in Australia has tried feeding ammonium sulphate solutions and I think they were close to saturation, roughly 40% by weight ammonium sulphate solutions, that they have as feed to the pipe reactor. As well they have tried dilute acids and they have also tried the aqueous ammonia. The concentration of the aqueous ammonia was very low, a few percent, but again I do not know the number off hand. I can provide you with that information.

Q - 5/ This question is related to the recovering of ammonia. What fraction of ammonia do you recover in the scrubbing system ? I mean the ratio between the amount of ammonia which is recovered in the scrubber and the total amount of ammonia fed to the plant.

A - It is very small. We have not done any measurements to determine exactly what it is. Our ammonia slip is negligible to the atmosphere. Our feeling is that the ammonia slip from the pipe reactor is very small, based on sulphuric acid that we feed to the scrubber system.

Q - 6/But you also feed some ammonia directly into the drum granulator ?

A - Yes, and there is a very little slippage from that. The largest part

.../.../...

of it is absorbed in the granulator. It is only a few percentage points that actually slip into the scrubber system.

Q - Mr. P. ORPHANIDES, Duetag, France

1/ Can you please give the full analysis of the product ? In terms of ammonium sulphate, ammonium bi-sulphate, moisture, pH and other if any components.

A - I could tell you that the nitrogen analysis varies between 20 and 21. Sulphate analysis is typically 24%. The moisture content is about 0.1%. The pH also can vary anywhere from 3 to 4.5.

Q - 2/ To make the balance, there is something else in the product ?

A - We add a granulation aid to the process, and that is part of Incitec proprietary technology and that is part of our patent, so I cannot tell you what it is.

Q - 3/ In the flowsheet, it is not indicated that there is a granulating agent coming in.

A - There should be, it is mentioned in the paper.

Q - 4/ What is the pipe reactor material you use and what is the lifetime of such pipe reactors ?

A - Again I cannot comment on the material we use, but we improved dramatically on the lifetime that Incitec used to get. We can run for a couple of months without any failure. When we started out we were looking at monthly failures.

Q - 5/What is the granulation bed temperature you are working with ?

A - It runs between 200 and 230 ° F

Q - Mr. B. CHRISTENSEN, Superfos Fertilizer, Denmark

1/ Can you tell to what extent crystalline ammonium sulphate can be absorbed in the process.

A - We have not actually tried to do that again it has been tried in Australia by Incitec. I would think 20 or 30% crystalline or more. There are technologies developed by TVA in which they use up to 80% crystalline and only 20% sulphuric acid and ammonia. So I am very conservative when I say 20 or 30%. I am sure it is a lot more, but we have not personally tried it.

Q - 2/ Can you tell what is your Size Guide Number compared to Sherritt Gordon's ammonium sulphate ? They stated that it was the grade 19:3:0 with something like 20% sulphur.

A - According to Sherritt Gordon, their product contains about 3% ammonium phosphate and has a size guide number of about 250, which is approximately the same size as our product.

Q - Mr. H.J. HERO, Kemira Oy, Finland

1/ How do you control or adjust the crystal size of ammonium sulphate

before granulation ?

A - There are no crystals that are visible to the naked eye formed in the process. There is some crystallization in the scrubber liquid and that is controlled by controlling the pH and density of the liquid. But the product itself does not have any visible crystals at all.

Q - 2/ Can you say what is the liquid-solid ratio for the granulation ?

A - After the pipe reactor, I do not know what the liquid-solid ratio is in the slurry. We put in stoichiometric amounts of sulphuric acid and ammonia that we need, and roughly 0.7 ton of water for every ton of product. The water flushes off so the moisture content would be very low in the slurry as it exits the pipe reactor.

Q - 2/ Is any additive used for granulation, if so what type ? Could you tell anything about the type, if it is a surfactant or something else ?

A - I cannot really discuss the type. There is a whole family of materials that can be used and be fed into the liquid system or into the solid system. It is commonly and readily available, but I cannot really discuss the chemistry of it.

Q - 3/ You mentioned that your material is very free flowing, what is your coating agent ?

A - We do not use a coating agent at all. We had occasionally to lightly oil it because we oil our phosphate products occasionally to suppress dust. But with ammonium sulphate, as far as I know, we do not typically oil it, so there is typically no coating agent at all. If we use one it is a fraction of a percent of oil.

Q - Mr. A. BARBERA, Agrimont, Italy

1/ Have you ever granulated ammonium sulphate derived from organic production ?

A - No we have never done that. We only use fresh sulphuric acid that we manufacture and ammonia that we manufacture.

Q - 2/ Can you describe problems, if any, encountered to optimize ammonium sulphate high quality production ?

A - We encountered a lot of problems. The optimization centered quite a bit around the solids handling system. If the process is not run exactly at the right optimum operating point, you end up with excessive amounts of dust being formed and that was probably one of our biggest problems when we first started the plant up. There was a tremendous amount of dust being formed, plugging up our cyclones, and even getting into the air in the building where we had leaks and things were not sealed up well. So it is primarily a dusting problem and maintaining the product size. But we do not have a lot of corrosion problems, we do not have those types of problems. The service factor right now is very high. The plant is extremely easy to start up and shut down. And once we start up and run it, it stays running. We do not have a lot of maintenance problems. The service factor is probably as good as or

.../.../...

better than it is for making ammonium phosphate in that plant.

Q - Mr. D.S. LOVELACE, Allied-Signal Inc., USA

1/ Do you have a cooler ?

A - Yes we do.

Q- 2/ Is that your basic reason for not having caking ?

A - No

Q - 3/Is it the low moisture content then ?

A - Until our patents are approved I can only say at this point that it is a combination of everything really. It is not one specific item. You can readily cake with a cooler or without one. Both Incitec and Esso have had caking problems before understanding how to run properly. We have a cooler, they do not, so you can cake with or without one. Certainly, if your moisture content goes high, you will cake, that is not a secret, that is quite obvious.

Q - 4/ So your granulated product functions differently in moisture heat relationship to caking than does crystal ammonium sulphate ?

A - We have not really done any comparative testing. We have basically done caking test under specific conditions, but I have not compared them specifically to crystalline. I would say, qualitatively the answer is yes, it does perform better.

Q - 5/ What test method did you use to determine crushing strength ?

A - We use Pfizer hardness method. I think it is 50 granules, -7, +8 size, and we crush them and take the average crushing pressure, using a Pfizer hardness tester.

Q - 6/ Do you run SGN on your crystalline by-product ? And, if so, what is it ?

A - We do not manufacture crystalline by-product. We used to purchase it and resell it. We purchased actually yours at a time.

Q - Mr. J. PRIAT, Grande Paroisse, France

1/ What is the concentration of the sulphuric acid you introduce in your pipe reactor ?

A - We use both 93 and 98%.

Q - 2/ Another question about the concentration or the density of the liquid going from the scrubbers and that you recycle to the pipe reactor.

A - I cannot comment on that point.

Q - 3/ What is the humidity of the product at the exit of the granulator ?

A - Again, I cnanot comment on that. It is very low. The product has 0.1% moisture, and the humidity at the granulator is part of our technology

so I cannot reveal that.

Q - 3/ Do you use gaseous or liquid ammonia ?

A - Both can be used. I does not make a difference.

Q - 5/ What is the temperature in the pipe reactor ?

A - As an order of magnitude, about 300 ° F.

Q - 6/ What is the consumption of fuel or gas per ton of product ?

A - I do not know the answer to that.