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

CONTRIBUTION TO THE IMPROVEMENT OF SUPERPHOSPHATE
MANUFACTURING CONDITIONS BY MEANS OF THE USE OF
CATIONIC SURFACTANTS

By Messrs. Boutault, Bruyneel and
Kalinovski (Société de Produits
Chimiques d'Auby, France).

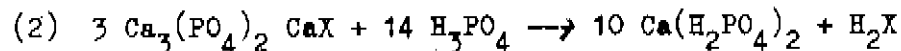
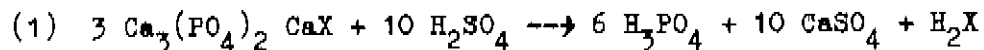
Although the first patents relating to the manufacture of ordinary superphosphates were taken out over a century ago, the physico-chemical processes which take place are still the subject of considerable debate which we do not wish to revive in this paper.

Basically, the process aims to solubilize the P_2O_5 in phosphate rock by sulphuric acidulation.

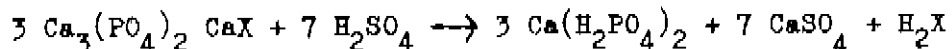
In calculating the amount of acid required for a specific phosphate rock, due allowance must be made for all factors likely to be affected during the reaction with sulphuric acid, assuming that all the P_2O_5 is converted to monocalcium phosphate.

Although the mixing of the phosphate and the acid presents no particular difficulties because of the progress achieved in mixer design, the importance of achieving an accurate feed of acid (which is relatively simple) and of phosphate (which may be more difficult) should not be underestimated.

It is theoretically admitted that the conversion of phosphate rock into monocalcium phosphate takes place in two stages during the reaction with the sulphuric acid, with the temporary formation of phosphoric acid, giving reactions of the following type:



or, summarizing



in which X represents groups such as F_2 , $(\text{OH})_2$ or CO_2 , according to the phosphate involved.

The heterogeneous and exothermic reaction (1) occurs on the surface of the phosphate particles: it is important that it should be carried through as completely as possible.

To this end, a strong ventilation is provided to evaporate a certain quantity of water. This permits the evacuation of part of the heat of reaction and the reduction of the moisture content of the product obtained.

One also aims to increase the speed of the reaction by increasing the fineness of the grind within the limits set by the economics of the operation.

Reaction (2) is of the same kind (heterogeneous and exothermic) as reaction (1) and is favourably affected by the same factors. Experience acquired in the manufacture of triple superphosphate tends to prove that it proceeds fairly easily.

As is well known, the solubilization of the P_2O_5 is never entirely completed when the superphosphate is taken from the den. The product then has a considerable free acid content (2 to 6%) and begins a more or less long and complicated evolution which reduces the free acidity and the insoluble fractions to water- and citrate-soluble forms of P_2O_5 .

During this period of curing, processes of solidification ensue, resulting, in particular, from the formation of monocalcium phosphate. In these circumstances, considerable caking can occur during storage.

Although in our above remarks we have deliberately reduced to its simplest expression the description of the main stages and difficulties in superphosphate manufacture, the production of a good quality superphosphate is, in short, not a simple problem.

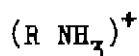
With a view to improving the quality of their product, many producers have, over the last twenty years, been led to try various different additives. As soon as they appeared on the market, surface activating agents, also called wetting agents and surfactants, were used as a possible solution to the problems arising. Many patents were taken out, particularly in the U.S.A., and important publications and studies dealt with the subject.

In particular, at the ISMA Technical Conference in 1955, a very interesting paper presented by Dr. R. Kaack drew the attention of our members to the potential benefits to be obtained from a large-scale programme of trials relating to the specific properties of surfactants, the composition and structure of raw materials, the characteristics of the processes used, the nature of the finished products and their moisture contents, and even the climatic conditions in the producing countries. In his paper, Dr. Kaack correctly distinguished between so-called anionic surfactants and non-ionic surfactants and concluded that the latter were better suited to be used in the manufacture of superphosphates.

Anionic surfactants where the lypophilic group - i.e. the aliphatic chain - constitutes the anion are, in fact, not stable at a pH of less than 7, whilst the non-ionic surfactants - mostly condensates of the aliphatic chains on ethylene oxide - are sensitive only to extreme pH.

We have taken particular interest in this question, because the group incorporating our company, which plays an important part in the French superphosphate and complex fertiliser industries, has also begun the manufacture of special surface activating products.

These products are cationic, and the lypophilic group constitutes the cation according to a formula of the type



(R representing a hydrocarbon chain). They are stable throughout the range of acid pH.

The oxyethylated aliphatic amines, which we manufacture, are of a non-ionic nature in alkaline pH and are slightly cationic in acid pH. Their wetting and emulsifying capacity is considerable, as well as their filmogenic capacity. The programme of trials, which is the subject of the present paper, was conceived on two levels - in the laboratory and in the factory. Our trials mostly related to the solubilisation of Moroccan phosphates. In particular, they aimed to make a systematic study of the incidence of our surfactants on

- the fineness of grinding of the phosphate
- the rate of reaction
- the acceleration of the process of manufacture in dens
- the reduction of the curing period
- the improvement of solubilisation
- the improvement of the physical properties of the finished products.

The first stage of our trials was conducted jointly in two of our laboratories. Each laboratory was equipped with a small batch den, capable of dealing with about 1 Kg of superphosphate. After the mixing, the den was placed in a thermostatic enclosure regulated at about 90°C and under about 25-30 mm water. These conditions were designed to approximate to the industrial working conditions of batch dens.

After a denning period of 4 hours, the superphosphate was de-denned and left to cool in the air before proceeding with the operations of sieving, sampling and analysis. Table 1 is given as an example and shows the practical results of one of our experiments designed to determine, in particular, the possible influence of the fineness of grinding.

As the laboratory results were, in general, satisfactory, the trials were then taken to a second stage in two factories, the first of which was equipped with a continuous rotary den, with a capacity of 20 t/h, and the second of which had a batch den with a capacity of 130 tons.

Table 2, which is again provided as an example, shows the results obtained in a recent experiment in a batch den designed to make a particular study of curing conditions.

In general, our experiments demonstrate the importance of carrying out a considerable number of trials if one wishes to derive valid conclusions.

As has been already indicated, various raw materials can contain wetting agents in small quantities. Certain residual acids, for example, can contain anionic detergents which are absolutely incompatible with cationic surfactants. Certain phosphates may have been flotated with fatty acids, and this leads to the formation of a hydrophobic film on the surface of the phosphate particles, making them more resistant to the attack of sulphuric acid. Conversely, certain phosphates may have been subject to a cationic flotation and thus react more easily. The incidence of possible variations in raw materials and the inevitable errors of analysis - particularly important in the comparison of trials carried out in two different factories - leads to certain anomalies in the results obtained.

Although, for all these reasons, our work cannot be considered to be yet complete, we may summarize as follows the substance of our results:-

- 1). The surface activating agent should preferably be introduced either directly into the head mixer or into the acid before its entry into the mixer.
- 2). There is no evidence that the addition of the surface activating agent allows any reduction in the grinding fineness of the phosphate without affecting the rate of reaction.
- 3). On the other hand, the surfactant seems to have a beneficial effect in accidental cases of errors in the feed or of irregularity in the working of the apparatus feeding the den.
- 4). The reaction of the phosphate with the sulphuric acid is accelerated in the presence of the surfactant.
- 5). The slurry at the outlet of the head mixer is more homogeneous and flows more easily into the den.
- 6). It is possible to use acids of a higher concentration than normal without blockage in the dens, and hence one obtains a lower moisture content in the superphosphate obtained.

TABLE 1

Results of Laboratory Tests

	Water at 100°C	P ₂ O ₅			Free acid fraction (NaOH)	Available P ₂ O ₅ fraction
		Water and citric acid soluble	Total	Insoluble		
<u>Analysis 12 h after de-denning</u>						
Rock phosphate reference without Noramox	11.27	18.55	19.98	1.43	6.13	92.8
" with 0.3°/oo Noramox	11.41	18.50	19.87	1.37	6.00	93.1
Phosphate sieve 40 reference without Noramox	11.58	18.78	20.11	1.33	6.02	93.4
" with 0.3°/oo Noramox	10.22	18.92	20.31	1.39	6.43	93.15
" normal crushing ref. without N	11.34	19.09	20.10	1.01	5.91	95
" " with 0.3°/oo N	9.24	19.40	20.43	1.03	5.95	95
<u>Analysis after 10 days' storing</u>						
Rock phosphate reference without Noramox	10.71	19.42	20.11	0.69	4.60	96.6
" with 0.3°/oo Noramox	10.85	19.28	19.87	0.59	4.35	97
Phosphate sieve 40 reference without N	10.45	19.64	20.44	0.80	4.40	96
" " with 0.3°/oo Noramox	10.22	19.25	20.23	0.60	4.26	96.7
" normal crushing reference without N	10.10	19.36	19.98	0.62	4.22	96.8
" " with 0.3°/oo N	9.03	19.80	20.38	0.58	3.41	97.15

NOTES: Rock phosphate Morocco 80

Normal crushing (80% through 65 mesh Tyler sieve)

Sieve 40: the whole phosphate passing through 35 mesh Tyler sieve

Sulphuric acid 53° Bé at 35°C

"Wetting" by the acid: $\frac{\text{Acid weight at } 53^{\circ} \text{ Bé}}{\text{Phosphate weight}} = 94\%$

TABLE 2

Results of Industrial tests

		At the beginning of excavation	At the end of excavation	After 2 days' storing	After 3 days' storing	After 10 days' storing	After 20 days' storing
<u>Reference manufacture</u> Super 20% Den no. 192 Weight 123 t.	Water at 100°C	11.42	11.35	11.00	11.11	10.81	9.85
	P ₂ O ₅ total content	20.92	20.99	21.18	20.96	21.05	21.43
	Water and citric acid soluble	18.88	18.95	19.48	19.66	19.84	20.22
	Non soluble	2.04	2.04	1.70	1.30	1.21	1.21
	Free acid fraction	3.72	3.44	2.36	2.16	2.15	1.70
	Available P ₂ O ₅ fraction	90.3%	90.25%	92%	93.8%	94.3%	94.4%
Manufacture with addition of 2% co Noramox Den no. 193 Weight 123 t.	Water at 100°C	12.22	12.50	11.94	11.39	11.20	10.96
	P ₂ O ₅ total content	20.29	20.13	20.32	20.47	20.48	20.45
	Water and citric acid soluble	18.61	18.71	19.10	19.44	19.44	19.51
	Insoluble	1.68	1.42	1.22	1.03	1.04	0.94
	Free acid fraction	3.66	3.51	2.63	2.43	2.36	2.19
	Available P ₂ O ₅ fraction	91.7%	92.45%	94%	95%	94.9%	95.5%

NOTES: Phosphate Morocco 80/82
Normal crushing (80% passing through 65 mesh Tyler sieve)
Sulfuric acid 53° Bé at 15°C
Acid wetting: 93%.

7). De-denning is greatly facilitated and blockages of the excavator are practically eliminated and are, in any case, less violent.

8). Curing appears to be accelerated to a variable extent, depending on the raw materials used: generally the product obtained has a lower moisture content.

9). The improvement in the physical qualities of the superphosphate thus treated is indisputable: the products always have an excellent appearance, and although they are practically in powder form, they do not cake and present no difficulties in subsequent handling.

10). The reduction in the manufacturing time in continuous dens enables rates of production to be accelerated by more than 25%. In our opinion, this result is of primary importance, because it implies the possibility of increasing the production capacities of existing plants without new investment, when they are equipped with continuous dens.

11). In the manufacture of binary and ternary fertilisers, the treated superphosphate can be used without difficulty after only four or five days of curing and even, if need be, immediately after emerging from the den. Its composition remains virtually constant between the 4th/5th day and the 15th/20th day. Thus the need for large storage sheds for the curing of superphosphate over three or four weeks is eliminated.

12). The granulation of the treated superphosphate and of the binary and ternary fertilisers manufactured with this product raises no problems and even seems to be improved. However, we have been unable to show the possibility of any substantial reduction in the amount of water or steam used in this operation - contrary to the affirmations of certain authors.

In addition, in conjunction with certain of our clients, whom, without naming them, we should like to thank, we have carried out industrial trials on the manufacture of concentrated superphosphate. This is, of course, produced by reacting phosphate rock with phosphoric acid. The introduction of a surfactant into the phosphoric acid used in the manufacture of concentrated superphosphate, in the proportion of 100 to 400 grams per ton of superphosphate, improves the physical structure of this product, which becomes considerably more friable. The main effect of the surfactant in the mixture of phosphate and acid consists in the extension of the possible duration of the mixing without any breakdown in the alveolar structure due to the evolution of CO_2 . Otherwise, this stage would be very short (a few seconds) without the strong mixing necessary for good homogenisation, and one would observe the formation of hard pellets.

CONCLUSIONS

As we have already indicated, we are still continuing our studies. The results which we have reported above may be of more or less interest to producers, according to circumstances. It is certain, for example, that the reduction in the curing period will not interest manufacturers who have surplus storage capacity.

But the use of cationic surfactants has so many simultaneous advantages that it seems to us that it will systematically become generalised. This is all the more likely because, although these additives are, in themselves, relatively expensive (about 5 French francs per Kg ex-works - present economic conditions in France), the rates of application of our currently available products (about 150 to 300 g/ton) are sufficiently low for the cost of the treated superphosphate to be only 1 to 2% more than that of normal superphosphate.

DISCUSSION

Mr. H. BOUTAULT (Sté de Produits Chimiques d'Auby, France): Our paper does not claim to offer any exclusive solution to the problems discussed. We were particularly interested in improving superphosphate manufacturing conditions by the use of surface activating agents. Our interest stemmed from the fact that the group to which we belong produces both superphosphate and complex and compound fertilisers on the one hand, and cationic surface activating agents on the other. We believe it is necessary to have this double activity in order to undertake a worthwhile experimentation in this field. Experimentation is, in fact, difficult, and it must be recognised that the results are significant only in so far as each is supported by several distinct experiments and comprises only a kind of statistical average of these experiments.

We are now continuing our work and are trying to differentiate between the effects of the surfactants available to us as a function of the precise aims to be achieved in each particular case. In view of the large number of components which offer themselves to such an experimentation, it goes without saying that our progress is very slow. We often think that we are only at the start of our work. This, to our mind, should in future cover the study of the improvement of manufacturing conditions in respect of granular binary and ternary fertilisers. As we have stressed in our conclusion, we consider that the use of cationic surface activating agents simultaneously offers so many advantages that they must finally become quasi-systematically generalised.

Mr. A. CORELA (S.A. Cros, Spain) : I wonder if you could give further information on the following points. It seems that the correct application of your surface activating agent varies from 150 to 300 g/ton of rock phosphate. What is the effect of varying the proportion of the activating agent on the rate of the reaction between phosphate rock and sulphuric acid? Similarly, what is this effect on the curing time of the superphosphate? Also what influence does it have on the physical qualities of the final product?

Finally, could you give the exact chemical composition of your surface activating agent?

Mr. BOUTAULT: The amount of surface activating material to be added should be determined in each particular case, depending on the particular characteristics of the plant and the raw materials used. In general, good results are achieved with doses of 200 - 250 g/ton. Too small a quantity, e.g. about 50 g/ton, produces no improvement. In addition, improvements are not proportional to the amount of material used. Beyond a certain point, they appear to level out, so that an excess of surfactant no longer gives any substantial advantage. In these circumstances, it is naturally preferable not to exceed the prescribed ceilings, and even to keep slightly below them.

With regard to the nature of our products, I should say that, without entering into detail, the cationic agents which we have developed also generally present a non-ionic character favourable to the development of physico-chemical processes. These products are mostly selected within the family of long chain, oxy-ethylated, fatty amines. One can also use the salts of these amines. To quote an example, the product mentioned in our paper is a condensation product of ethylene oxide on an amine, the hydro-carbonated chain of which comprises 18 atoms of carbon. This product is obtained from fatty acids of animal or vegetable origin. The mixture of fatty acids is treated with ammonia and dehydrated to form a nitrile, and by the subsequent hydrogenation of this nitrile the primary fatty amine is formed, on which we fix the ethylene oxide. In this particular case, we fix 11 molecules of ethylene oxide.

Mr. A. SINTE MAARTENSDIJK (Albatros Fertilizers Ltd., Ireland):

I should like to ask a few questions relating to the summary of results given on pages 4 and 7. The following paragraph numbers relate to the corresponding paragraphs in the summary.

- 6) Has it been proved that, for the same fineness of grinding of the Rock Phosphate, a more concentrated Sulphuric Acid can be used for production. What is for instance the maximum concentration at a certain fineness of grinding?
- 8) Table 2 does not show that curing is accelerated when using 0.2% of Noramox. For instance for den no. 192 the available P_2O_5 fraction has increased by 3.9% after 3 days of storing, while for den no. 193 these increases are only 2.8 - 3.6% since leaving the den. Moreover the acidulation of the Rock Phosphate for den no. 193 has undoubtedly been higher than for den no. 192, which also shows up in the moisture contents, which are higher for den no. 193. Because of this higher acidulation the available P_2O_5 is in the case of den no. 193 still slightly lower than for den no. 192.
- 10) How has the reduction in the manufacturing time in continuous dens been determined. If in fact this is about 25%, does it mean that the time necessary for the conversion of all free sulphuric acid has been reduced by 25%.
- 11) You state that, for the manufacture of binary and ternary fertilisers, "treated" Superphosphate can be used immediately after emerging from the den. This can be done - and is in fact done in a great many plants - with ordinary superphosphate, provided that it is of a decent manufacture (i.e. by using the correct concentration and temperature of H_2SO_4 , fineness of rock grinding and thorough mixing).
- 9) You state that treated superphosphate - and we have some experience in this direction ourselves - does not cake. Is it unlikely to expect that in view of this non-caking property a granule produced from this material would disintegrate earlier than an ordinary superphosphate granule?
- 12) Although the granulation of the treated superphosphate does not raise any problems, how is the quality of the granulated product?

How for instance is the hardness of the granules compared to those made from untreated superphosphate?

Mr. BOUTAULT : With regard to your first point, i.e. the fact that we could have used a more concentrated sulphuric acid, we used acid at concentrations exceeding 53° Bé. We carried out experiments going up to 58° Bé., but in practice we consider that at this point working conditions become very difficult, and the improvement should not exceed concentrations of 55 - 56° Bé. This is equivalent to a decrease of 1% in the water introduced into the system. We have not carried our investigations far enough to know whether this decrease in water content is carried right through into the superphosphate. We would suppose that the exact equivalent is not carried through but that the super must gain about half a unit.

With regard to the fact that our Table 2 presents certain anomalies, we completely agree on this point. In general, our conclusions are based on the average results of numerous experiments, and within these averages such anomalies disappear. We have observed fairly frequent anomalies in the detail of each of our industrial experiments in batch dens. We attribute this firstly to the conditions of manufacture which necessitate manual operation and which are therefore difficult to reproduce from one day to the next. Secondly, the plants in question are fairly old. They were not modified for the purposes of the experiment, and the measurement of the sulphuric acid feed is made by weighing and is relatively inaccurate. The importance of this objection has not escaped us, and I can now tell you that our most recent industrial experiments, which have been carried out in continuous dens, have fortunately and fully confirmed the statistical results we obtained in batch dens.

With regard to the reduction in manufacturing time, this is precisely an item based on experiments carried out in continuous dens. The present case involved moving belt dens, and we simply controlled the speed of the belt. We observed that with an increase of 25% in belt speed, the superphosphate at the outlet of the den was, let us say, somewhat retarded, in so far as its free acidity was somewhat higher than normal superphosphate, but this retardation is practically eliminated after about two days, and after this the two superphosphates are practically identical.

With regard to the production of binary and ternary fertilisers, using superphosphate fresh from the den, this is possible but has certain disadvantages. I think the main problem is to obtain a superphosphate of constant quality, but in addition the use of a fresh superphosphate is always accompanied by an unreacted proportion of the P_2O_5 .

As far as the granulation of treated superphosphate is concerned, this raises no particular problem. We measure granule hardness on an apparatus which is fairly peculiar to our company. We have noticed nothing with regard to possible variations in hardness of the granules of either treated or untreated superphosphate. Thus, to answer your other point, the granules of treated superphosphate do

not disintegrate more quickly than the granules of untreated superphosphate.

Mr. M.E. PEDEMONT (Australian Fertilisers Ltd., Australia) : We have carried out a number of trials using fluorinated hydrocarbon anionic surfactants on the superphosphate reaction. Although they are not cationic, they are particularly stable in acid, and our phosphate rock was Nauru, Christmas Island and Florida concentrates. It was ground to about 60-70% -100 Tyler mesh. We found that the treatment actually slowed down the reaction, rather than speeded it up : the rate of setting in the den definitely tended to decrease. I can only attribute this to either the rock type or its sizing, and I should therefore like Mr. Boutault to comment on the influence of these two factors on the addition of surfactants to the superphosphate reaction.

Mr. BOUTAULT: Our experiments involved Moroccan phosphate almost exclusively. This is the phosphate which we have used virtually exclusively up to now. I am therefore badly placed to discuss other phosphates.

I think there are two distinct aspects of this question: firstly, the nature of the phosphate, and secondly the treatment which it has undergone, particularly by flotation. I think a slowing down in the reaction is scarcely conceivable apart from a counter indication originating from flotation.
