

# **ISMA**\* Technical Conference

Sandefjord, Norway 8-11 September 1970

\*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

By :

J.M. De Long P.W. Casperson

Occidental Chemical Company U.S.A.

#### INTRODUCTION

Not since the early 1960's when diammonium phosphate made its commercial entry into the U.S. as a high-analysis, multi-nutrient, granular product, has a new phosphatic fertiliser material made such dramatic impact on world markets. Diammonium phosphate growth could be directly associated with the rising popularity of bulk blending in the U.S., as well as increasing export demands. Since 1965, Super Acid popularity has been similarly related to a vigorous increase in liquid fertiliser consumption. This market is currently growing at a rate of 15-20% per-year in the U.S. in contrast to the total fertiliser market which is growing about 6% per year.

In the last five years, numerous marketing and technical articles have related the popularity of liquids and the commercialisation of wet process superphosphoric acid, a relatively inexpensive form of polyphosphates capable of sequestering troublesome metal impurities in wet process acid.

During this five-year period, both producer and consumer's experience has generated improved technology leading to higher quality products, more intensive marketing concepts, and a comprehensive investigation of the economics of manufacturing Super Acid. This led to a search for new Super Acid markets including use in granular fertiliser production, liquid feed supplements, and numerous industrial applications. Many of the latter are still under investigation.

It is the intent of this paper to deal with Super Acid as an ingredient in mixed granular fertilisers, describing the handling procedures, general costs, and overall benefits available to the fertiliser manufacturer.

Table I - ANALYSIS OF TYPICAL STREAMS

<u>Item</u>	Phosphoric Acid feed	Superphosphoric Acid product %			
Total P <sub>2</sub> 0 <sub>5</sub>	54.2	72.49			
Ortho P205	100.0	31.37			
Conversion	0	56.7			
Fe203	1.0	1.33			
A1 <sub>2</sub> 0 <sub>3</sub>	1.9	2.47			
MgO	0.3	0.40			
so <sub>3</sub>	2.6	1.90			
F	1.0	0.30			
CaO	0.01				
κ <sub>2</sub> ο	0.09	-			
Na <sub>2</sub> 0	0,.03	<del></del>			
SiO <sub>2</sub>	0.015	<del>.</del>			
Solids	1.50	0.37			

Wet process superphosphoric acid is today marketed in the U.S. as a green (or black) dense liquid, containing 70-74% P205, of which 50-60% is in the poly form. Table I shows typical analysis of ortho acid feed and Super Acid product. Note the reduction of S03 and F, as well as the 75% decrease in solids. The latter represents the effect of poly sequestration of metal phosphate insolubles in the feed acid. Approximately half of the remaining solids are inert, sub-micron particles of charred organic matter which are totally suspended and cause no handling problems.

Table II outlines some of the physical properties of Super Acid, used in designing process equipment to effectively handle and process this new product in liquids or granular fertilisers.

### Table II - PHYSICAL PROPERTIES OF SUPER ACID

Heat of dilution to 54% P205, B.T.U.'s/Lb. P205	135
Heat of ammoniation, B.T.U./Lb. NH3	2,400
Ammoniation capacity, Lbs. NH3/20 Lbs. P205	7.2
Specific Gravity @ 60° C	2.04
Viscosity @ 60° C, centipoise 2,400 -	5,000
Maximum safe storage temperature	70° C

Occidental Petroleum Corporation has developed a process for manufacturing superphosphoric acid which has been in commercial operation at White Springs, Florida for the last four years. Dubbed the Oxy-Nordac Process, it may be distinguished from other submerged-combustion systems by its distinctly different dip-tube arrangement and scrubbing train, patented features which have contributed greatly to improved operation and superior product quality. Figure I represents a simplified flowsheet of the Oxy-Nordac Super Acid Process. Reprints of an article more thoroughly describing the process are available on request.

Since the Fall of 1965, Occidental engineering and technical staffs have solicited the cooperation of several U.S. fertiliser manufacturers in the utilisation of Super Acid as a new and valuable ingredient in the manufacture of superior quality fertilisers. To date, 14 plant-scale tests have been conducted, 14 more are scheduled for completion before the end of the year, and approximately half of the cooperators to date are successfully incorporating Super Acid into their product lines, emphasizing the premium characteristics through widespead promotional programs. TVA has conducted similar tests, using both furnace and wet process Super Acid in a small continuous ammoniation-granulation plant2. Their conclusions indicated Super Acid is a practical approach toward granulation of superior products with inherent benefits in manufacturing costs and operating efficiencies.

Occidental also manufactures and sells a premium ammonium polyphosphate granular product containing zinc and iron and sold under the registered trade-name, ZIPP. This product has generated profitable sales in the areas of both agriculture and lawn and garden products, having demonstrated agronomic superiority in both of these areas.

## FORMULATION AND FORMULA ECONOMICS

In the early 1960's when Super Acid was first incorporated into granular fertilisers, strong emphasis was placed on its contribution to higher analysis products and the agronomic benefits contributed by polyphosphates. Is was also discovered that Super Acid could eliminate or at least reduce the investment in drying equipment because of its anhydrous characteristics and its affinity for free moisture. At that time, relatively large quantities of Super Acid were used in formulation (up to 700 lbs. per net ton) and economics of formulation were rather unfavorable because of the wide price spread between orthophosphoric and superphosphoric acid<sup>3</sup>. An up-charge of \$3.50 per ton was not uncommon and, as a result, the tangible benefits offsetting increased raw material costs were insufficient to generate wide-spread interest in this new approach. It was equally difficult to translate intangible benefits into

cost savings or increased profits.

Today, the formulation of granular fertiliser materials with Super Acid has been greatly simplified. Multi-plant experience has shown that considerably smaller quantities will accomplish those objectives which make use of Super Acid technically and economically attractive. Both process and product information, later described, involves the use of 50-150 lbs. of SPA per ton, making no attempt to totally replace other supplemental PoO5 in the formula. At these rates, Super Acid has been found compatible with all of the standard fertiliser raw materials in conventional manufacturing processes. After a formula is written and the raw material costs are compared with and without Super Acid, it is possible to show actual raw material savings from use of Super Acid. Even under the most extreme cost conditions, the use of 100 lbs. of Super Acid (72 lbs. P205) should increase raw material costs less than \$ 1.00 per ton of finished product. It will be shown that this incremental increase can be off-set by substantial process savings and improved physical-chemical product characteristics, justifying proportionately larger sales realisations on the product. Table III shows comparative quantities and costs of raw materials in a typical fertiliser grade manufactured with and without Super Acid.

Table III - FORMULATION WITH SUPER ACID - 10-20-10

STANDARD I	FORMULA		FORMULA		
Material	Lbs/tor	<u>Cost</u>	Material	Lbs/tor	Cost
Sol'n 440	373	5.71	Sol'n 440	373	5.71
DAP (18-46-0)	200	6.08	Amm. Sulphate	171	1.50
Normal Super	784	7.84	Normal Super	726	7.26
Triple Super	329	7.19	Triple Super	354	7.73
Muriate of Pot.	334	5.68	Muriate of Pot.	334	5.68
Sulfuric Acid 93	3% 54	•55	Super Acid	100	520
	2074	\$33.05		2058	\$33.08

As Super Acid is totally anhydrous, formulation practices must take into account its tendency to absorb free moisture in the reaction: Poly + H2O = Ortho. The key to preparing good formulas with Super Acid involves control of temperature and plasticity in the ammoniator bed. This is a function of moisture and heat released from hydrolysis and from chemical heat of reaction with ammonia. As plasticity is critical to the degree of granulation and over-all tonnage through-put, it has been convenient and sometimes necessary to use scrubber water (if available), hot water, or steam to control consistency of the ammoniator discharge.

Experience with several types of plants and a variety of products has confirmed Super Acid's strong affinity for ammonia, allowing frequently as much as two additional units of ammoniacal nitrogen to be used as opposed to incorporation of solid nitrogen forms. This may decidedly improve formula economics in those plants which do not incorporate a slurry or pre-neutralizer type reactor preceeding the granulation operation.

Because raw material requirements vary in each plant, it has been OXY's policy to provide in-plant technical assistance in process design, equipment installation or modification, formulation, and plant start-up. This includes training of both management and operating personnel in the use of Super Acid.

## PROCESS DESCRIPTION

## Transporting Super Acid

OXY Super Acid is shipped from White Springs, Florida in 100-ton insulated stainless steel tank cars to both liquid and dry fertiliser manufacturers throughout the entire United States. These tank cars are insulated with 3-4 inches of polyurethane foam designed to structurally support the cargo and eliminate metal contact between inner and outer tank. As a result, the acid should not lose more than 1-2° F per day in transit through a mean ambient temperature of 0° F (-18° C). The cars are equipped with a bottom-unloading 4" ball valve and connecting flange, a steam coil on the inner tank and pressure and vacuum relief systems with emergency provisions for unloading through the car's top hatch.

This car provides the manufacturer with a means of storing acid but it is important that the Super Acid is properly scheduled and continuously converted to minimize excessive delay on the plant's railroad siding. The Super Acid may be pressured directly into process or into a positive displacement pump with a variable speed drive. The entire granulation process is portrayed in Figure II.

## Transferring Super Acid

A mild-steel, quick-couple hose is used to connect tank car and acid pump. This hose should be steel-reinforced 4" butyl rubber. All acid lines are insulated and preferably steam or hot water traced to maintain temperature and fluidity throughout the transfer system.

Figure III provides a more detailed description of

the tank car connecting system. Because of the low corrosion characteristics of Super Acid, manufacturers may use schedule 80 black iron pipe between pump and granulator. The stipulation here is that moisture should not be allowed to come into contact with the interior walls of the black iron pipe. Lines must therefore not be steam-cleaned. It is preferable to leave them filled at between 100 and 130° F to prevent complete solidification and/or polymerization of the acid.

Where extended pipe runs between tank car and process are exposed to severe cold, a simple and inexpensive means of maintaining acid temperature in these lines may be used. Figure IV portrays the use of wooden sheeting and vermiculite which is constructed in the form of a trough to completely enclose and insulate both acid and steam (or hot water) lines from the ambient environment. This form of insulation is estimated to cost approximately \$ 0.50 per running foot. Its design permits ready access to the transfer line for repair and re-assembly when necessary.

## Sparging Super Acid

Perhaps the most critical equipment design involves the proper size and placement of the Super Acid sparging system. Although Super Acid has been successfully introduced into granulation systems via direct addition to phosphoric and/or sulfuric acid lines, experience indicates superior results when the acid is sparged over the bed as shown in Figure V. A flexible rubber connection is illustrated which permits rapid replacement or relocation of the sparger to obtain best granulation characteristics. Note that the sparger bar is constructed of stainless steel to minimize corrosion/ erosion and ensure uniform distribution of acid over the entire ammoniating portion of the rotary unit. The length of the acid sparger, number of holes, and size of holes must conform to each individual granulator unit. It is desirable to distribute the Super Acid over the entire length of the rolling bed to obtain maximum control of temperature release and plasticity in granulation.

Figure VI relates the flow rate and acid pressure to the size of a single orifice in the sparger system. This is useful in varying sparger design to the individual plant, production rate, or product line.

## Metering Super Acid

Because of the temperature-viscosity relationship, Super Acid flow rates must be carefully controlled to ensure continuous, trouble-free operation of the granulation unit. When air pressure is used to transfer acid from the car to process,

a recording magnetic flow meter is required with a downstream control valve. Although a positive displacement pump with variable speed control has been used in tests to regulate acid flow, it is recommended that a magnetic flow meter again be used in conjunction with the positive displacement pump to ensure accurate calibration and consistent flow rates.

#### Summary

The key to simple and efficient handling of Super Acid depends on observing the following rules:

#### DO:

- 1. Avoid exposing Super Acid to atmosphere to prevent polyphosphate deterioration and equipment corrosion.
- 2. Inspect and record condition of car, product, and equipment prior to each start-up.
- 3. Carefully observe each step of the unloading procedure in OXY's Super Acid Handbook.
- 4. Observe normal maintenance procedures for parts, replacement, lubrication, equipment adjustments, and housekeeping.
- Maintain records of operating including temperatures, pressures, flow rates, and moistures for standardizing limits of control.

#### DO NOT :

- 1. Expose Super Acid to prolonged or excessive heating (above 150°F) unless immediately prior to total conversion of entire heated portion.
- 2. Transfer Super Acid in pipe smaller than 3 inches in diameter unless line is shorter than 20 feet.
- 3. Leave pressure and heat source on transfer lines when not in use.
- 4. Use steam or "wet" air to purge acid lines unless they are made of stainless steel.
- 5. Leave cold, untraced lines filled with Super Acid longer than necessary to avoid cooling and hardening.
- 6. Start up acid transfer equipment before inspecting car, acid lines, and acid handling equipment in plant.

## Granulation with Super Acid

The introduction of Super Acid into the granulator is immediately evidenced by a rapid increase in the granulator discharge temperature, accompanied by the appearance of a semi-tacky agglomerate of fertiliser granules. Although the discharge product gives the appearance of being excessively wet, moisture analyses indicate this is not moisture but an ammonium polyphosphate melt coating the granules of NPK fertiliser. Depending upon the grade of fertiliser manufactured, optimum granulation can be controlled by regulating the discharge temperature within the range of 180-220° F (82-105° C). Since the bulk of the ammoniator discharge will be on-sized product (essentially no dust), product recycle will consist primarily of screen over-sized material which has been crushed in the hammer or chain mill. In some instances, it is necessary to return modest quantities of onsized material to maintain the proper plastic state of the granulator discharge. Some manufacturers have increased the mesh size of the lower deck screen from 20 to 14 mesh Tyler.

Temperatures in the ammoniator-granulator may also be controlled by the addition of scrubber water or low pressure steam. Table IV provides operating temperatures for ammoniator, dryer, and cooler for a variety of product grades. Because of the reduced moisture inputs, coupled with the anhydrous nature of Super Acid, these products have allowed fuel savings in the dryer operation of from 30 to 70% over identical grades using no Super Acid. Significant reduction in recycle rates has increased production capacities as much as 50%, allowing higher production goals or reduced operating time.

Without exception, every grade produced much harder pellets. Using a spring-loaded, calibrated scale to measure pellet hardness, products manufactured with Super Acid showed pellet hardness increased more than 30%. This was found beneficial to both plant operation and field distribution of the product.

Several plants found that the harder pellets were responsible for maintaining cleaner equipment, minimizing shutdowns to clean equipment (screens and bagging equipment) and for eliminating the reprocessing of degraded products.

Without exception, bulk storage of products made with Super Acid eliminated caking problems in both the manufacturing facility and in field warehouse facilities. One manufacturer noted that, for the first time, no material was returned for reprocessing because of bag set or product degradation in spreader equipment due to moisture absorption or pellet degradation. This manufacturer also observed considerable reduction of in-plant dust and obnoxious fumes in

Table IV - OPERATING CONDITIONS AND PRODUCTION IMPROVEMENT USING SUPER ACID

a	1	1			т	·		·					·	
Prod. increase	50 %	"		\ \	.   '	10 T	25.	1	50 %	50 %		0	ار ا	i
Prod. TPH With	24	25	30	30	30	35	30	30	30	30	30	30	30	30
Normal prod.	16	20	20	25	ı	25	25	,	20	20	20	20	25	25
Fuel savings	10 t	b¢ 0.‡	50 %	50 2	£ 0.7	\$0 <b>%</b>	× 09	₩ 09	50 %	10 Ja	Λ 84	\$\$ 0.7	50 %	50 %
Cooler exit temp.	38	£ #	64	38	38	1,3	£ <del>1</del>	617	94	32	38	t 3	29	1+3
Dryer exit temp.	88	88	66	93	88	93	88	88	93	7.7	88	93	77	93
Amm. exit temp.	104	66	88	107	102	101	107	107	93	93	66	93	93	66
Ammoniator Granulator	TVA Drum	TVA Drum	TVA Drum	TVA Drum Pug mill	TVA Drum	TVA Drum	TVA Drum	TVA Drum	TVA Drum	Pug mill	TVA Drum Pug mill		Pug mill	TVA Drum
Plant	Æ	ტ	4	Ð	A	Þ	t•;ì	4	ഥ	ပ	[ <b>*</b> .	Ç	೮	ſŦ4
GRADES	10-6-4	16-8-8	6-12-12	12-12-12	8-16-24	5-20-20	10-20-10	10-20-20	8-20-0	5-23-27	6-24-24	7-31-12	8-32-16	8-36-10

the manufacturing area. It was felt that this has helped reduce shrinkage and in-plant losses.

### Reduced Air Pollution

Stack emissions can be significantly reduced by using Super Acid. Test comparisons on one of the major grades produced are shown in Figures VII and VIII. These tests indicated a substantial reduction in dust loss from the dryer. Using only 100 lbs. Super Acid per ton of fertiliser reduced the dryer dust losses from 0.4 grains/ft3 to 0.1 grains/ft3. Although ammonia losses were higher in the case of Super Acid, approximately two units more anhydrous ammonia per ton were used and production was increased 66%, off-setting the slight increase in ammonia loss. This may be further corrected by slight reformulation and closer control of dryer discharge temperatures.

#### SUMMARY

The benefits from using Super Acid may now be summarized.

- 1. Small amount of Super Acid enhance granulation and allow use of lower-cost standard raw materials to off-set its premium cost.
- 2. Improved granulation provides higher production rates through reduction of off-sized recycle.
- 3. Reduced drying requirement eliminates stack losses and provides fuel economies approaching 50 %.
- 4. Increased product hardness eliminates in-plant dust losses, clean-out and maintenance shutdowns, and product degradation in storage and distribution.
- 5. Product size uniformity and superior condition eliminate bin and bag set and increase storage life.
- 6. Polyphosphate content (7-30%) in product offers premium quality aspects by sequestering inexpensive inorganic micronutrients required for improved crop response and higher yields.
- 7. Less recycle, lower drying requirements, and more durable pellets contribute to reduced solids emission and less air pollution via gaseous exhaust streams.

\* \* \* \* \*

### REFERENCES

- 1. "Processing Problems Pared for Super Acid", D.R. Stern, J.D. Ellis, Chemical Engineering, pp. 98-100, March 23, 1970.
- 2. "Use of Superphosphoric Acid in Small Ammoniation-Granulation Plants", F.P. Achorn, J.S. Lewis Jr., Croplife, pp. 10-15, March, 1969.
- 3. "End Use of Superphosphoric Acid", R.G. Powell, I.S.M.A. Technical Conference, Edinburgh, September, 1965.

#### DISCUSSION

Mr. J. AUSTIN (Occidental Chemical Company): Firstly, I would like to convey to you the regrets of Mr. DELONG and Mr. CASPERSON that they have been unable to come to Oslo to present their paper.

The name "Super Acid" is now generally used in the United States as an abbreviation of "Superphosphoric Acid" which, of course, refers to a mixture of Ortho, Pyro and Polyphosphoric acids. The main impact of this material in the fertiliser industry has been in the preparation of concentrated liquid fertilisers. Messrs. DELONG and CASPERSON introduced their paper with a brief description of Occidental's production of super acid in Florida and they mention also Occidental's production of a special granular monoamonium phosphate which contains Polyphosphate in conjunction with zinc and iron additions.

The use of superphosphoric acid in granulation has been studied for a number of years and there are several well known papers on this subject. The "new approach" of the authors was to develop the use of superphosphoric acid in smaller amounts than had previously been considered. In most of the fourteen trials referred to in the paper, the super acid supplied only a part of the total  $P_2O_5$ .

In their paper, Mr. DELONG and Mr. CASPERSON give a great deal of practical information concerning the transporting, handling and means of introduction of super acid into granulation plants, the key factor here being that the super acid is always sprayed onto the bed so that it tends to cause the formation of a coating of ammonium polyphosphate on the granules.

The principal advantages found in the industrial trials are as follows:

- 1. Up to 50% increase in production due mainly to the lower recycle when operating with super acid.
- Savings in fuel in the dryer due to the higher heat of re-action between super acid and ammonia and the less amount of water introduced compared with merchant phosphoric acid.
- 3. A decrease in dust formation.
- 4. Harder granules with resultant benefits during storage and handling.

5. Probably a certain agronomic advantage, under certain circumstances, due to the polyphosphate content which is retained in the product, provided that the acid is sparged directly onto the bed.

Most of the work of Mr. DELONG and Mr. CASPERSON and their collaborators in many companies in America has been based on low nitrogen compounds. It would be very interesting to know if members here who have experience of the granulation of high nitrogen compounds feel that any of the advantages of super acid would in fact be obtained in that case.

Mr. M. SICARD (Asturonia, France): The interesting paper by Messrs. DELONG and CASPERSON shows the progress which has been made in the use of superphosphoric acid for the manufacture of solid fertilisers and confirms the advantageous influence of this use in granulation. It therefore seems that one can envisage, because of the provision of some of the P<sub>2</sub>O<sub>5</sub> with superphosphoric acid, a significant increase of the capacity of plants by suppressing or reducing the recycling of fines, economy in fuel consumption and finally a better looking product. The economic balance shown in table 2 shows that these advantages may be obtained without any increase in the cost of the raw materials.

In this paper the agronomic advantages of polyphosphates have also been mentioned. It is on this subject that I should like to put my first question. Table 3 shows a use of 50 Kg superphosphoric acid per tonne of granulated 10-20-10. This corresponds to the introduction of about 20 Kg of  $P_2O_5$  in the non-ortho form per ton of product i.e. perhaps only 10% of the  $P_2O_5$  in the fertiliser. Can we assume that at this concentration the sequestering power of polyphosphates is sufficient to give special qualities to the product?

The fertiliser temperatures on leaving the cooler, which are shown in table 4, usually lie between 38° and 43° C. These temperatures seem to favour hydrolysis of polyphosphates during storage. Has such hydrolysis been noted?

My third question concerns the behaviour of the equipment in the special conditions of granulation. The temperatures of the product at the output of the ammonia granulator as noted in table 4 are in the region of or even greater than 100° C. Has an increase in the corrosion of the equipment materials been noticed? Have you been able to establish a corrosion level relative to a plant working without superphosphoric acid?

The final question concerns superphosphoric acid itself.

The viscosity of this acid at 60°C shown in table 2 is between 2,400 and 5,000 centipoise. This viscosity seems to me to be very low for an acid containing 72% P<sub>2</sub>0<sub>5</sub>. Since this value has great importance for the choice of the actual equipment, can you confirm that this viscosity in fact does correspond to that of the acid, the analysis of which is shown in table 1 ? Finally, can you tell me exactly what kind of pump is used for transporting the superphosphoric acid ?

Mr. AUSTIN: The example given in table 3 is a typical example of a formulation using a small amount of super acid and I believe the quantity of super acid which is present there would probably be insufficient to give the necessary sequestration of impurities and, therefore, one could certainly not claim that this particular formula would give agronomic advantages. However, I would say that this is not established or determined. Where there has been a definite indication that agronomic advantages have been obtained is when the monoammonium phosphate contains ammonium polyphosphate and in that case the quantities of polyphosphate are considerably higher than in the case of the examples in table 3. These are not the same products.

The next question concerned the temperatures in table 4. It is perfectly true that the temperatures at the exit of the granulator and at the exit of the dryer are higher than those which would be used in the storage of superphosphoric acid. However, the rate of reaction in the granulator is very high and, after neutralisation, the hydrolysis of the polyphosphates does not proceed at an appreciable rate even at temperatures over 100° C. It is only in the acid state that the hydrolysis can continue, leading to the formation of insoluble compounds.

The next question concerned corrosion. I am sorry I cannot answer that question - I just do not know the answer.

The fourth question concerned the viscosity of superphosphoric acid. I can confirm that the viscosity shown in table 2 does refer to superphosphoric acid of the composition shown in table 1.

Concerning the pumps used for superphosphoric acid, a number of different types have been tried and probably the most successful are positive displacement pumps running at a slow speed. The normal type used would be one with a loop type configuration using either stainless steel or special alloy moving parts. In other cases, particularly for the unloading of tank cars, the progressive cavity pump, generally known as the monopump, has been used very successfully.

Mr. MORAILLON: I should like to refer to table 3. The formulae given there would generally be considered too expensive for European conditions. To make a 10-20-10 fertiliser in France, and I presume that this applies to the rest of you, one uses a very different formulation with anhydrous ammonia instead of 440 solution, ammonium nitrate, orthophosphoric acid and a charge consisting either of ordinary superphosphate or by using the sludge from the production of phosphoric acid. The composition, whose formulae is given in table 3, may be valid for certain conditions in the U.S.A. for small fertiliser manufacturers far from the sources of primary materials, but it would not be economic in Europe.

Mr. AUSTIN: I believe that everything you have said is perfectly true. Under European conditions we would certainly not normally expect such a formulation to be used. It is the situation in North America where the basic raw materials are transported long distances, particularly the phosphates from Florida to the Mid-West and where the basis for production of granular compounds is very different from that in Europe. It is, as I mentioned myself at the end of the presentation, of interest to know whether in fact the use of superphosphoric acid in European type granulation, where nitric acid is more generally used, could bring similar benefits. However, I am afraid that, on this point, I can only agree with you.

 $\underline{\text{Mr. J. FROCHEN}}$  (Pierrefitte-Auby) : In table 2 the authors indicate maximum safe storage temperatures of 70° C. What does safe storage mean ?

Concerning the transport of superphosphoric acid they indicate insulated tank cars of stainless steel. What kind of stainless steel?

Mr. AUSTIN: On the question of the safe storage of superphosphoric acid, at temperatures over about 70° C reaction with the impurities present can continue. It is normally the longer chain components in the acid which continue to react and eventually the chain links and molecules formed can give a type of polymer which causes the acid to set into a gel. Thus one must not store superphosphoric acid, particularly superphosphoric acid with a high level of metallic impurities, at temperatures above about 70°.

Ordinary 316 quality stainless steel is perfectly satisfactory. In fact there is a considerable debate whether stainless steel is needed at all.

Mr. B. CARLSEN (Dansk Svovlsyre-og): Can you explain why the granules get harder with the addition of a relatively small amount of super acid?

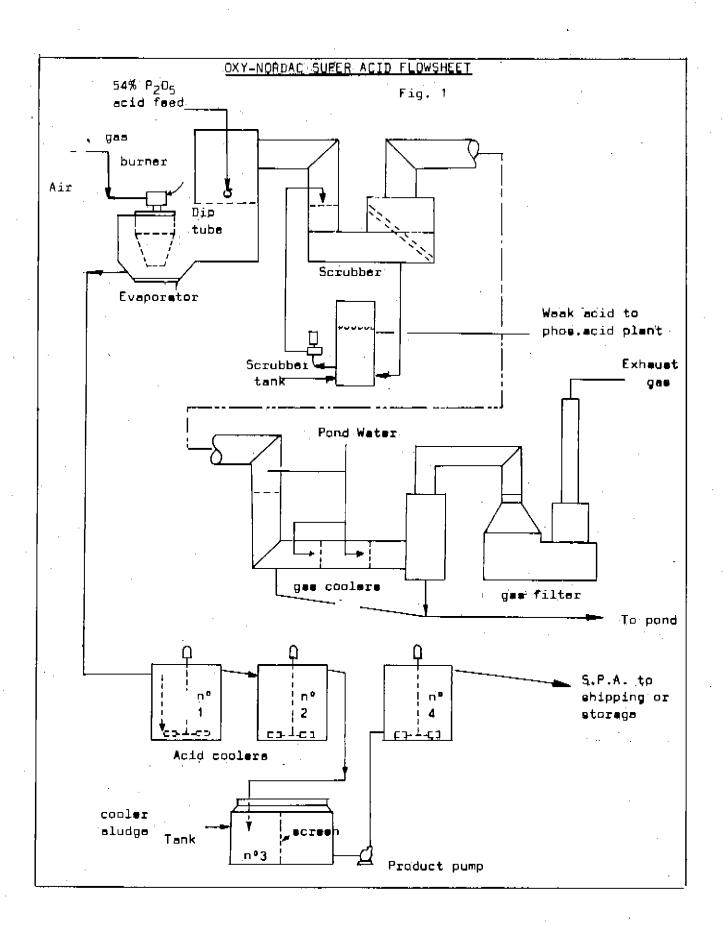
Mr. AUSTIN: We believe that this is because, when sparging the super acid into the granulator, it tends to form a coating on the outside, a molten coating, which, on cooling, sets to a hard mixture of monoammonium phosphate and ammonium polyphosphate. However, the work on this has not been very comprehensive and this is only a tentative explanation. Certainly the granules are much harder.

Mr. M. BONGAARD (Windmill, Netherlands): I would like to refer once again to table 2, on the cost aspect of the formulation. Apparently the super acid used has been valued at \$5.20 for 100 lbs. The essential thing here is that the phosphate coming from diammonium phosphate has partly been replaced by this super acid. As the P2O5 of diammonium phosphate is essentially coming from normal phosphoric acid, I would like to know how the price of normal phosphoric acid compares with \$5.20 per 100 lbs. super acid.

Mr. AUSTIN: This is a typical pricing of the various components under U.S. conditions. The price of  $P_2O_5$  in super acid is generally valued at the plant at about \$ 12 - 13 per ton  $P_2O_5$  higher than the equivalent in 54% merchant acid. The situation may be rather different if the formulation is being done in the Mid-West where the price of 54% acid may be closer to that of super acid because the transportation costs from the centres of manufacture are higher.

Dr. RAISTRICK: In the paper you have spoken about the use of super acid for sequestering zinc and similar heavy metal cations and say this offers a benefit and this kind of fertiliser is now being sold for garden fertilisers and horticulture and so on. We understand that in the U.S. a great deal of the garden fertiliser quickly finds its way into ditches and rivers and my question is this: if the use of ammonium polyphosphate becomes prevalent do you visualise any problem in the environment when we are introducing into it a material which can solubilise, which can mobilise dangerous heavy metal cations such as zinc and mercury, and one wonders what will be the effect on fish and perhaps on human beings? Have Occidental given any consideration to this problem and, if they have, what do they believe is the safety of this kind of practice?

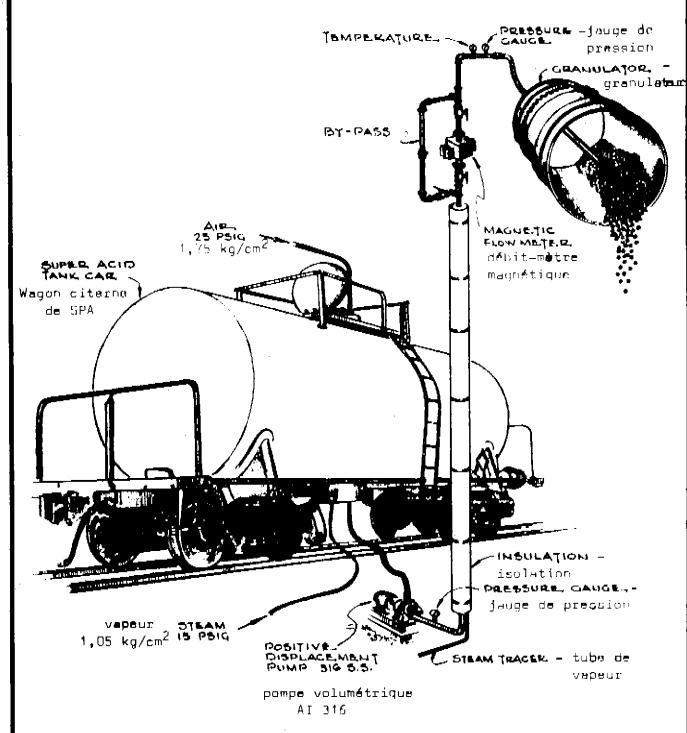
Mr. AUSTIN: This is a very difficult question. I believe that, regarding the agronomic position, it has been shown that polyphosphates do tend to migrate a little further in soil than the orthophosphates. Similarly the rates of hydrolysis of ammonium polyphosphates under conditions in the garden or in the field is relatively slow. I think this is really a question of the particular soil conditions and particular location. Possibly in soils where fertilisers are very mobile and phosphates are not tied up quickly and in tropical conditions with heavy rain, there polyphosphates may be leached rapidly through the soil and this could cause such problems. At this moment I do not know whether our own people in the United States are in fact aware of this possibility and are doing any work, but I can obtain an answer for you.

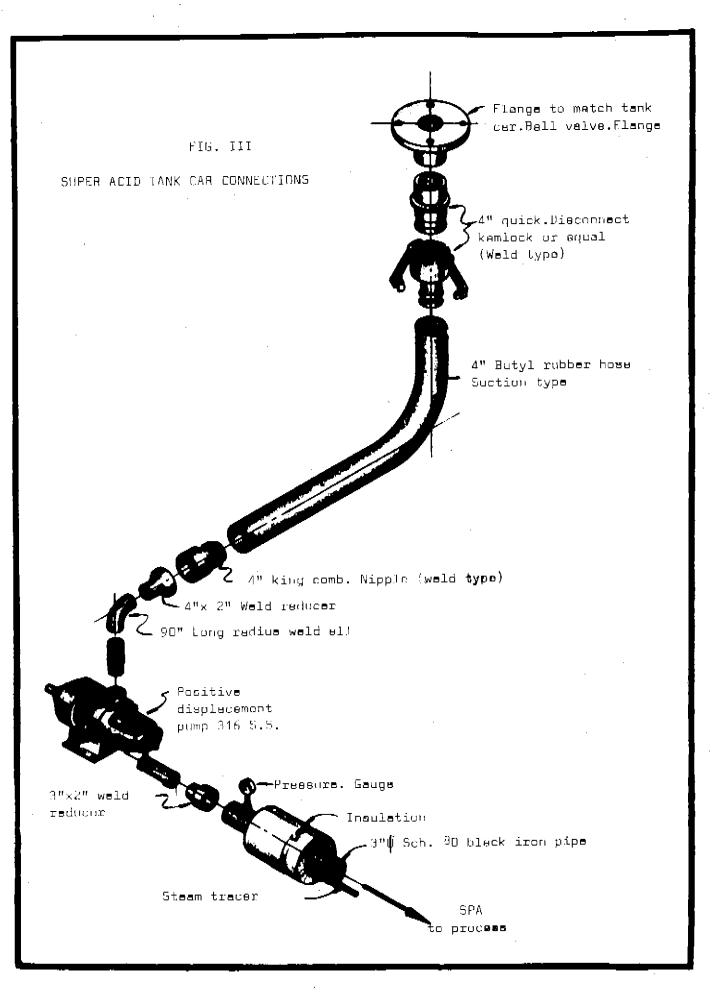


F16. II

## ILLUSTRATION I SUPER ACID IN GRANULATION

GRANULATION AVEC SPA





#### FIG.IV

# ILLUSTRATION III INSULATED SUPER ACID TRANSFER SYSTEM

SYSTEME ISOLE DE TRANSFERT DU SPA

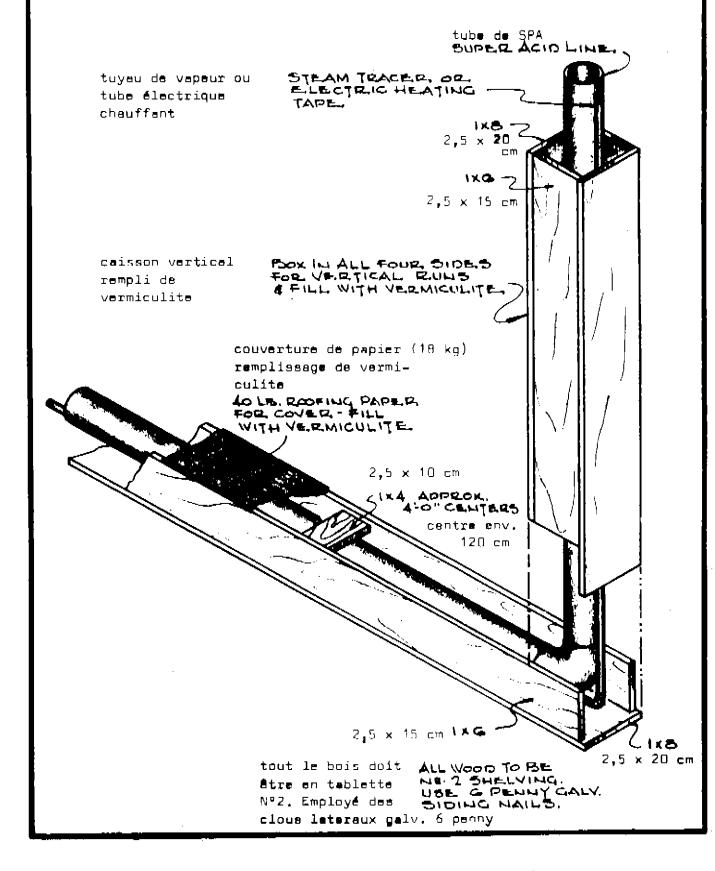
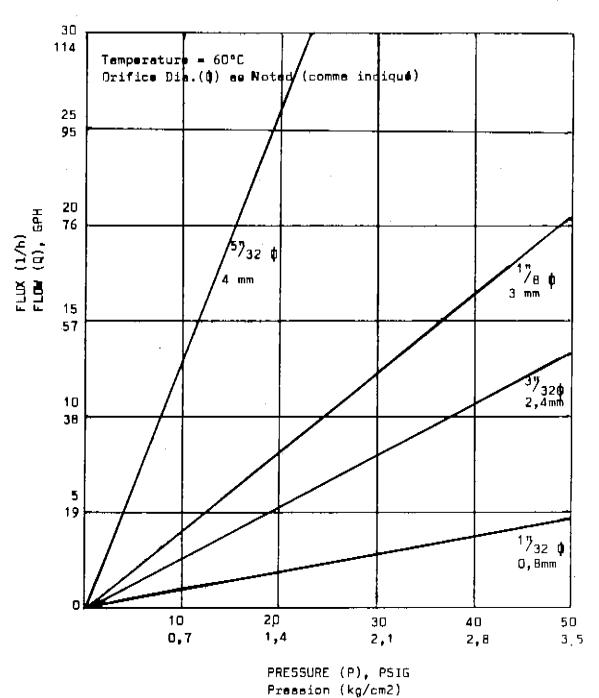


FIG. V SUPER ACID SPARGING SYSTEM 2" 5.5. hose ⊈Z" S.S. coupler with shank adaptor nat. pipe thread 2"🗘 pipe Advisable alternate Drum granulator Pressure gauge 3"x2"reducer 1"5.5. pipe 1"5ch. 80 black SPA sparger iron pipe above bod Insulation 1" coup Steam tracer rubber hose Holes in 5.5. pipe only ——Day material flow below bed Drum rotation S.P.A. sparger section contains 1/8" Dia. holes on 1" to  $1^{1}/2$ " centers 5.P.A. sparger (spacing depends on length of ammobia sparger }

Ammonia sparger

# Appersion de SPA à travers un seul orifice dans un tube 40, 2,5 cm SPARGING SUPER ACID THROUGH A SINGLE ORIFICE IN 1-INCH SCHEDULE 40 PIPE

FIG. VI GRAPH.VI



## DRYER STAUK LOSSES WITH SUPER ACID

NUMBER <u>1</u> COMPANY ABC Fartilinar Company SYSTEM <u>Dryer</u>  $D^2$ 1.  $.7854 \times (1144) = 6.24$  AREA OF STACK IN SQ.FT. AREA CFM 2. FRM 530°F × 6.24 - 17,206 × 60 1,032,360 460+ MEASURED TEMP. CU.FT. SAMPLES 3. CFM  $\times$  MIN. X VACUUM CORRECTION <u>1.08</u> × <u>10</u> 12,241 <u>1.00</u> × <u>15</u> 0.076 <u> 29.9 – 5.75</u> <u>1.00</u> × <u>10</u> 29,9 29,311 NH3/CU.FT.AIR 4. ML ACID N ML BASE N  $(487 \times 0.5) - (402.1 \times 0.5) =$ 26,656 x <u>29,311</u> CU.FT.SAMPLED 5. CFH ₩NH3/EU.FT.AIR # NH<sub>3</sub>/HR  $1.032.360 \times 5.43 \times 10^{-5}$ 6. FREE NH. /TON TPH NH3/HR. IN FORMULA × <u>25</u> <u>2681.25</u> % NH\_ LO55 <u>x 100</u> = Nº 6 2681.25 % DUST LOSS B. WT. DUST #DUST/CU.FT.  $N_0 S$ .2206 GRAMS =  $\frac{1.66 \times 10^{-5}}{1.032360} \times 1.032360 = \frac{17.117 \times 100}{1.032360}$ 0.034 50,000  $454 \times 29.311$ ⊨ PROD./HR. GRAINS/CU.FT. 9. ♣/CU.FT.

 $1.66 \times 10^{-5} \times 7,000 = .1162$ 

## DRYER STACK LOSSES WITHOUT SUPER ACID (CONTROL.)

COMPANY ABC Fertilizer Company SYSTEM Dryer NUMBER 2

1. .7854 x ( D<sup>2</sup>) - AREA OF STACK IN SQ.FT.

144

2. FPM AREA CFM CFH
3201 x 530° + x 6.24 - 17.074 x 60 1.024.485

MEASURED TEMP.

4. ML ACID N ML BASE N NH<sub>3</sub>/CU.FT.AIR  $\frac{(500 \times 0.5) - (470 \times 0.5)}{26,656 \times CU.FT.5AMPLED} = 2.23 \times 10^{-5}$ 

- 5. CFH  $\frac{1}{2}$  NH<sub>3</sub>/CU.FT.AIR  $\frac{1}{22.85}$  ×  $\frac{10-5}{22.85}$  =  $\frac{22.85}{22.85}$
- 6. FREE NH<sub>3</sub>/TON TPH NH<sub>3</sub>/HR. IN FORMULA

  88.50 × 15 = 1327

  7. N° 5 22.85 × 100 = 1.7 % NH<sub>3</sub> LOSS
- 9. # /CU.FT. GRAINS/CU.FT. 5.46 x 10-5 x 7,000 = \_\_\_3822