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THE USE OF SURFACE ACTIVE AGENTS IN THE PREPARATION OF FERTILIZERS

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In the hope of improving the quality of their products, fertilizer manufacturers in the U.S. began some years ago to watch developments in the use of wetting agents, already widely used in soap factories. Their efforts were enthusiastically seconded by the manufacturers of wetting agents who saw an opportunity for increasing their business. As a result, both fertilizer and wetting agent industries have carried out many trials, part of which gave good results, with some isolated bad results, but the majority showed no influence one way or the other. This diverse behaviour of the wetting agents is hardly surprising when the following points are kept in mind:

1. both chemical and physical factors are at work
2. raw materials treated vary greatly in composition
3. a multiplicity of end-products is produced by a variety of methods and frequently show strongly contrasted characteristics

The real cause, however, appears to lie in the structure of the surfactants and their specific properties, as established by the trials carried out by the U.S. Dept. of Agriculture. It is known that surfactants lower the surface tension between air and aqueous solutions by forming a boundary film on the surface of the aqueous solution, The hydrophilic groups of the wetting agent are orientated towards the aqueous solution, while the hydrophobic components penetrate the surface in the form of innumerable minute projections and so destroy the film between the aqueous solution and the air. The hydrophobic content of modern wetting agents is a hydrocarbon residue, which may be chain-like, linear or branched, saturated or unsaturated, and made up of 10-30 C-atoms. The hydrophilic component is usually the solubilising group in a terminal position and may be of an anionic or nonionic type. the solubility of substances in water is effected in the first case by the anionic groups: $-\text{COO}.\text{Na}$, $-\text{SO}_3.\text{Na}$, etc., and in the second case by the nonionic binding forces of the hydrophilic molecule positions (accumulated OH-groups). Thus, wetting agents fall naturally into two groups, those which are anionic in solution or nonionic, and consequently react quite differently to any given medium (acid, alkaline.) A representative sample of the types in commercial use at the present time is given by the following list:

Anionic Surfactants

- 1) Na-salt of dodecylbenzene cyclohexanol sulphonate
- 2) Na-salt of decylbenzene pentahydro benzene sulphonate.
- 3) Na-salt of polyalkyl naphthalene sulphonate
- 4) Alkyl benzene triethanolamine sulphonate

Nonionic surfactants

- 5) Alcohol-ethylene oxide condensation product
- 6) Mercaptan-ethylene oxide condensation product
- 7) Alkyl phenyl polyethylene glycol ether
- 8) Alkyl phenoxy polyoxyethylene ethanol.

Surfactants of this type are offered in all countries under proprietary names as more or less viscous solutions or in the form of pastes and powders.

By the use of these wetting agents, producers of ordinary and triple superphosphate (and multiple-nutrient fertilizers prepared from them) expect to satisfy the most varied demands.

- 1) Quicker reaction between phosphate and acid, using less acid with higher output.
- 2) Reduction in curing time
- 3) Improved physical properties in the finished superphosphate.
- 4) Advantages in ammoniation
- 5) Easier granulation
- 6) Improved physical properties in the finished compound fertilizers.

The manufacturers were encouraged in such hopes by the blandishments of the detergents industry, whose affirmations were not always based on actual experience. Understandably, the decomposition of phosphates by sulphuric acid or phosphoric acid occupies a great deal of space in the extensive program carried out in the U.S. by the superphosphate manufacturers to investigate the usefulness of wetting agents of this type. Both anionic and nonionic surfactants were used in these tests, and all stages of the process of decomposition were observed.

For the laboratory tests a reaction vessel with stainless steel change-cans with a capacity of approx. 30 litres has proved very satisfactory. These mixers are fitted with a thermocouple, which is carefully insulated from the larger supporting tube, so that high accuracy of measurement can be achieved. A drying-oven of 6-can capacity specially designed to circulate heated air at 70°C over the contents of the cans was used for quick curing.

The cured superphosphate is excavated by means of a cutter which is inserted into the can when it has been tilted to slightly below horizontal. The relative hardness of the product was measured by its resistance to the cutter-bar which is pivoted in the centre and connected to a tension spring over a graduated scale. Two interchangeable springs registering a pressure of 0-5 or 0-10 lbs were used, depending upon the hardness of the product.

For each experiment, 10 lbs of various kinds of phosphate were used and were decomposed on an average by 8 lbs of sulphuric

acid at 56°Bé, one with the added surfactants and one without.

The fines content fluctuated between 87-97% on a DIN 40 sieve and 58-78% on a DIN 80 sieve.

The surfactants were used in amounts of 0.25-1.25 per ton of superphosphate (908kg). Where the surfactants were soluble, a concentration was used equal to 10 ml. per 10 lbs. or a ratio of 0.25 lbs. of surfactant to every ton of superphosphate (908kg). If the amount contained less than 50 ml. of surfactant solution (equivalent to 1.25 lbs. of wetting agent, per ton of superphosphate) water was added to keep the volume of solution plus water constant at 50 ml.

Anionic surfactants which were incompatible with acids were added to the phosphate in the can, while the acid-sensitive surfactants plus added water were mixed with the acid before acidulation. Average period of agitation was 45 secs.

The temperature of the decomposed mass was recorded at one-minute intervals until it reached its maximum and began to decline. Can and contents were then weighed and the volume (bloating) calculated from this.

Before the drying oven was started, duplicate samples of approx. 2 g. were taken from each reactive and titrated with sodium hydroxide against methyl orange to determine the residual free acid at this stage (about one hour after mixing). These tests were repeated with further samples of 1 g. taken 24 hours later (after curing overnight at 70°C) when the weight of the cured product was determined and the charge excavated from the can. During the latter procedure, the hardness of the product was determined, as previously described. At the same time, analytical samples were taken, screened on a 2mm. sieve and tested on the afternoon of the same day for residual free acid and citrate-insoluble P_2O_5 .

(Translator's note Dr. Kaack's text has "citrate-soluble", but the article describing the work & reference 2. - has "citrate-insoluble" with the explanatory phrase: "considered as a measure of unreacted rock".)

The preparation of triple superphosphate was carried out in the same apparatus, but instead of one part of H_2SO_4 (100% basis) per unit of phosphate, two parts of titratable H_3PO_4 were used.

Plant-scale trials were carried out in the U.S. with phosphate with a fines content of 85% on a DIN 40 sieve and 55% on a DIN 80 sieve, with 58% of H_2SO_4 (100%) in the form of an acid of 56°Bé (T. = 57°C). Anionic and nonionic wetting agents

were used at the rate of 0.5 lb per ton of superphosphate (908 kg). The anionic surfactant was added to the acid used for decomposition, while the nonionic type had to be added to the phosphate-acid mixture, since this material caused excessive frothing when added to the acid direct.

The phosphate and acid were mixed together in 2-ton capacity pans, the batches being limited to 1 ton of superphosphate per charge. Immediately after filling, the 75-ton capacity dens were excavated by dragline. Control and treated materials consisted of 225-450 ton lots:

Samples of the superphosphate, taken about three feet below the surface of the piles at one week intervals starting 24 hours after mixing, were immediately analyzed for total, water-soluble and citrate-insoluble phosphate, free acid and moisture contents. Pile temperatures observed at the time the samples were also recorded. After six weeks curing in the piles, the superphosphate was tested for hardness. This was done by measuring the rate of vertical penetration of a star-drill under pressure of the weight of the electric hammer into undisturbed material in the pile at an elevation of about four feet above floor level.

At the same time, i.e. after maturing for six weeks, the superphosphate was used to make compound fertilizers and, contrary to normal practice, no conditioners were used. Portions of the finished mixtures were bagged 2, 3, 8, and 16 days after manufacture in asphalt-laminated four-ply paper bags and stored

in tiers 10 bags high and 15 cm. apart.

After two, four and eight weeks, the 1st, 5th and 9th rows, counting from the top of the pile, were tested for bag set. In this test, the bags were dropped four times from a height of about 3 feet on to different sides and then screened for coarse particles on a 5 mm. light mesh box-type sieve.

Other tests undertaken in U.S. superphosphate works concern the use of an anionic surfactant, an alkyl aryl sulphonate, in the manufacture of compound fertilizers, the wetting agent being added at the rate of 1 lb. per ton of mixture (908 kg).

There is also much information available on the use of wetting agents, where details of processes, apparatus and methods used have not so far been published. These results are discussed in the section that follows.

Effects of Wetting Agents

For ease of arrangement, it is better to deal separately with its influence on manufacture and treatment of superphosphate (ammoniation, mixing and granulation).

^{under}If we begin with the acidulation of phosphates, it is obvious that ~~experimental~~ conditions better results were obtained with nonionic surfactants than with the anionic products, as they do not disintegrate in the acid medium. Moreover, considerable differences have been established, even within the same type, and these are due to the different methods of chemical synthesis.

So far, analytical tests have failed to establish with absolute certainty that either type of surfactant influences acid consumption or yield. However, the higher temperatures recorded on mixing all types of phosphate with acid in the presence of surfactants indicates that the initial reaction, i.e. the attack of the sulphuric acid on the rock, is accelerated: the second phase of acidulation (between phosphoric acid and residual phosphate), however, appears to be affected hardly at all during the first week after acidulation. Appreciable differences begin to appear only 1-4 weeks after acidulation in the content of free acid and the yield of treated and untreated superphosphates. This is due to the fact that the use of wetting agents apparently facilitates the release of water from the curing piles, and this evaporating action lowers the temperature in the piles.

This reduction in the temperature of the free water further encourages the tendency towards a lower content of free phosphoric acid in the liquid which is in equilibrium with solid monocalcium phosphate. If this equilibrium is upset, the concentration of the free acid in the solution is raised, so that it is able to react with the residual raw phosphate to give a higher yield.

A reduction in the curing time for fresh superphosphate benefits the producer only if he is not in a position to wait for the normal curing period of 6-8 weeks, for example, during the peak season. If he is able to leave the superphosphate to cure for six weeks and over, then it makes no difference whether he uses wetting agents or not, as untreated superphosphate, with normal drying and cooling, reached the same stage of reaction and curing in 6-8 weeks as the mixtures with added wetting agents.

The best result obtained was the production of a free-flowing, non-caking product of low density and increased volume, this improvement was even more apparent in the production of triple super.

Against this, the anionic wetting agents delayed the reaction between the phosphate and the acid in the mixer, in the den and in the curing pile, hindered the conversion of the superphosphate and gave a harder and denser product.

When judging the favorable characteristics of certain non-ionic wetting agents, it should be mentioned that various raw materials, such as flotation phosphate, or waste sulphuric acid from oil-refineries, already contain small amounts of wetting agents.

The tests discussed above have shown that such impurities may be just as effective as the best wetting agents added for the purpose.

Thus, it is important, if we are to avoid muddled and erroneous conclusions from the testing of wetting agents, to examine the raw-material first for the presence of such waste products; this applies to potash salts and solid and liquid nitrogen compounds as well as to phosphates and sulphuric acid.

The grades of triple and ordinary super obtained by using nonionic surfactants possess greater volume and are therefore lighter and more porous, and appear to have advantages in ammoniation. At any rate, a super produced in this way showed a 6% increase in absorption of ammonia, as against the untreated super, and no reversion or increased losses of ammonia could be established. In another case, it proved possible by adding wetting agents to compound fertilizers to get a better distribution of moisture, so that the material was drier and easier to handle, better for drilling, too.

Nonionic surfactants, which produced a less dense structure in superphosphates treated with them, and even more with triple super, transferred this good quality, though in greatly reduced degree, to the compound fertilizers prepared from the treated super. However, this was not true of all types of compound fertilizers - an indication of the extent to which hardening depends on the composition of the individual varieties.

Anionic surfactants answered better in the manufacture of compound fertilizers if they were added, not at the stage of acidulation of the phosphate, but at the time of mixing the various nutrient ingredients. In such cases - for example, when using an alkyl aryl sulphonate - it was able to accelerate the chemical reactions, reduce the reaction temperature by better conduction of heat, and consequently to produce more rapid cooling in the curing pile.

In this way, a number of users of this wetting agent have been able to effect better N utilization without reversion of phosphoric acid, and without higher ammonia losses, and also without lowering the quality. As a result of this more rapid conversion, the compound fertilizers obtained showed less hardening, so that Payloaders could be put on to shifting the piles, whereas previously the material had to be blasted and excavated before it was ready to load.

So far, no details have been published on the effect on the granulation of super and compound fertilizers of the addition of wetting agents. This is rather surprising, since even some brochures put out by surfactant manufacturers refer to these advantages, moreover, a lowering of surface tension in the solutions to be used for the granulation process ought to be beneficial, and thus their use would appear to hold promise. The literature of two manufacturing firms claims that in the granulation of super and compound fertilizers their wetting agents will prevent agglomeration of the finished granules without affecting their hardness, and will further allow granulation to be carried out with less water.

CONCLUSIONS

From various points of view, it is expedient that these surfactants should be thoroughly tested to discover their effect on granulation (even anionic surfactants may be of value here), and this should be a priority task for all who are interested.

- (1) If it is true that their use reduces the amount of water needed for granulation, then it is possible that the drying period following this can be shortened, or the drying temperature reduced. The advantages to be derived from this would be: less reversion of phosphoric acid and less hardening in the end-product. (Fertilizer Journal 41 (8) 295 1954)
- (2) Since the presence of wetting agents ensures a more even distribution of moisture within the individual granules, this obviates the fear that moisture will collect on the surface of the granules and dissolve any very soluble salts, which will crystallize out when the temperature drops and weld the separate granules into a compact mass.

Generally speaking, it may be said that the addition of surface active agents is indicated only when the raw material contains none, or not enough.

The reduction in the curing time is of little importance, since the normal reactions occur in untreated mixtures if they can be left for the usual period, and the end-product is of satisfactory quality.

Of real advantage is the improvement in the physical properties of superphosphate, and even more in triple super (less caking with more bulk, lower fuel consumption, cleaner working conditions, less hardening in the curing pile).

An improvement in the ammonia process and the physical properties of compound fertilizers appears to be within reach.

A pre-requisite for the more general use of wetting agents in the manufacture of fertilizers is the carrying out of an extensive programme of trials. It should be planned to include the study of the specific properties of different types of surfactant, the composition and structure of the raw materials, any special procedures to be adopted, also the type of end-product and its nutrient and moisture content, and the climatic conditions in the country of manufacture.

In these circumstances it is probable that the optimum conditions for the use of wetting agents can be worked out. It will also be necessary to establish the quantity of surfactant needed to obtain the best results.

The last is a key point, because the price of wetting agents is so high that their use is not an economic proposition unless the quantity to be used can be kept as low as possible.

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