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

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A NEW PROCESS OF CONTINUOUS SUPERPHOSPHATE MANUFACTURE.

by Etablissements Kuhlmann (28th June, 1949).

Since the inception of the Superphosphate industry, now already a century old, manufacturers have always regarded it as an essential condition that the mixture of phosphate and acid should flow into a container of great volume, the "den", and that the superphosphate should be left there to complete the reaction.

The designers of apparatus for a continuous production, whose main object was to reduce the cost of construction and operation of superphosphate plants, have relied on the same principle which they considered to be unassailable. They have, therefore, retained the den by giving it various shapes and contented themselves with a plant having a simultaneous flow of the phosphate-acid slurry and extraction of solidified superphosphate.

However, in their desire to reduce the volume of the den - in order to limit initial cost - they have endeavoured to accelerate the process of setting by prolonging as much as possible the mixing of phosphate and acid. The advantage thus derived has been of little importance because the mixer had become a complicated apparatus, heavy and expensive, without any considerable reduction in the size of the den. In the majority of processes the reaction mass still represents a multiple of the production per hour.

Towards 1934 H. LOISEAU and G. CARTIGNY sought to accelerate the reaction of the superphosphate formation and solidification by limiting the increase in temperature in such a manner as to form a semi-hydrate and gypsum; it is known that the water of crystallisation of these substances separates out in the liquid phase of the reaction slurry.

They verified that the maturing of superphosphate manufactured by this method was in no way retarded and that it was, on the contrary, more rapid than in the usual conditions of manufacture.

In order to eliminate the heat generated in the course of reaction they realised that the most simple procedure consisted of emulsifying the slurry by air prior to setting and of breaking down the formed superphosphate as rapidly as possible.

It then became unnecessary to use a den seeing that the two operations of mixing and breaking down followed each other within a very short space of time and it was even harmful to leave the superphosphate in the den because in such an enclosed space heat disperses only with great difficulty. H. LOISEAU and G. CARTIGNY made the superphosphate set on a simple conveyor thereby evolving the KUHLMANN process.

In this process already described in patents granted by numerous countries in the course of years preceding the war, the acid and phosphate used are distributed and measured continually by fool-proof apparatus which are manipulated conjointly; for the acid a volumetric feed and for the phosphate a constant weight feed of a special type are used which ensure adequate accuracy.

The phosphate and the acid are intimately mixed in a mixer following the distributing apparatus. This mixer consists of a sheet-iron vessel of very small dimensions in which an agitator with turbine paddles revolves in order to mix intimately the constituents and to emulsify the slurry by the introduction of air. This frothy slurry is expelled from the mixer through an outlet aperture, which is constantly open, and drops on to the manufacturing conveyor belt.

The rollers supporting this belt are arranged in such a manner that, near the mixer, its cross-section is in the shape of a trough becoming progressively horizontal as the belt travels in a continuous movement towards the other end.

The superphosphate slurry thus spreads in a thin layer and allows an intensified reaction and a rapid set. Due to the thinness of the layer and also to the introduction of air and release of CO_2, the solid form acquires great porosity and a very slight density.

On arrival at the end of the belt opposite the mixer, the superphosphate is subjected to a disintegrating device consisting of steel wires tightly drawn between formers at each end of the shaft, the axis of the cylinder being at right angles to the line of movement of the belt.

Both the belt and the disintegrator are covered by a hood in order to collect the gases and the water-vapour generated by the reaction. The end of the belt near the disintegrator is subjected to strong suction which by increasing the removal of water, dries and cools the divided superphosphate thus facilitating the crystallization of gypsum.

The superphosphate dropping from the disintegrator is conveyed to the storage shed; its quality is such that it can be transported with equal facility by a rubber belt, in skips on a mono-rail, or by elevators, etc.

The return section of the belt is suitably cleaned by a rotating brush. The reaction mass remains in this apparatus for a very short time; some fractions of a second in the mixer and a few minutes on the belt conveyor.

In order to obtain this result of a revolutionary character it had been necessary to realise the importance of regulating the feed of phosphate and acid and of using sufficiently precise apparatus so that at any given time the quantities of the raw materials reacting upon each other would be available in exact amounts and that the materials could be mixed intimately.

From that moment the process of H. LOISEAU and G. CARTIGNY came into being.

The phosphate is distributed by a weigher i.e. gravimetrically not volumetrically, a procedure which hitherto has been deemed satisfactory. An efficient volumetric feed of acid is connected with the weigher, the mixture of acid and phosphate is energetically mixed and aerated in a small mixer fitted with paddles, the "den" disappears, as the belt conveyor on which the superphosphate sets cannot very well be called by that name; and the disintegrator which has to divide a very thin layer of material is only a small apparatus of a very simple construction.

The apparatus is therefore considerably lightened; it requires foundations to carry very little weight and it can even be installed on the upper floors of a building, for example, above the storage shed.

In these circumstances the outcost is very small as the user effects an appreciable economy on accessory expenses with which he is usually confronted.

The wear and tear of most of the apparatus is almost nil; periodically the vessel and the paddles of the mixer as well as the wires of the disintegrator need replacing with little cost on account of the very small dimensions of these parts. Only the replacement of the conveyor belt represents an appreciable expense but in view of its long service which is effectively assured and which in a 20 ton-per-hour unit attains 100,000 tons of superphosphate, the corresponding charge does not exceed 10 French francs per ton of superphosphate produced. It is more economic than the wooden or metal conveyor which had been used during trials.

No component of the machine is of delicate construction or difficult to adjust on the spot. On the contrary, every apparatus consists of parts which are of simple design and of which there is a ready supply.

Finally, none of the components runs the risk of sudden deterioration due to wrong handling or any other cause as it has been the case with processes prior to the KUHLMANN process: enormous horizontal and lateral transporters, cog-wheels of very considerable diameter, etc.

It is equally unnecessary to envisage long stoppages in order to repair the solid masses of concrete, walls or arches damaged by acid vapours generated in large quantities.

Thus a very great measure of improvement is obtained which has been borne out by years of operation with a high performance.

The simplicity, the safety in regulating the manufacture and the absence of breakdown makes it possible for a single workman to run and supervise the installation.

The cost of labour is, therefore, much lower than in any other process; this is all the more so owing to the fact that the putting into operation of an empty installation is very rapid and, inversely, the plant can be stopped and emptied of its contents in a few moments.

The consumption of energy is higher to mix the slurry of phosphate and acid for a lengthy period, to shift great quantities of superphosphate or to scrape the large surfaces of a material which is too compact; for the same production capacity the motive power drops from 1 to 2 KWH/T to 0.2 - 0.3 KWH/T.

The KUHLMANN process results in a product of superior quality without requiring more than the other processes as far as the strength of acid, the fineness of the phosphate or the duration of the maturing of the superphosphate is concerned.

The accurate regulation of the raw materials, their energetic mixing and aeration, the setting of the superphosphate in a thin layer in the absence of any pressure, the intense evaporation of the moisture promoted by the small thickness and by the fissures formed when the set material travels along the belt and, finally, the division into fine particles, gives the superphosphate an excellent physical aspect, light, sandy, dry, hardening very little during storage, very soluble, homogeneous and of a quality which always remains constant.

During several months of operation and with only plus or minus differences corresponding to relative day to day errors of analysis the following has been obtained:

Raw Materials:

Morocco phosphate with 2.5% H_2O
ground with 15% residue on sieve No. 100
Sulphuric acid Baumé 15° : 54.5° T = 35° C.

Superphosphate:	After three weeks' storage:
Moisture (loss at 100°) %	9.9
Phosphorus anhydride, free	2.5
" " water-soluble	18.30
" " water and citrate soluble	18.75
" " total	19.15
Solubilisation $\frac{\text{(water and citrate soluble)}}{\text{total}}$	97.9

The above results as well as those obtained with all the other phosphates treated demonstrate that it is possible to manufacture a superphosphate of good quality by pulverising it only a few minutes after mixing.

Published in 1937, the KUHLMANN process has remained little known until late owing to the war and its consequences and only one 20 ton-per-hour unit has been in operation during this period.

But, at present, several 10-ton and 20-ton-per-hour units are under construction and it may be rightly assumed that the process, the advantages of which are undeniable, will enjoy a certain popularity.

The continuous running of a thin layer of superphosphate which facilitates taking samples of a definite age as well as the homogeneity of the product, have enabled Mr. SZEJNBERG to study the reactions of superphosphate formation.

The results of that study are shown in the annexed graph:

92% of the sulphuric acid applied enter into reaction after 2 to 4 minutes of contact and the whole of it after 10 to 15 minutes. At the same time phosphoric acid forms rapidly which in its turn reacts upon $Ca_3(PO_4)_2$ resulting in mono-calcium phosphate, the principle constituent of superphosphate.

Mr. SZEJNBERG furnishes proof on an industrial scale of the double reaction of the mono-calcium phosphate formation;

$$2\ Ca_3(PO_4)_2 + 6\ H_2SO_4 \rightarrow 4\ H_3PO_4 + 6\ CaSO_4$$
$$4\ H_3PO_4 + Ca_3(PO_4)_2 \rightarrow 3\ Ca\ H_4(PO_4)_2$$

hypothesis formulated for the first time by KOLB in 1874 and considered as being very likely by several other authors.

The examination of the curve showing the variations in terms of time of the free P_2O_5 content and of $Ca\ H_4(PO_4)_2$ - the first passing through a maximum the moment the sulphuric acid has more or less completely entered into reaction - is very significant in this respect.

Every phosphate has its own set of curves which vary with the concentration of the sulphuric acid and above all with the finess of grinding, but with normal conditions of operation their general aspect remains always the same.

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- SUPERPHOSPHATE -

Procédé continu Kuhlmann.