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CAKING MECHANISM OF PHOSPHATIC FERTILIZERS AND ITS CONTROL AT GNFC BY THE APPLICATION OF ANTICAKING AGENTS AND THEIR MODE OF ACTIONS¹

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SUMMARY

The cause of caking of most fertilizers is the growth of crystal bonds between fertilizer particles. These crystals develop during storage due to continuing internal chemical reactions or thermal effects which result in the deposition of crystals, from minute amount of salt solutions present in fertilizer. Inter-growth of such crystals between granules or between particles of a non-granular product result in caking.

The paper will describe the mechanism of caking of phosphatic fertilizers and its prevention by using the anticaking agents.

RESUME

La cause de la prise en masse de la plupart des engrais est le développement de liaisons cristallines entre les particules d'engrais. Ces liaisons se développent durant le stockage du fait de la poursuite de réactions chimiques internes ou d'effets thermiques provoquant le dépôt de cristaux, à partir de quantités minimes de solutions salines présentes dans les engrais. La croissance interne de ces cristaux entre les particules non granulées provoque la prise en masse.

L'exposé décrit le processus de prise en masse d'engrais phosphatés et sa prévention par les agents antimassants.



INTRODUCTION

The phenomenon known as caking or setting is the formation of a coherent mass from a particular array, due to some finely divided solids, whether powdered, granulated or prilled, under certain conditions, losing their fluidity and forming hard blocks or lumps. The caking phenomenon usually appears during storage, handling or transport operations of the material. Recently caking and its inhibition has received great attention, by its importance in fertilizer industry due to following points:

1. Return of lumps or caked products to the manufacturer.
2. Reconditioning of rejected products.
3. Extra transport, handling and packing costs.

PHYSICOCHEMISTRY OF CAKING CHARACTERISTIC

The caking characteristic can be described essentially as a superficial process of crystallisation, which occurs in two stages:

• HUMIDIFICATION

The surface of the granules/prills (solid) is covered with a thin layer of water, which is produced either:

- By absorption of relative humidity,
- By movement towards the surface of the water occluded in the particles,

¹ *Mécanisme de prise en masse des engrais phosphatés et de son contrôle à GNFC par l'application d'agents antimassants et leur mode d'actions*

OR

- By both above phenomena at the same time.

- **PHASE CONTENTS OR SALT BRIDGES**

When the humidity of the air alternately rises and falls, or the temperature of the material undergoes changes, the absorbed water re-evaporates and the "liquid bridges" of saturated solution become "crystalline solid bridges", which cause the crystals to stick together and the most trouble some caking of fertilizers is believed to be caused by "crystal-bridging".

- **MAIN FACTORS INFLUENCING CAKING OF FERTILIZERS**

There are number of factors influencing the tendency of a fertilizer to cake:

1. Internal Factors

Internal factors related to the physico-chemical properties and constitution of the fertilizer are:

1.1 Chemical composition

The chemical nature of fertilizer (formula, concentration, impurities, etc.) changes their hygroscopicity and their tendency to cake.

1.2 Specific surface area

Caking tendency of fertilizer closely depend upon the particle size and shape of the material.

(A) Particle Size

When the particle size increases, the specific surface area decreases, which causes the reduction of the forces of attraction and the point of contact between adjacent particles and lower their tendency to cake.

(B) Particle Shape

When particle surface is smooth and well formed, the caking will be delayed due to the limitation of the contact points between the particles.

(C) Mechanical Strength

The mechanical strength or hardness of the particles has an effect on the caking tendency. Weak granules under the pressure of storage piles tend to deform and form relatively large areas of contact between the granules. Also fracturing of granules can form fines which promotes caking.

1.3 Moisture Content

The amount of moisture allowed to remain in a fertilizer at the time of its manufacture has a great effect on its tendency to cake in storage. For most caking mechanism, the presence of moisture in the form of solution phase is essential. The higher the degree of drying at the time of manufacture, the less active the caking mechanism will be. The extent of drying required to effectively inactivate caking mechanisms varies widely with the composition and physical make up of the fertilizers.

1.4 Temperature

The temperature of the product when placed in storage is another important factor having an effect on caking tendency. If the product undergoes high temperatures or sudden thermic variations, it tends to cake badly due to:

- Water re-evaporation (recrystallisation and establishment of crystalline solid bridges)
- Development of internal reactions, promote plastic like particles that deform under pressure.
- Promotion of crystal bridging and capillary adhesion due to deformation.
- Crystal habit changes.
- For the above reasons, it is advisable to cool freshly make product adequately before storage in bags or bulk. The maximum advisable bulk storage temperature for ammonium nitrate is probably about 54°C (130°F). If the product is to be bagged directly from production, cooling at least 54°C is advisable to avoid damage to the bags.

1.5 Hygroscopicity

The hygroscopic properties of the product can have an effect on the degree of caking. All fertilizers have a maximum relative humidity, referred as critical relative humidity-(CRH) above which they will absorb moisture. Caking as a result of moisture absorption, is usually along the pile surface and with prolonged exposure to relative humidities can become quite deep.

2. External Factors

External factor related to the environmental conditions of the fertilizer exposed during handling and storage.

The storage temperature of warehouse is important with respect to caking tendency. Higher ambient temperature lower the CRH of a fertilizer material and thereby increase its hygroscopicity. For example the CRH of a 15-15-15, nitrophosphate is approximately 55% at 30°C, whereas it is approximately 45% at 40°C. Conversely, raising the temperature of existing warehouse air will reduce the relative humidity (RH). This method is employed to lower the warehouse RH below the CRH of the fertilizer.

3. Other Factors

1. Humidity
2. Time of Storage
3. Pressure

3.1 Humidity

(A) Initial moisture content

Relatively small changes in moisture content have a marked effect on the caking of fertilizer.

A high initial moisture content, favours the atmospheric moisture absorption and consequently the formation of liquid bridges.

Below an initial moisture content of 0.5%, products normally do not show any tendency to cake under the pressure applied in storage. Therefore a careful control of humidity is especially recommended in the fertilizer industry.

(B) Relative atmospheric humidity

Caking depends closely on atmospheric relative humidity variations. Every salt or mixture of salts has a definite critical relative humidity. Above CRH, the moisture absorption will take place while below CRH, moisture evaporation will take place.

The rate of the absorption is dependent of factors such as:

1. The difference between the RH of the air and the CRH of the fertilizer.
2. The movement of the air with a constant RH over the fertilizer.
3. The moisture holding capacity of the fertilizer as influenced by the granulometry and porosity.
4. The rate of penetration into the bulk of fertilizer.

3.2 Time of Storage

The time of storage has a great effect on caking. Caking is found to increase rapidly in the first few weeks after the production, then slows down, and finally reaches an almost constant value.

3.3 Pressure

Degree of caking, frequently is quite dependent on storage pressure. Pressure tends to increase the contact points between the particles, inducing material to cake. Similar to storage time, an excessive and prolonged pressure will result in significant increase in the caking. Under pressure, particle deformation may occur, resulting in increased contact area. Pressure can be limited by limiting the height of the bag stacks or bulk storage piles. A 20 bag stack is considered moderate in height.

SOLUTIONS FOR MINIMISATION OF CAKING PROBLEM OF FERTILIZERS

Various measures are taken by fertilizer industry to overcome or minimise the caking problem. They are:

- The adoption of drying process, to obtain the product of low moisture content.
- The use of different cooling process to obtain a product with low temperature at the time of bagging.
- The adoption of granular technology to produce larger particles and there by reducing the surface area and number of contact points between the particles.
- The control of storage conditions such as storage time, temperature, stacking height and RH.
- Modifying the packaging by up-gradation of bags quality and filling of mixed fertilizer in moisture proof bags.
- Coating of fertilizer by anticaking-agent, and there by reducing the abrasion characteristic of the product.
- Using of double liners in bags as packing material and sealing them by heat sealing machine, to avoid the moisture ingress into the product during prolonged storage.

However, there is practical and economical limits to improvements. Therefore, in number of cases, the use of anticaking-agent, in combination with process and storage control is the answer to caking problems. But its use does not compensate for a poorly produced or handled fertilizer.

THE EFFECT OF ADDITIVES (ANTICAKING AGENTS) ON THE CAKING PROCESS

Active anticaking additives (agents), are those whose chemical constitutions is of more importance, than their physical nature. The possible mechanism by which the anticaking-agents do function are listed as under:

1. Spreading of the liquid film over the particle surface.
2. Preventing saturated solutions on the surfaces of the two adjacent particles from coming in contact.
3. Modification of crystal habit/behaviour during dissolution and recrystallisation process.
4. Inhibition of dissolution and crystallisation.
5. Inhibiting nucleation of small crystals during dissolution or recrystallisation process.
6. Reduction of capillary adhesion between particles.
7. Protection of the particles, by developing a hydrophobic barrier on its surface.
8. Modification of the bond tensile strength.
9. Reduction in the strength of the salt bridges between particles.

THE MODE OF ANTICAKING ACTION

The mode of action which prevents caking of a specific fertilizer is determined by the type of anticaking-agent used and to some extent the type of fertilizer being conditioned.

Amines and the amines derivatives are the active ingredients in the anticaking-agents. The alkyl group (which increases with chain length) forms a hydrophobic coating on fertilizer particles and prevents caking. Being cationic in nature they are easily absorbed on the fertilizer moiety and bulky alkyl group effectively prevents bridge formation and ingress of moisture.

The action of alkyl radical which controls bridge formation and the amine group which provide a strong affinity for the surface of fertilizer and mineral particles to which the surfactants are bonded by chemisorption, is shown in Figure 1 and the hydrophobic characteristic is shown in Figure 2.

TYPES AND CATEGORIES OF ANTICAKING AGENTS

The material called anticaking-agent is applied to an agent that maintains its flowability during storage and handling. They can be classified in two categories, according to the method of application.

- Inert charges or inert dusts
- Organic surfactants or surface active agents

1. Inert Charges or Inert Dusts

Inert additives are those compounds whose chemical constitution is less important than their physical nature. Such additives are normally applied as fine powders to the surface of the granule and they work on following possible mechanism:

- Diffusion of the crystallising phase over the granule surface.
- Nucleation of small, finer crystals during a solution/recrystallisation process.
- Removal of moisture by absorption.
- Reduction in the formation of visible contact area.
- Reduction of the tensile strength of the bond across the visible contact area.

These substances are micronised and have a very low bulk density and high covering and adherent power.

IN SPITE OF THEIR SIMPLE APPLICATION AND LOW PRICE, THEY OFTEN HAVE IMPORTANT DISADVANTAGES SUCH AS

- Low anticaking effect on formulas with a serious tendency to cake.
- In order to get the good results, it is necessary to add higher concentration of the inerts than the fertilizer can absorb.
- The excess charges produce dust in the storage, and handling become difficult.

2. Organic Surfactants or Surface Active Agents

The surfactants are chemical products that alter or modify the phenomenon of surface forces, by lowering the surface tension of its solvents.

Reductions of the surface tension between liquid phase and the solid phase helps the liquid phase to adhere and penetrate the solid phase particles of the mixture.

The surfactant molecule consist of both the hydrophilic and hydrophobic functional groups. The classification of surfactants depends upon whether the active species is a molecule (non-ionic) or an ion bearing a positive (cationic) or negative (anionic) charge.

2.1 Non-ionic Surfactant

The largest class of nonionic surfactants are the poly-oxyethylene condensates, but Iancellic (1966) found that these have only a moderate effect and are not widely used. Compounds such as silicone fluids may be regarded as non-ionic surfactants

2.2 Cationic Surfactants

The cationic surfactants are dominated by the fatty amines, especially those with a long chain carbon atoms.

They have the physical properties like, hydrophobic power, polarity and toxicity, etc.

They are effective in preventing the caking by three different mechanisms:

- By the formation of a hydrophobic coating on the surface of the particles. This improves water repelling characteristics.
- By reducing capillary adhesion between particles.
- By inhibiting nucleation or modifying crystal growth and reducing the number of contact points.

2.3 Anionic Surfactants

The anionic surfactants are dominated by alkyl aryl sulphonates. Due to their hydrophobic nature they act as anticaking agents and increase the contact angle of fertilizer solution and reduce tensile strength of caking bond.

CRITERIA FOR SELECTION OF ANTICAKING-AGENT AT G.N.F.C.

G.N.F.C. has used different anticaking agents from the commissioning stage of ANP\CAN plants. The name of the anticaking agents along with the name of their suppliers are as under in Table 1.

Table 1

SR. No	NAME OF ANTICAKING	AGENTS PHYSICAL STATE	NAME OF SUPPLIERS
1.	Lilamine	Semi-solid	Uhde Germany
2.	Boroflow	Semi-viscose	Bombay Oil Ltd.
3.	Filcon-108	Semi-solid	Transmetal India
4.	Canpol-16	Semi-solid	-----do-----
5.	Lubrash AA-B	Semi-solid	Tashkent Oil (P).Ltd.
6.	ZadeL-20	Liquid	Transmetal. India.
7.	Lubrash-LL	Liquid	Tashkent Oil (P). Ltd.

G.N.F.C. has developed sufficient experience in the evaluation and application of different anticaking agents on ANP\CAN products, and finally set up its own technical specifications of semi-solid and liquid anticaking agents (Appendix I) which are strictly followed for product evaluation and approval at G.N.F.C. Laboratory by accelerated test method (IFDC / ICI / Kao. Corp. & BASF).

Since July 1995, G.N.F.C. has changed the coating material from semi-solid to liquid due to the following comparative edge:

1. Cost effectiveness.
2. Safety consideration of employees to toxicity.
3. Pumpable at room temperature.
4. Minimisation of laborious occupancy when handling drums.
5. Minimisation of sludge formation at the bottom of the day tank.
6. Reduction of charging tank temperature from 85-120°C to 55-65°C.
7. Low temperature of coating drum, leads for uniform coating and loss of product through vapour phase is minimised.
8. No product loss during handling.
9. Crystallography of the granules remains intact.
10. Packing material (empty drums) is reusable.

The crystallisation curves of semi solid and liquid anticaking-agents are shown in Figures 3 and 4 which indicate their flowability at R temp.

Application of anticaking-agent as coating material on ANP and CAN produced at G.N.F.C.

(A) Coating System of ANP Plant

The process flow diagram (PFD) of charging system of anticaking-agent of ANP plant, is shown in Figure 5. The coating material is taken in the tank (36D1) and the tank product temperature is brought to 80-110°C, in case of semi-solid and 55-65°C in case of liquid, with the help of the steam. The services of agitator (36N001) is used for mixing the coating material as and when required. The product dose level is set through the stock pump (36P001). The stocks are adjusted as per production level of the plant at 0.05%, anticaking-agent through nozzle, which is attached in 36P1, A\B discharge line and placed in the coating drum at a suitable height and angle. The uniform coating on granules is achieved by having sufficient baffles in the coating drum and is observed by analysing the product for fluorescence characteristic in ultra-violet region. From coating drum the product moves on conveyor belt (36H018) and is sent for bagging in bagging plant.

The coating by anticaking-agent improves the flowability, minimise dust level, caking tendency, intra-molecular force of attraction, contact points, and porosity of the granules. Thus, the coating by anticaking-agent has proved helpful in maintaining the above characteristics of the product.

(B) Coating System of CAN Plant

The principal of anticaking agent coating is the same as that of ANP plant. Here the anticaking material is charged in the charging tank (60D1) and heated from 80-110°C in case of semi solid and 55-65°C in case of liquid. The agitation of the product is done by agitator (60N001) and the dose level of anticaking-agent is maintained by the pump (60P001A\B). To check the uniformity of coating, the fluorescence property of the product is checked in ultra-violet region. CAN product after coating drum (50 S004) moves on, to the conveyor belt and finally to bagging plant for bagging. The process flow diagram(PFD)of the system is shown in Figure 6.

(C) Monitoring of coating efficiency of anticaking-agent on Plant Scale

The plant scale monitoring of anticaking-agent coating is done by laboratory, by collecting weekly samples of ANP\CAN products, and analyse them for anticaking-efficiency and for fluorescence property, for uniform coating. The detail of analysis, of coating efficiency pertaining to the year 1996, is placed in Appendix 2.

CONCLUSION

- The probable cause of caking in phosphatic fertilizers is the process of deformation brought about by stress on the solubility of fertilizer salts.
- The application of anticaking-agents on phosphatic fertilizers, restrict the movement of crystal by inhibiting the crystal dissolutions and growth, and by reducing the tensile strength of caking bond by surfactant action.
- The anticaking-agents work in hydrophobic form on wetting which makes the surface of the granule resistant to water, so that rate of moisture absorption by the granules is reduced. Further, a hydrophobic barrier between two granules is provided to prevent bonding due to capillary adhesion, restricting caking under the influence of humid conditions.
- In view of above and to serve the customers need for a free flowing fertilizer without loss of properties even after prolonged storages in warehouses, the fertilizer industry needs to use anticaking-agents (additives) coating on their fertilizer products.

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(A) SPECIFICATIONS OF SEMI-SOLID/LIQUID ANTICAKING AGENT

SR. No.	TEST	UNIT	SPECIFICATION	
			SEMI-SOLID ACA	LIQUID ACA
(1)	Colour/Appearance	-	Yellowish/ Brownish	Yellowish/ Brownish/ Blackish
(2)	Flash Point	°C	150 min	150 min
(3)	Viscosity at 70 °C	cst	25 max	25 max
(4)	Reduction on crushing load on ANP Prod.at 0.05% coating	%age	50.0 min	50.0 min
(5)	Reduction on crushing load on CAN Prod.at 0.05% coating	%age	50.0 min	50.0 min
(6)	Fluorescence at 0.05% coating	-	Slight visible on ANP/CAN	Slight visible on ANP/CAN
(7)	Homogenity at Room temp.	-	Fully homogeneous	Fully homogeneous
(8)	Is the material pumpable at RT	-	-	Pumpable
(9)	Liberation of free Ammonia at RT	-	Not desirable	Not desirable

APPENDIX 2

(B) ANTICAKING EFFICIENCY OF ANP AND CAN COATED PRODUCTS AT PLANT SCALE IN G.N.F.C.FROM JAN 1996 TO JAN 1997

SR.No.	DATE OF SAMPLING	PRODUCTS	
		ANP % EFFICIENCY	CAN % EFFICIENCY
(1)	3.1.96	51.9	53.4
(2)	8.1.96	51.2	51.6
(3)	22.1.96	51.2	52.3
(4)	30.1.96	51.0	50.5
(5)	13.2.96	51.0	50.0
(6)	19.2.96	51.6	51.1
(7)	26.2.96	51.3	50.8
(8)	6.3.96	52.3	51.1
(9)	18.3.96	50.0	51.0
(10)	22.4.96	52.6	51.4
(11)	13.6.96	52.4	55.0
(12)	5.7.96	51.1	52.3
(13)	14.8.96	52.0	50.8
(14)	22.8.96	51.2	50.7
(15)	18.9.96	50.0	50.9
(16)	25.9.96	52.4	51.9
(17)	16.10.96	51.5	52.0
(18)	23.10.96	51.5	52.9
(19)	29.10.96	51.9	52.2
(20)	14.11.96	51.6	51.7
(21)	09.12.96	50.6	50.0
(22)	15.1.97	51.2	51.0
(23)	18.1.97	52.5	53.6

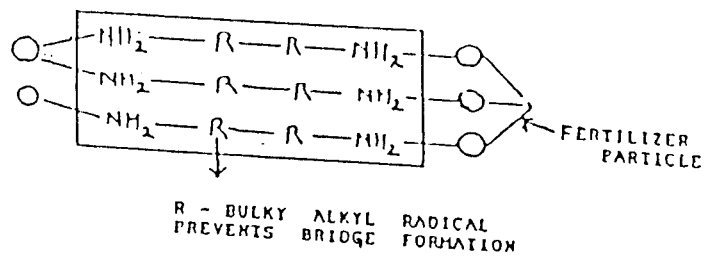


Figure 1 - A typical hydrophobic bonding of a fertiliser particle with an anticaking agent

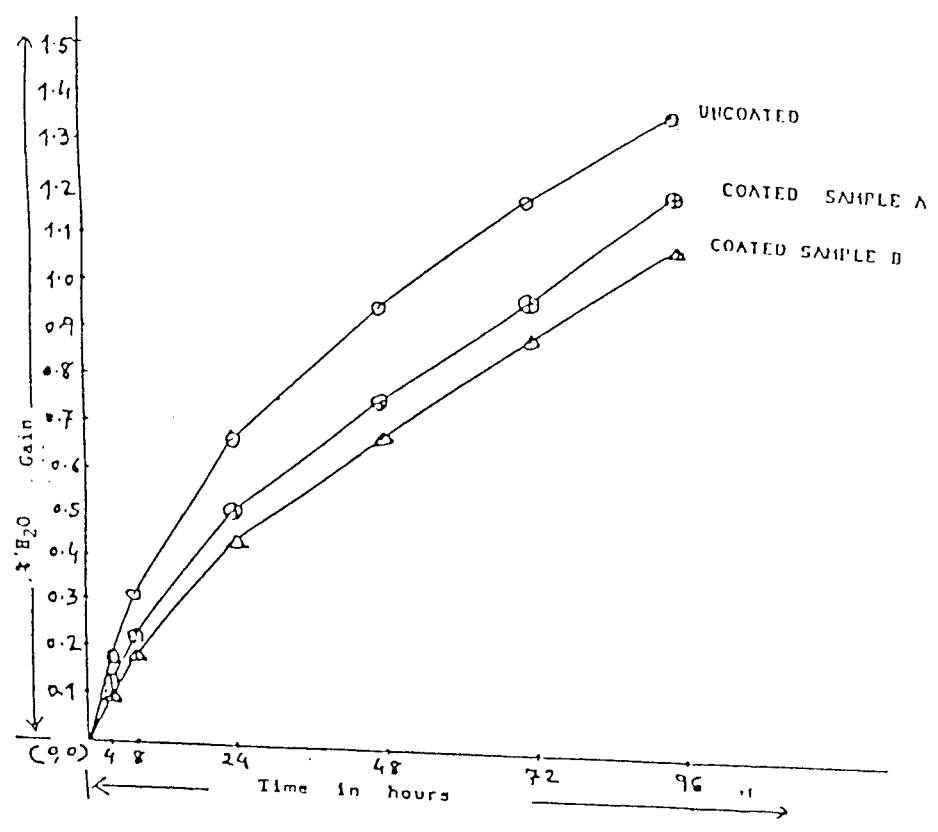


Figure 2 - Hydrophobic characteristic of anticaking agent (with 0.05% w/w coating) on complex fertiliser ANP at 90% RH and 30°C (as per IFDC method)

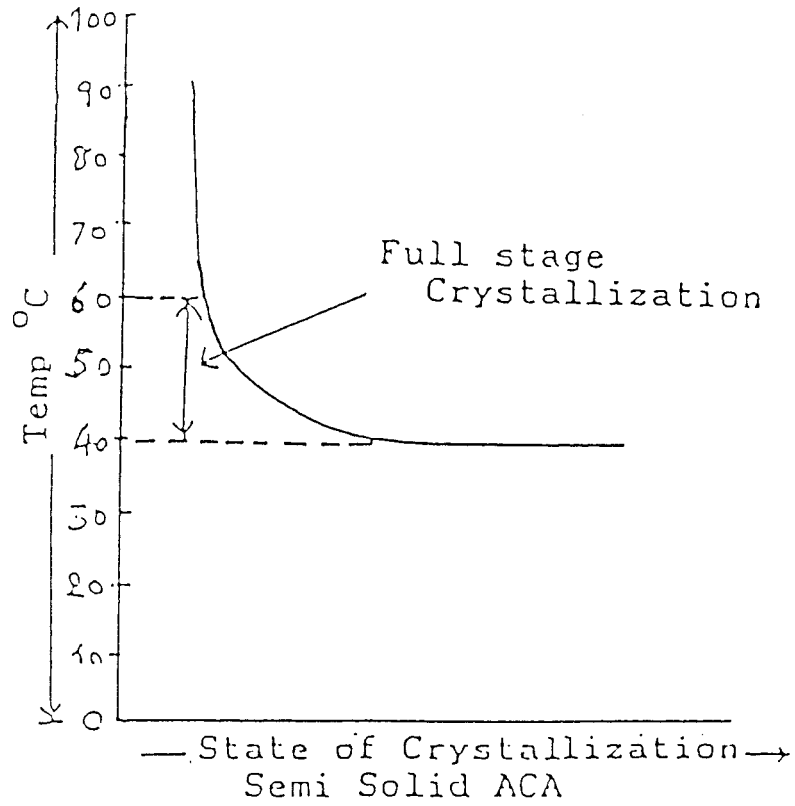


Figure 3 - Crystallisation curve of semisolid ACA

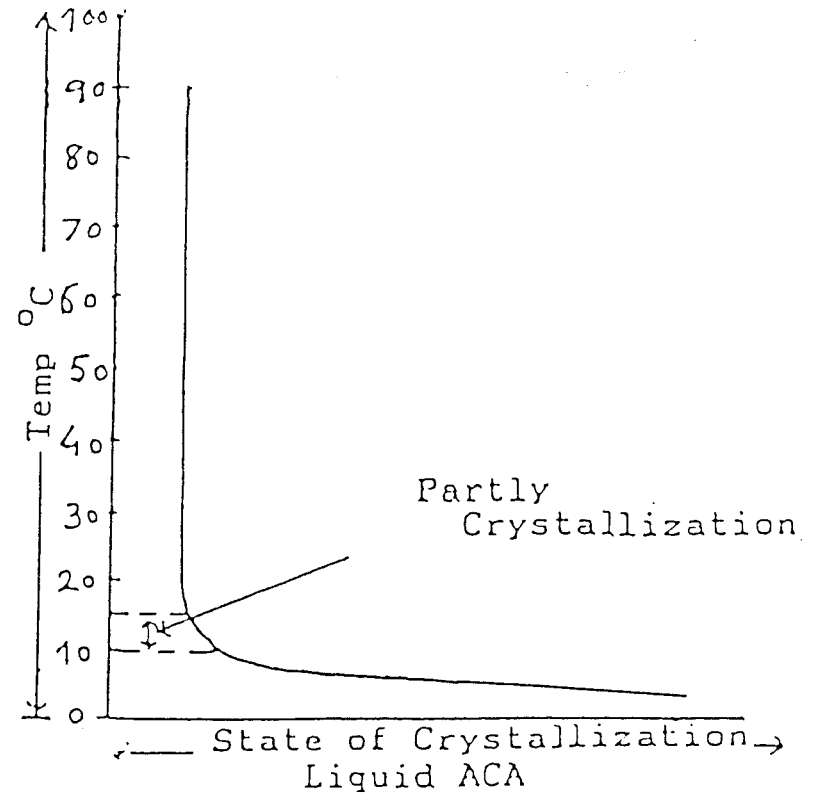


Figure 4 - Crystallisation curve of liquid ACA

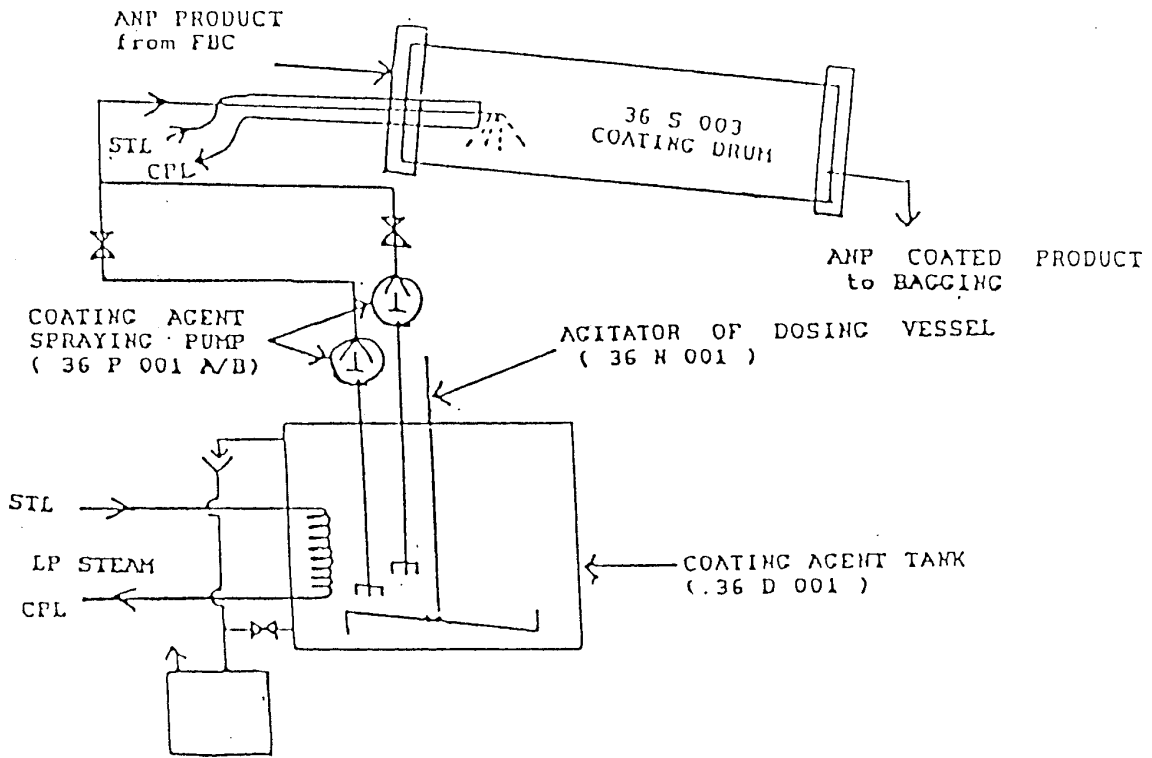


Figure 5 - Coating system for ANP plant

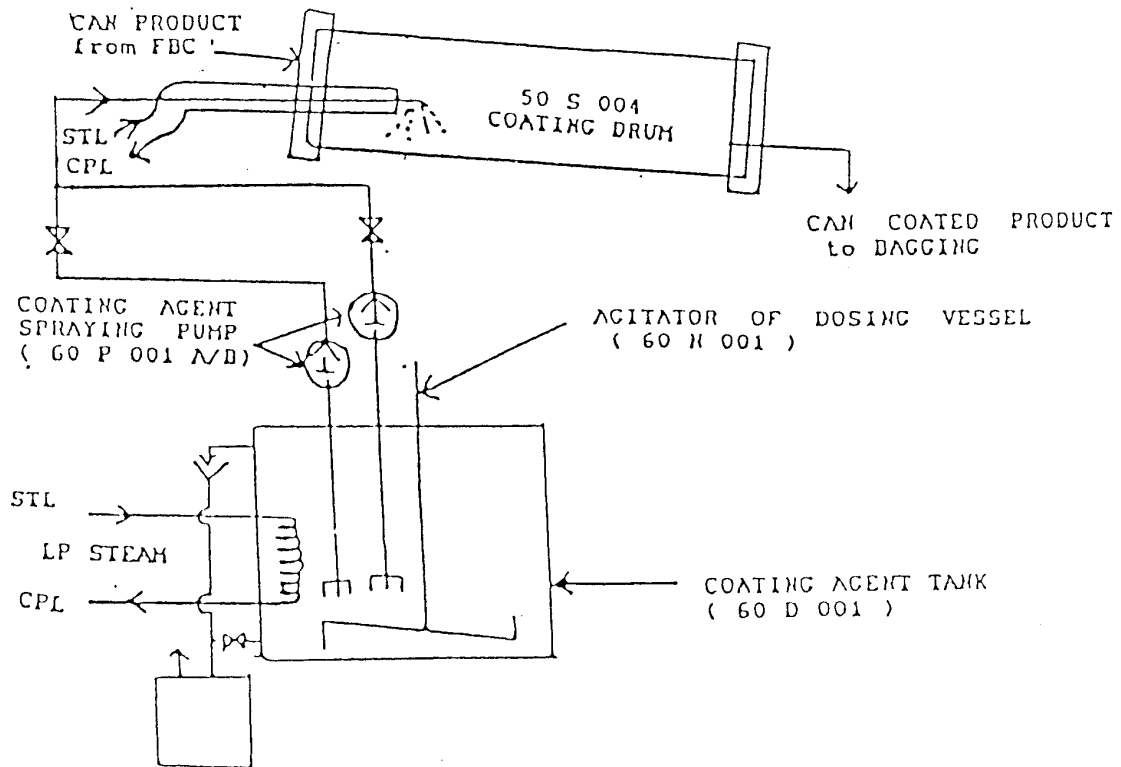


Figure 6 - Coating system for CAN plant