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MELT OIL COOLING PROCESS FOR THE PRODUCTION  
OF UREA BASED COMPOUND FERTILISERS

By

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Mitsui Toatsu Chemicals succeeded in the commercial production of urea in 1937 and is now one of the largest producers of urea in Japan. In 1952, Mitsui Toatsu began the large scale manufacture of urea-based compound fertilisers. It is well known that the production of urea-based compound fertiliser by the traditional method is difficult and expensive. The drying conditions are especially critical and inefficient.

For this reason, in 1965, Mitsui Toatsu started fundamental studies to develop a new process to make urea-based compound fertiliser. In the process, potash and phosphate suspension in the molten urea is prilled to disperse droplets of a uniform size, which solidify in the oil cooling tank. Experiments were completed at a pilot plant last year and a technical and economic evaluation of the results has been carried out. This report is based on the results of the experimental work at the 0.5-ton-per-hour capacity pilot plant.

#### PROCESS DESCRIPTION

##### Raw Materials

The materials initially required to produce urea-based compound fertiliser with the Melt Oil Cooling Process are urea, mono-ammonium phosphate and potassium chloride or ammonia, urea, phosphoric acid and potassium chloride.

The raw urea is weighed, melted at 135°C and pumped up to the mixing tank. Mono-ammonium phosphate and potassium chloride are also weighed, crushed and fed into the mixing tank by a pneumatic conveyor.

Heat must generally be supplied to prepare the slurry. Mono-ammonium phosphate and potassium chloride are dried and pre-heated to 100-250°C in the pneumatic conveyors. They are heated in separate chambers to prevent the melting of mono-ammonium phosphate.

Either 30 per cent P<sub>2</sub>O<sub>5</sub> or 54 per cent P<sub>2</sub>O<sub>5</sub> phosphoric acid may be used as an initial raw material. The acid

is neutralized in a preneutralizer into a slurry with a molar ratio of approximately one. The resultant mono-ammonium phosphate slurry is then concentrated in an atmospheric-pressure falling film evaporator. Following this, it is mixed with urea melt and potassium chloride in the mixing tank. The resulting mix is finally concentrated until moisture content is reduced to 0.5 per cent.

Typical raw material formulations are shown in Table 1 and the flow sheet of the Melt Oil Cooling Process is shown in Figure 1.

TABLE 1  
Formulation of Melt Oil Cooling Process

Raw materials	Product Grades (Kg/MT)	
	18.6-18.6-18.6	28.0-28.0-0
Urea (46-0-0)	307	471
Mono-ammonium phosphate (12-50-0)	372	-
(12-53-0)	-	529
Potassium chloride (0-0-60)	310	-
Filler (0-0-0)	11	-
Total	1,000	1,000

#### The Mixing Tank

In the mixing tank, urea melt, mono-ammonium phosphate, potassium chloride and a small amount of recycle fines are treated to create a homogeneous suspension. The most important function of the mixing tank is efficient heat transfer. This is because the viscosity of the suspension increases rapidly in a short time and a hard heat-resistant layer of scale forms on the surface of the heat transfer jacket. Mitsui Toatsu has developed special mixing and heating devices that eliminate these problems.

For the slurry material to produce 18.6-18.6-18.6 grade fertiliser, the maximum mixing retention time is limited to four minutes and the optimum temperature of the suspension is approximately 125°C. The relationship between the viscosity of slurry and mixing time is shown in Figure 2.

Otherwise, suspension viscosity would increase too much and cause great difficulty in the transportation and dispersion of the slurry for prilling. Delicate mixing is also important in order to prevent urea decomposition

and the condensation of mono-ammonium phosphate into polyphosphate. Special precautions are taken to prevent clogging in the pump and transfer pipe when the suspension is pumped from the mixing tank to the prilling device.

### The Prilling Device

The prilling device is essential for the success of the Melt Oil Cooling Process.

The highly viscous suspension must be dispersed into droplets of a uniform size to increase the production rate and reduce the recycle ratio. Conventional prilling devices are of the nozzle-plate or the rotating-basket type. Because fertiliser suspension is very viscous and contains undissolved potassium chloride and ammonium phosphate, traditional prilling methods could not process the slurry satisfactorily. Clogging and scale formation were frequent problems.

Therefore, Mitsui Toatsu developed a distinctively different type of prilling device to obviate the difficulties formerly encountered. The new device reduces the recycle ratio to 10 to 15 per cent and ensures continuous operation over a long period of time.

Complete details on both our mixing tank and device will be disclosed after patent protection is established.

### Cooling and Oil Separation

A low viscous oil was used at the pilot plant for cooling purposes. The oil temperature was fixed so as to produce spherical products of a uniform size.

The cooling tank proved to be extremely efficient and an oil depth of only one to two meters was sufficient to cool and solidify a 5-millimeter diameter product. This greatly enhances investment saving.

The cooled and solidified product is removed from the bottom of the cooling tank (in oil mixture form) and sent into the centrifugal oil separator. Several types of continuous centrifugal oil separator were tested but it was found that none could prevent the crushing of the spherical products.

It was, therefore, decided to employ a batch-type centrifuge for oil separation. With the centrifuge, residual oil was reduced to 0.5 to 1.0 per cent and product crushing was almost completely eliminated.

Such a problem is overcome by using the Melt Air Cooling process. But the selection of the most suitable cooling process will depend on investment costs, climatic conditions, and product characteristics.

### Screening and Recycle Fine Treatment

After oil separation, the finishing steps leading to the final product do not differ remarkably from those in the more conventional processes. Some 10 to 15 per cent of over- or under-sized products are returned to the mixing tank for reprocessing. Screened products are conditioned with diatomaceous earth to preclude caking during storage. Since the separated oil from the centrifuge contains a small amount of fertiliser materials, these materials are separated in the settling tank and are returned to the mixing tank.

## MELT OIL COOLING PROCESS CHARACTERISTICS

### Investment Costs

A case study has been made to determine the profitability of our new process. The savings were between 20 and 30 per cent when compared with investment necessary for ordinary processes. The savings are possible because the process renders unnecessary the use of certain expensive equipment, e.g., granulators, rotary dryers, rotary coolers, and additional associated accessories. Other advantages of the process include the compactness of plant and the minimization of dust and noise pollution.

### Product Grade

In this process, solid materials such as phosphate and potash are mixed with molten urea. Therefore, it requires more than 250 kg. of urea to produce one ton of the final product. However, the urea content is expected to be reduced in future as a result of process improvement.

Limitations in regard to raw materials include (i) the use of materials with a high dissociation pressure, such as diammonium phosphate; (ii) the use of materials with a high water content; and (iii) the use of alkaline raw materials.

At the same time, the use of such above-mentioned raw materials in the process is very limited. Nevertheless, high  $P_2O_5$  content grades and low N content grades are difficult to produce. But it is possible to manufacture several basic fertiliser grades. We have succeeded

in producing the following: 18.6-18.6-18.6, 18-21-17, 28-28-0 and 23-0-32.

Product variety will be increased by bulk blending with granular diammonium phosphate or other granular fertiliser products.

#### Granulation Yield

Granulation yield for a +5 to -16 mesh product is around 85 per cent. This means that the recycle ratio is equivalent to 17.7 per cent to one ton of product. There is no segregation of the plant nutrients during mixing and dispersing. And the final product has a homogeneous structure. For these reasons, only a small level of overformulation is required to guarantee product quality.

#### Product Physical Properties

The superior physical properties of the product produced by the Melt Oil Cooling Process is the strongest point in its favour. The free moisture content ranges between 0.5 and 0.8 per cent and is considerably lower than that of products manufactured by conventional processes. A typical example of the product is shown in Figure 3. This low moisture content prevents caking and moisture absorption from the atmosphere. It also contributes to the high crush resistance of the product.

The appearance of the product is smooth and lustrous - like a pearl. The fertiliser is free flowing and suitable for use with application machinery in the field. The residual oil subsequent to the centrifugal separator process is less than 1.0 per cent. To date, the oil has shown no harmful effects on crops or soil structure.

#### CONCLUSION

The Mitsui Toatsu Melt Oil Cooling Process is suitable for the production of compound fertiliser with a high urea content. Plant investment is lower and the operation of the process is easily controlled.

Mitsui Toatsu is experienced in the Melt Air Cooling Process in the production of urea prill incorporated with herbicides such as Pentachlorophenol or Nitrophenyl chlorophenyl ether. We have also produced NK fertiliser by our Melt Air Cooling Process.

Our company now seeks new opportunities in urea-based compound fertilisers through the newly developed Melt Oil Cooling Process.

DISCUSSION

PROFESSOR J. ANDO (Chuo University, Japan): Mr. Akio Hatakeyama of Mitsui Toatsu Chemicals Inc., the author of this paper, is unfortunately unable to be here and, in the absence of another company representative, I have been asked to present the paper.

Mitsui Toatsu Chemicals started production of urea based NPK fertilisers in 1952 and now there are many Japanese companies who produce NPK fertilisers based on urea. In a year, more than 100,000 tons of urea are used to produce NPK compound fertilisers in Japan. All these companies use a pugmill or TVA type ammoniator-granulator rotary drum or a pan granulator for granulation. But, as you know, there is a problem in drying to low moisture content to ensure good physical properties. It is quite easy to decrease the moisture content to 0-1% but caking may ensue. For this reason Mitsui Toatsu recently developed the new process of melt oil cooling. I know that, in many European countries, this oil cooling process has been developed and used for various purposes. We know also that, at TVA, melt oil cooling for urea ammonium polyphosphate was demonstrated some years ago. The main characteristic of the Mitsui Toatsu process is the treatment of highly viscous slurry which contains urea, ammonium phosphate and potash to make it prill. This means of prilling and mixing, is a very important point of the Mitsui Toatsu process.

NOTE: Slides were shown during the presentation.

Slide 1 - A general view of the pilot plant for the melt oil cooling process which Mitsui Toatsu developed in Japan; it produces 500 kg/hour of product either 18.6 - 18.6 - 18.6 or 28 - 28 - 0. At the top is a cyclone, in the middle, a mixing tank and below is an oil tank for cooling.

Slide 2 - The switch panel.

Slide 3 - The urea melter.

Slide 4 - A mixing tank. In it are molten urea and pre-heated ammonium phosphate, powder or slurry, and pre-heated potassium chloride powder all mixed.

Its size is 0.7 m in diameter and 1 m in height.

Slide 5 - The viscosity of the 18.6 - 18.6 - 18.6 mixture based on urea and mono-ammonium phosphate and potassium chloride at 125°C.

As you see it is just over 2000 cps at first but after about 4 min. it goes up markedly. This means that both mixing and prilling should be done within 4 min. For the 28 - 28 - 0 which does not contain potash the viscosity is rather low.

- Slide 6 - This big tank is the oil tank which cools the prill.
- Slide 7 - The centrifuge. Mitsui Toatsu have several types of centrifuge and have found that, if they use the continuous centrifuge, some of the prills are broken and none of the continuous centrifuges were satisfactory. They now use the batch type centrifuge.
- Slide 8 - This round vessel is an oil settling tank.
- Slide 9 - The NPK grade 18.6 - 18.6 - 18.6. The size of the granules is between 3 mm and 1.5 mm. They are very round and therefore satisfactory.
- Slide 10 - This is another grade, 28 - 28 - 0, also with very good looking prills.
- Slide 11 - Another Mitsui Toatsu plant which is actually producing prills based on urea. Most of the time, they make special grades such as 20 - 0 - 20 based on urea, ammonium sulphate and potash: the mixture is molten, sprayed and cooled by air. This special type of product is used mainly for the top dressing of rice. Occasionally, they produce NPK fertilisers based on urea in this prilling tower. The grade is 20 - 10 - 20. The height of this tower is 22 m in effective height and they produce 200 tons/day of product, but when it is hot and humid in summer 22 m is not high enough to produce good quality 20 - 10 - 20 prills based on urea, ammonium phosphate and potash. Therefore Mitsui Toatsu think that oil prilling is better for the production of NPK grade fertilisers based on urea.

DR. P. KAASENBROOD (D.S.M., Netherlands). The literature mentions several processes for the manufacture of granular urea based compound fertilisers. These include processes in which granulation of solid or



molten urea, together with solid MAP or a slurry of MAP in water and (optionally) crushed potassium chloride, takes place in a pugmill, a rotary drum or an ammoniator-granulator. In these processes the granulation step is followed by a drying and a cooling step. Drying is costly, as it has to be done at relatively low temperatures, due to the low softening temperatures of Ur-P and Ur-P-K products.

Production of these compound fertilisers may become more economic when a melt of ammonium polyphosphate is used as a starting material. This is because the production of polyphosphate, e.g. by concentrating and ammoniating wet process phosphoric acid, is cheap compared with drying of a granulated Ur-P-K product. One drawback of this type of granulation however remains. Due to the relatively low granulation efficiency of pugmill and rotary drum, handling of large quantities of solid material as recycle is necessary.

Improvement of the granulation efficiency may be obtained by prilling. As regards the technique of prilling in oil, I may refer to a few papers published by TVA a few years ago.

Now a new oil prilling process, the MOC process, is being introduced. In this process ammonium orthophosphate containing Ur-P's and Ur-P-K's are produced. To this end, a melt or a homogeneous suspension of molten urea, mono-ammoniumphosphate and potassium chloride is made by intimate mixing of the three components in a special mixing tank. The melts or the suspensions are allowed to have high viscosities as, in addition to the mix-tank, a special prilling device has been developed, to obviate the difficulties formerly encountered in prilling viscous liquids and suspensions.

It would seem that the merits of the MOC process lie precisely in the fact that it uses a new type of mixing tank and prilling device, although I still wonder whether these will do away with all difficulties that may crop up. One of these difficulties is caused by the hydrolysis of urea. Even when the starting materials contain no free water, hydrolysis takes place due to reaction of urea with the water content of the MAP. Polyphosphate, ammonia and carbon dioxide are formed. The ammonia and polyphosphate remain in solution, the carbon dioxide however forms finely divided gas bubbles in the melt. Escaping of the gas from the melt or suspension may happen with formation of a foamy layer, especially when, as in the case of the MOC process, the recycle stream contains oil. On the point of these problems and some other aspects concerning technology and product quality I am very glad to have the opportunity to put some questions to Professor Ando who replaces Mr. Hatakeyama.

1. The first question refers to the statement on page 2 of the paper: Delicate mixing (in the mixing tank) is also important in order to prevent urea decomposition and the condensation of mono ammonium phosphate into polyphosphate. How can mixing prevent the reaction between urea and MAP, as this reaction takes place in the liquid phase, and the consequence of mixing is the dissolution of MAP in the urea melt.
2. How can the statement on page 4 (limitations in regard to raw materials include the use of materials with a high water content) be reconciled with the text on page 1.

Phosphoric acid with 30% P<sub>2</sub>O<sub>5</sub> may be used as an initial raw material and the text on page 2 which holds open the possibility to finally concentrate the resulting mix until moisture content is reduced to 0.5 per cent.

3. According to the diagram the oil containing recycle goes back to the mixing tank, which as stated on page 2, is kept at approximately 125°C. At this rather high temperature the oil will quickly oxidise, unless special precautions are taken. Oxidation has a strong reducing effect on the interfacial surface tension between the Ur-P-K melt and the oil in the prilling vessel, and consequently tends to deform the crystallizing liquid droplets. Are any measures taken to prevent this?
4. The paper does not mention formation of scale on the cooling surface, in pipes and pumps of the oil cooling circuit, though it is known that adducts between urea and oil may easily form and precipitate.  
Are there any ways in which scale formation and clogging in the oil circuit can be prevented?
5. Do the results of prilling and mixing, and also the physical properties of the end product not greatly depend on the purity of the raw materials. Are there any special requirements regarding these raw materials?
6. With respect to the physical properties of the product, it is stated on page 5, that the low moisture content prevents caking, though page 4 states that conditioning is necessary to preclude caking during storage. How do these statements fit in with each other? Can the prills be handled in bulk without silo-setting, and is ship-transportation in bulk to the tropics possible?

7. Would long storage of some end products, especially at temperatures higher than 30°C, not give rise to disintegration, initiated by double conversion between salts, (e.g. between potassium chloride and mono ammonium phosphate) which did not have enough time to attain equilibrium in the mixing tank.
8. It would be interesting to have some more information about the qualities of the end product. For example could you give us the urea and polyphosphate contents, the crushing strength of the prills and the caking tendency of a given compound.

PROFESSOR ANDO:

1. Delicate mixing is one of the most important steps in the Melt Oil Cooling Process, especially to produce NPK and NP compound fertiliser with high  $P_2O_5$  content grades. Here delicate mixing means the rapid and homogeneous mixing of raw materials and recycle materials. Generally raw materials are fed in both liquid and solid forms and local maldistribution of solid material causes the difficulties in resultant slurry transportation and also evenly distributed droplets formation.

But vigorous mechanical mixing promotes the decomposition of urea and formation of condensed phosphate, and too much mechanical mixing or long mixing results in foamy slurry and also foamy end products.

Therefore delicate mixing should be gentle enough to prevent foaming and scale formation with minimum back mixing and minimum retention time and also surface renewal function on the heat transfer surface of the mixing tank.

2. The Melt Oil Cooling Process starting with wet process phosphoric acid with 30 per cent  $P_2O_5$  concentration is incorporated with the neutralizer and ammonium phosphate concentrator prior to prilling.

There was insufficient presentation of this process and we appreciate your attention to this subject. We would like to provide further explanation.

Wet process phosphoric acid is neutralized with ammonia in the neutralizer and the resultant monoammonium phosphate slurry is concentrated in

the first evaporator to intermediate moisture content slurry and then mixed with urea and/or potassium chloride for further concentration in the second evaporator to give final mixed slurry with 0.5 per cent moisture content.

The rest of the process is the same as that of a conventional process as shown in the simplified flow sheet.

3. Recycle materials going back to the mixing tank contain less than one per cent of oil and this oil is not oxidized in the mixing tank even if the temperature is above 130°C at atmospheric conditions.

The oil is also emulsified in the fresh feed slurry material and is not separated to form an oil layer.

We have carried out degradation tests of oil mixed with fertiliser materials at high temperature of 150°C and found no meaningful oxidation at 120 to 130°C.

We have not thought about the strong reducing effect on the interfacial surface tension between the Ur-P-K melt and the oil in the prilling vessel which you have kindly indicated.

We will investigate this subject further.

4. At the beginning of our pilot plant study, we had been concerned about the formation of scale material in the cooling surface and in piping systems.

But after long-term operation, we dismantled the equipment to study the scale formation and found that only a small and very soft scale had formed on the surface of cooling circuit.

This scale was not formed as a result of adducts formation but was caused by a leak of water and steam to the oil system by improper operation and equipment failure.

5. In regard to the raw material specification, most of our study is based on the conventional fertiliser intermediates. Raw materials of specially high purity are not used for the pilot plant.
6. A small amount of coolant oil remains on the surface of the final product prills and the product gives an oily touch for a while after the oil separation at centrifuge.

This residual oil penetrates the plastic film of the fertiliser bag if the product is bagged shortly after oil separation.

Moreover this oil can be harmful to the colouring matter of bagging film in some cases, but by the use of special types of colouring matter, oil influence is minimised.

To prevent such phenomena, one to two per cent of diatomeaceous earth or talc coating is very effective and by this conditioning caking problem is also minimised.

We have made no extensive study on bulk storage in silos nor of bulk transportation especially to the tropics, but the critical relative humidity of Melt Oil Cooling Process products is lower than that of urea and they contain a little more moisture than fertiliser grade urea. More stringent precautions should be taken for bulk storage and transportation than those for urea.

7. The solid state double conversion between potassium chloride and mono ammonium phosphate will proceed even at 30°C, but its rate may be very small and no countermeasure will be necessary for practical purposes.
8. The concentration of condensed phosphate in the final products ranges from 20 to 25 per cent of total phosphate.

The crushing strength of the prill is measured from 4 to 7 kilogram per prill and no practical caking was observed after six month storage under 30 bags stacking of 20 kilogram content bags.

MR. M. NOIRBENT. (Docks Industriels, France.)

What are the advantages of oil prilling as opposed to air prilling? Are these advantages not eroded by the difficulty of :

- a) oil separation
- b) recycling of oil soaked microprills

I would like to have some explanations and details of the pulverisation and the granulometry of the finished product.

PROFESSOR ANDO : I understand that Mitsui Toatsu have another plant in which they make prills by air cooling. The height of the tower is 22 m and in most

cases this is not high enough to make good NPK fertilisers based on urea. It will work well when it is very cold and dry but in Japan, the weather is often hot and humid and it does not work well. Therefore, it depends on the weather. In European countries when it is very dry and less humid and temperature is low, air cooling in a prilling tower might be more economical than oil prilling, but in Japan, for NPK, Mitsui Toatsu consider oil cooling to be more economical than prilling in a very high tower.

The other question is on the form of atomizer. This is a patent of Mitsui, which treats highly viscous slurry and is quite different from the conventional type of atomizer for prilling. It is not a spray bucket type or prilling cup such as TVA uses but something quite different. Mitsui did not provide me with details.

The following questions and answers were the subject of correspondence after the Conference:

MR. I. KOTLAREVSKY. (Etablissements Gardinier, France.) May I please know:

1. The type of pump used for prilling.
2. Whether you have tried to add PPA.
3. What quality of oil is used and its degradation.
4. The rate of recycling.
5. How control is exercised over NPK grade (with recycling)?

ANSWERS received from MITSUI TOATSU Inc., Japan.

1. The type of prilling pump.

The essential points for the prilling pump are accurate flow rate control, enough discharge pressure and resistant to the cavitation due to the gas evolution during pumping.

We have tested five types of prilling pump and found three out of five unsuitable and two satisfactory.

The details of this type of pump are proprietary and we cannot release further details at this stage.

2. The addition of ammonium polyphosphate.

About 20 to 25 per cent of the phosphate is converted into condensed phosphate even if the product is manufactured by supplying orthophosphate.

The viscosity of the melt slurry will be increased by adding ammonium polyphosphate as a raw material.

We have noticed that too much condensed phosphate formation in the products caused super cooling of the slurry in the oil cooling vessel and longer retention time was essential for solidification in the vessel. We expect the amount of ammonium polyphosphate to be limited to a certain range.

3. The quality of oil and its degradation.

Less than one per cent of oil is retained on the surface of the final products.

The operating temperature of the oil in the Melt Oil Cooling Process is relatively low; no meaningful oxidation was observed.

A small amount of oil is discarded with condensed water and foreign matter which is removed regularly from the system.

4. The recycling rate.

As mentioned in the paper, the amount of recycle material is less than 20 per cent if the size distribution of the product is limited to 6 to 20 screen mesh.

5. The method of control of the NPK grade.

Product grade is controlled mainly by adjusting the feed flow rate of raw materials. The segregation of plant nutrients in the products due to the prill size is very small if compared with the conventional solid mixing granulation process. Control of product grade with recycling is almost negligible.

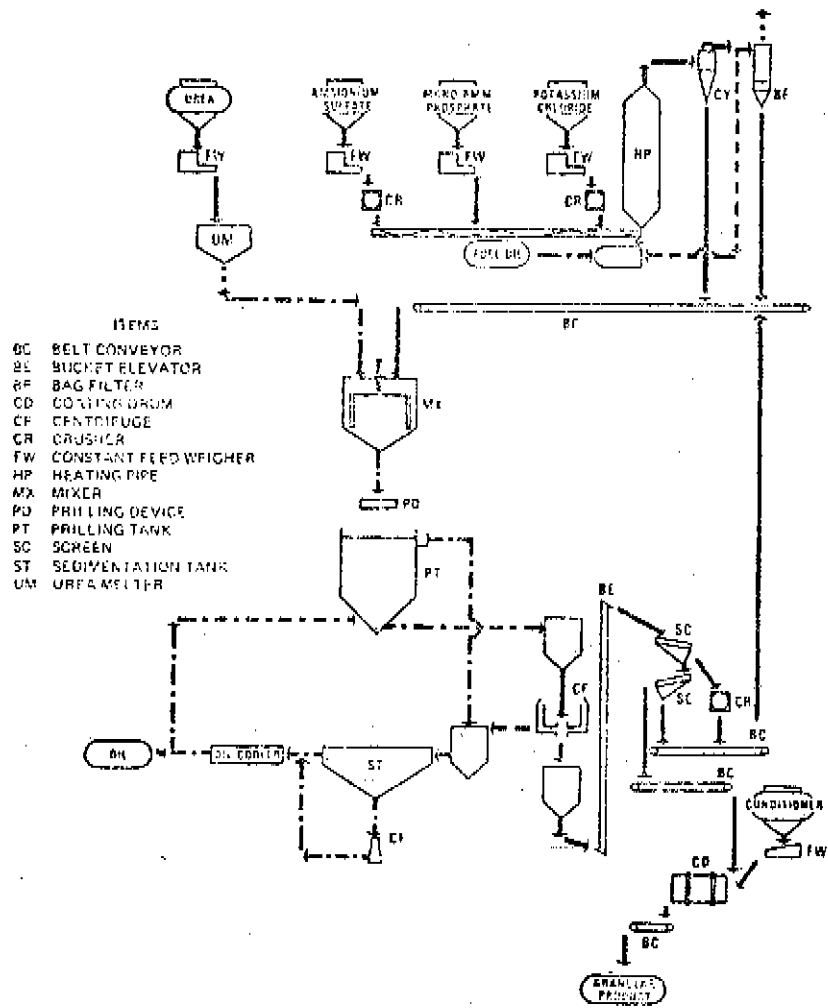


Figure 1. Flow sheet of Melt Oil Cooling Process  
(monoammonium phosphate route)



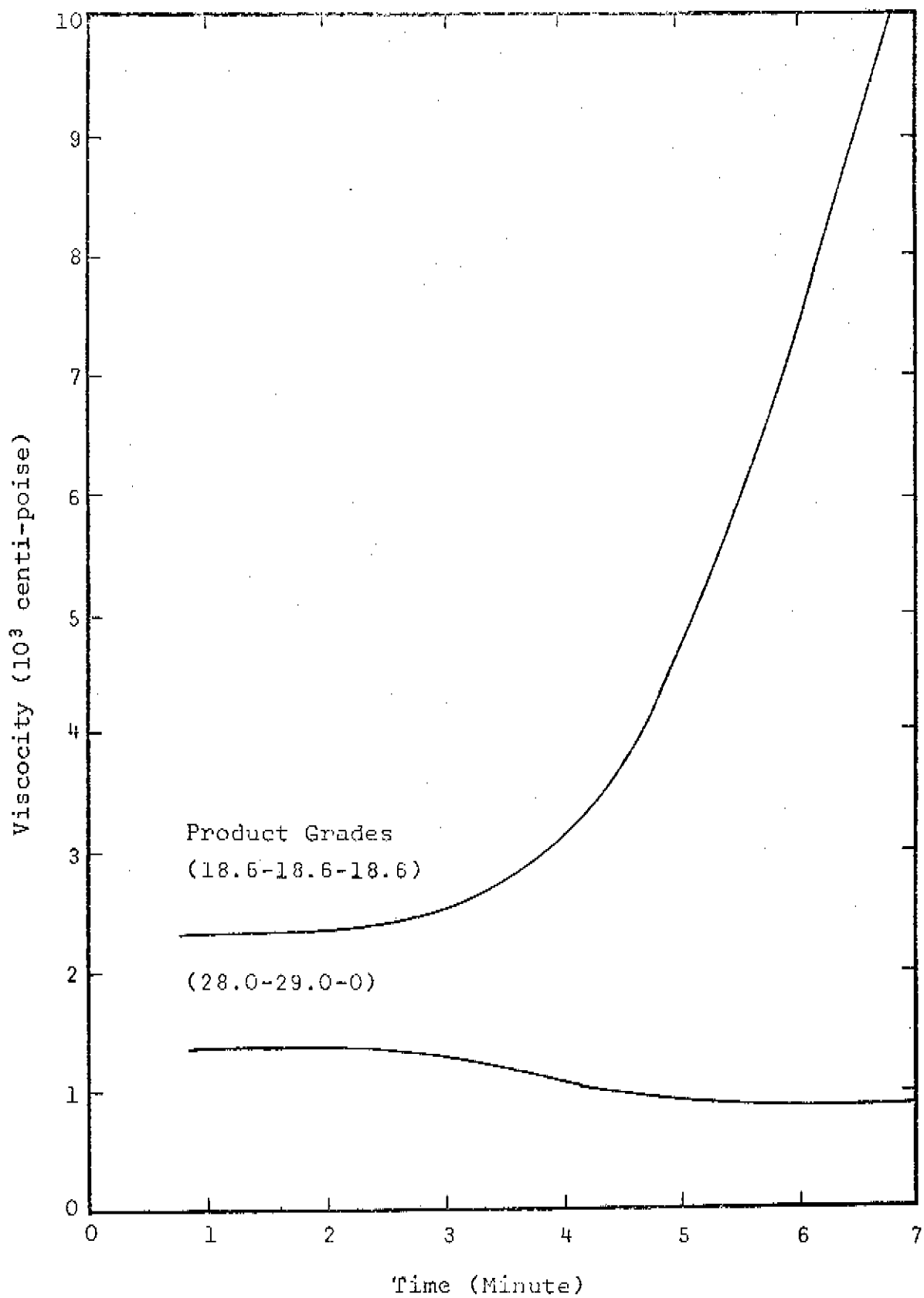


FIGURE 2

Viscosity of Slurry for Melt Oil Cooling Process



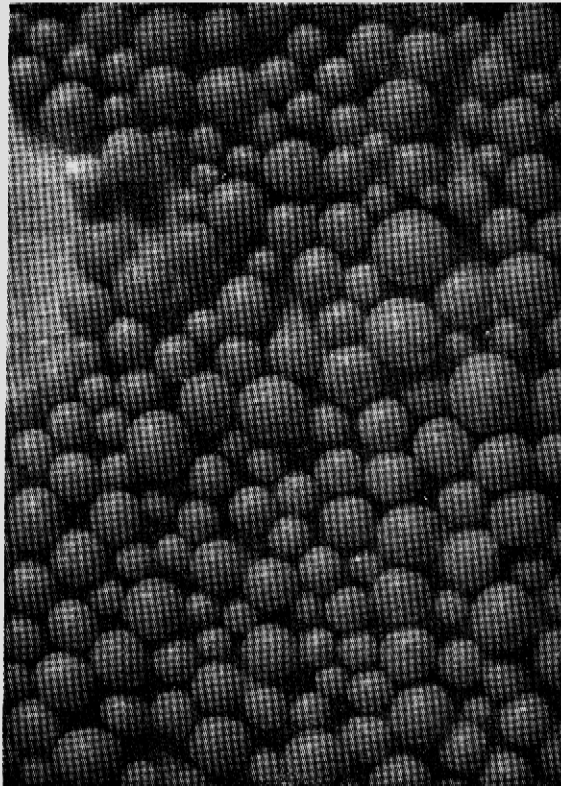


Figure 3. Typical example of the Melt Oil Cooling Process product

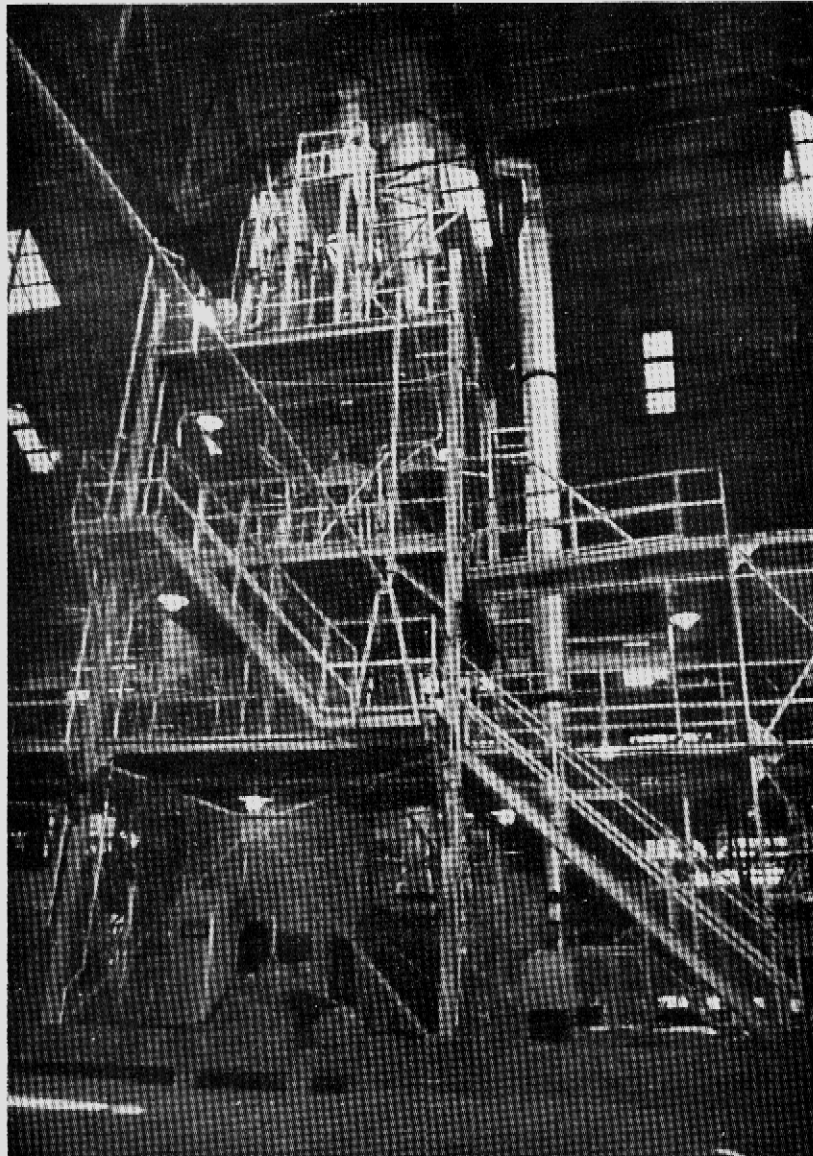


Figure 4. Pilot Plant of the Melt Oil Cooling Process (0.5 MT/H)

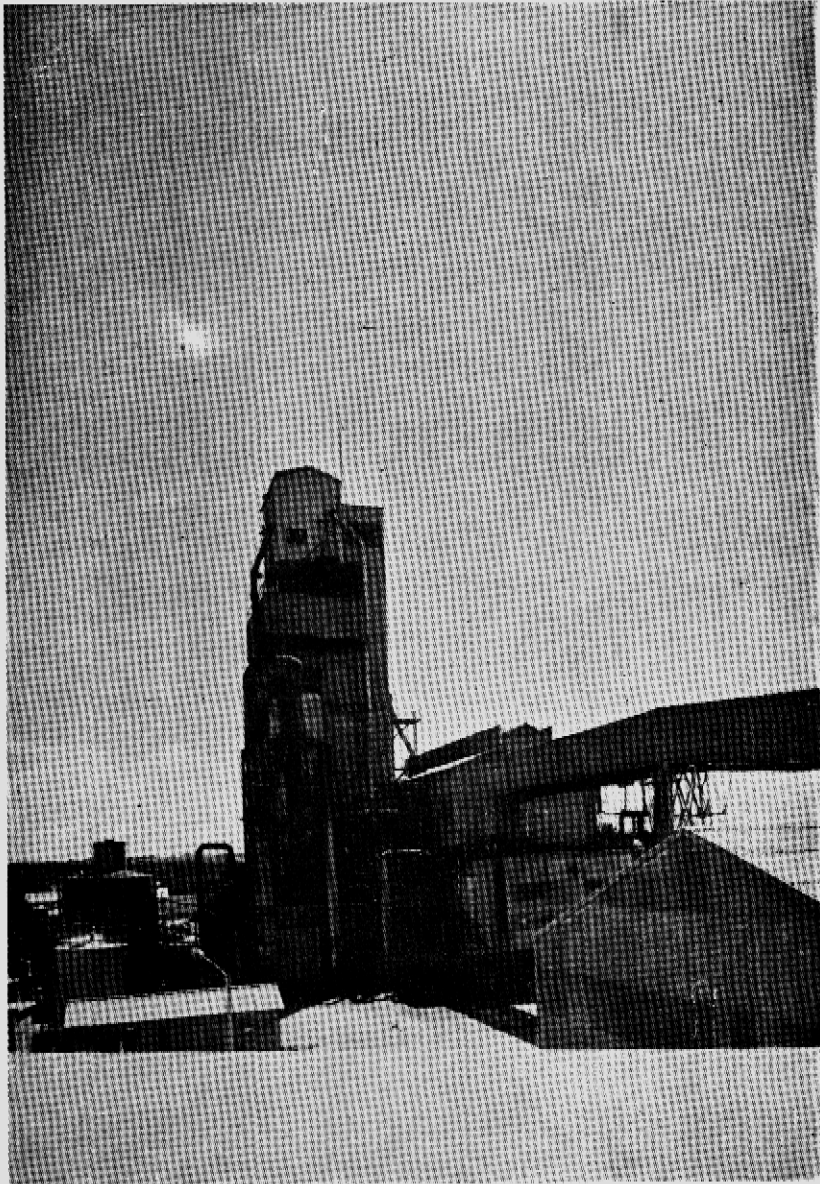


Figure 5. Semi-Commercial Plant of the Melt Oil Cooling