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SOME EXPERIENCES ON THE INTRODUCTION OF UREA INTO GRANULAR MIXED FERTILIZERS BASED ON SUPERPHOSPHATE

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INTRODUCTION

The work described in this paper was consequent upon the decision of the authors' company to build a urea plant and to use urea as the principal source of nitrogen in its mixed fertilizers. While it cannot be contended that the use of urea in granular mixtures is in any way original, it is hoped nonetheless that the experiences gained during this investigation will be of some interest.

The chief object of this work was the development of processes and techniques for the most efficient utilisation of urea in granular mixtures based on single superphosphate and it is of some importance, therefore, to appreciate the circumstances prevailing in the fertilizer industry in South Africa. The most important fact in this connection is the Government regulation regarding phosphate availability. We are perhaps fortunately situated in that the criterion of availability of phosphate in mixed fertilizers is solubility in 2% citric acid solution. In consequence it is possible to carry out a considerable amount of ammoniation of the superphosphate fraction of granular mixtures, which is naturally economically desirable. Though it is not a legal stipulation, it is the usual endeavour of South African producers to retain at least 50% of the citric soluble phosphate in water-soluble form.

The superphosphate used in South Africa is usually made from either Morocco rock or from the locally produced Phalaborwa concentrate. There is very little which needs to be said about Morocco rock, but the Phalaborwa concentrate, which may be unfamiliar to most of you, needs a little explanation.

The concentrate as received has a fairly high phosphate content, usually in excess of 36%, but is unreactive when used for the manufacture of single superphosphate. Mineralogically it is an igneous apatite, the main impurities being calcite, micaceous minerals and magnetite. Typical analysis of both rocks are shown in Table 1 together with analyses of superphosphate produced from them.

Table 1

a) Typical analyses of phosphate rocks used in South Africa.

		Phalaborwa concentrate	Morocco rock
P ₂ O ₅	(%)	36.54	33.30
CaO	(%)	49.84	51.18
Fe ₂ O ₃	(%)	0.67	0.29
Al ₂ O ₃	(%)	0.40	0.87
CO ₂	(%)	4.33	4.01
F	(%)	2.44	3.96

b) Typical analyses of superphosphate produced.

		Phalaborwa concentrate	Morocco rock
Total P ₂ O ₅	(%)	21.0	20.0
Citric-soluble P ₂ O ₅	(%)	19.6	19.3
Water-soluble P ₂ O ₅	(%)	19.0	19.0
Free acid P ₂ O ₅	(%)	4.0	2.0
Moisture	(%)	5.6	5.0
Ratio			
	$\frac{\text{w.s. P}_2\text{O}_5}{\text{t. P}_2\text{O}_5} \times 100$	90.5	95.0

It will be observed that the water-soluble P₂O₅ content of both superphosphates is identical but that the conversion of the Phalaborwa-based superphosphate to water-soluble form is significantly lower.

Table 2 shows the granular mixtures currently manufactured in South Africa. The compositions are such that they can be made from ammonium sulphate, superphosphate and potassium chloride.

Table 2
Currently produced mixtures
(% composition)

N	Citric soluble P_2O_5	K_2O
0	15	10
0	17	7
3	13	8
3	15	3
5	13	5
5	14	0
6	25	6
10	6	10
7	7	21
3	6	18
2.5	18.5	0

Of these mixtures the most important is 5-13-5. Urea is used in place of the normal ammonium sulphate, slight, though significant, upgrading occurs due to the higher nitrogen content of the urea. All the work described here has been based on either 5-13-5 or its urea-based near equivalent, 5-15-5. The authors' company is fortunate in having available ammonia made on its own factories. Consequently it is the usual practice to derive as much as possible of the nitrogen in a mixture from ammonia. Most mixtures, therefore, contain about 2% of ammoniacal nitrogen.

GRANULABILITY

A typical A.E. and C.I. granulation plant is shown as a line diagram in Fig. 1. It will be observed that the plant layout conforms generally to American T.V.A. practice though it must be emphasised that the low nitrogen content (and indeed the low analysis generally) of the local mixtures, is such that it is not necessary to add an acid in order to obtain maximum ammonia fixation.

Although it was the intention of the authors' company to utilise urea in granular mixed fertilizers in the form of a urea-ammonia liquor from the outset, such a liquor was not available until well on into this investigation, and in consequence it was necessary to add urea and ammonia separately to the remaining components of the premix for a considerable number of experiments.

Initial experiments using solid urea together with superphosphate and potassium chloride in the premix indicated that severe caking troubles during handling of the premix were likely to be caused by such a procedure. This was due to the formation of the very hygroscopic urea-phosphoric acid adduct from the urea and the free phosphoric acid in the superphosphate. In consequence it was then decided to make use of the urea in the form of an

aqueous solution which was added, after the ammonia, in the ammoniator of the plant. Experience on both full scale plants and on the semi-technical plant showed that the use of aqueous urea and ammonia gave rise to conditions most unfavourable to granulation and an upper ammoniation limit was found beyond which granulation efficiency fell prohibitively.

If we define a quantity "ammoniation level" as being the number of pounds of ammoniacal nitrogen added to each 100 lb of superphosphate in a prenex, we have available a scale which is of considerable utility. Our experience shows that if aqueous urea solutions together with ammonia are used to provide the nitrogen of the granular mixed fertilizer, there is an upper ammoniation level somewhere between 1.5% and 2%. If this is exceeded the appearance and feel of the material leaving the granulator are quite characteristic - very small granules, approximately $\frac{1}{8}$ mm in diameter, are formed which have a pronounced gritty feel and which cannot be persuaded to agglomerate into larger granules by the addition of either more steam or more water. Such efforts to improve granulation lead merely to formation of large lumps of over-size together with a slurry of the small granules. The granulation efficiency falls abruptly and it is impossible to continue operating the plant for more than a few hours, due to the build-up of recycle.

True urea-ammonia liquor the became available for experimental work and several more experiments were carried out on both plant and semi-technical scale to investigate the granulation behaviour of this material. It soon became evident that the use of UAL offered several notable advantages in regard to granulability and it was shown that when Morocco superphosphate was used all the nitrogen in a 5-15-5 or 5-13-5 mixture could be derived without difficulty from UAL. At this stage the procedure adopted for the introduction of UAL was to add the liquor in the ammoniator of the plant, after which water and steam were added in the normal way. The UAL manufactured by the authors' company is a low pressure type containing 33.2% total nitrogen, derived equally from urea and ammonia. In American terminology this is a 332 UAL (20-0-36). In American practice it is usual to add the urea-ammonia liquor below the bed of material in the ammoniator via an acrofoil distributor, the so-called T.V.A. header; and it is standard practice in A.E. and C.I. to use this type of distributor for ammonia. It was found, however, with our low pressure type of urea-ammonia liquor, that it was not necessary to resort to this type of distributor and a simple multiple pipe header mounted above the rolling bed sufficed. This gave very little trouble due to imperfect absorption of the ammonia (less than 0.25% escaping) and did not cause formation of oversize due to bad liquid distribution.

It was soon found, however, despite the successful experience with Morocco superphosphate, that when superphosphate made from Phalaborwa concentrate was used with urea-ammonia liquor that the familiar granulability difficulties were again evident. Various modifications of the granulation method finally led to a procedure which enabled all types of superphosphate to be granulated with UAL, even in the presence of large quantities of inert filler which had previously been found to depress granulability seriously. Our present technique for the use of UAL is to reverse the usual order of addition of the liquids. Thus the water necessary for granulation is added, in the granulator, to this pre-wetted powder. By the time the UAL is added the prenex is semi-granular, and it was feared that the consequent diminution in surface area would have a deleterious effect on ammonia absorption. This has, however, not been found to occur.

Surprisingly, and contrary to our experiences with Morocco superphosphate and the original UAL distribution technique, it has been found that the use of steam with our new procedure has

markedly deleterious effects on granulation, the causes of which are obscure. Little is known concerning granulability and we are hoping to resolve our problems by investigations on a laboratory scale, since it is obvious that a large scale plant is ill-adapted to this type of investigation.

Summarizing our conclusions on the subject of the granulability of mixtures based on urea it appears that:

- 1) Granulability is easily lost, a quite characteristic 'gritty' feel and appearance being then imparted to the material in the granulator.
- 2) Three factors determine the onset of this loss of granulability. These are ammoniation level, ammonia concentration at the surface of the solids at the moment of contact, and superphosphate type. Thus, for a Morocco superphosphate-based premix, an upper ammoniation level of 1.5 - 2.0% has been found in the presence of urea, when using anhydrous ammonia. When adding UAL to the dry premix the permissible ammoniation level is at least 3.75% when Morocco superphosphate is used. When Phalaborwa superphosphate is used, however, the permissible level is once again only 1.5%. If, however, the UAL is added to already wetted premix the permissible ammoniation level is restored to 3.75% even for Phalaborwa superphosphate.

BEHAVIOUR ON DRYING

One of the most interesting aspects of this investigation has been the behaviour of the urea on drying. In our first attempts to use urea on a semi-technical scale, it was discovered that the usual synthesis reaction in which ammonia and carbon dioxide are combined to form urea can, in the circumstances existing in the normal plant dryer, be very easily reversed, with the result that an alarming proportion of the urea present can be hydrolysed to ammonia and carbon dioxide. It was originally feared that the condensation reaction to form biuret might occur which would prove agronomically troublesome. Contrary to expectations, this has not proved the case: the proportion of biuret formed during normal processing is slight, less than 0.15% of biuret being present in mixtures which have been harshly dried. It was then necessary to develop our drying procedures to a point at which urea hydrolysis and consequent nitrogen loss should be insignificant.

In the days when ammonia and ammonium sulphate provided the nitrogen for granular mixtures it was common practice on A.E. and C.I. plants to operate so that material leaving the dryer was at a temperature of up to 140°C, in a praiseworthy endeavour to prevent setting troubles during storage by reduction of moisture content to a practical minimum. A considerable revolution in thinking was therefore necessary in order to preserve the urea.

Before describing the results of our investigations it is perhaps of interest to give some details of the experimental methods.

After start-up the plant is allowed to come to equilibrium, at which time all temperatures are steady and recycle is returned to the ammoniator at the constant rate at which it is produced. The time to attain equilibrium is of the order of 4-6 hours, and after this the plant is allowed to run steadily for a minimum of 12 hours before sampling is begun. The sampling period is usually 4 hours and the sampling frequency quarter-hourly. We have found that the most convenient sampling points for the determination of urea behaviour are across the dryer, i.e. at the granulator exit and at the dryer exit. The chief reason for sampling across the dryer is that the whole size range is examined, which is not

the case, if, for instance, only the on-size product is taken. The water content of material leaving the granulator is much higher than that at the dryer exit, and a correction is therefore made, either by means of a total phosphate balance or a potassium balance. Experimental error, as shown by sample to sample variation and experiment to experiment variation, seems to depend on the scale of operation, being considerably less for full-scale plants producing somewhere between 10 and 30 tons/hour than for the semi-technical plant producing 600-700 lb/hour.

It is reasonable to expect that the actual amount of hydrolysis of the urea which occurs would be mainly dependent on the temperature of exposure and the time of exposure. In the normal type of granulation process where both over- and under-sized material is returned to the process, and only that fraction of the total product which is within a certain size range is actually removed from the system, the determination of the effective exposure time is a problem of some subtlety.

If we consider a normally operating granulation plant having a retention time in the dryer of H minutes for a single pass, then the effective retention time is given by the expression $H/G \times 100$, where G is the granulation efficiency. In normal practice, at granulation efficiencies in the 60% region, this means that the effective retention time in a dryer with a single pass retention time of, say, 15 minutes is, in actual fact, 25 minutes. The derivation of this relation is shown in Appendix I.

It must be pointed out that there is an implicit assumption that the granulation process does not discriminate between fresh feed and recycled material.

It is our experience that the most satisfactory index of exposure intensity is the solids exit temperature from the dryer, this value being a better indication than either the arithmetic or logarithmic mean between the inlet and exit solids temperatures. A correlation has been found between urea hydrolysis, exit solids temperature from the dryer and effective retention time in the dryer, by treating the hydrolysis process as a zero order reaction.

i.e.

$$-\frac{d(U)}{dt} = Ae^{-E/RT} \dots\dots\dots(1)$$

- where (U) = instantaneous urea content,
- E = the activation energy of the reaction,
- A = the frequency factor of the reaction,
- R = the gas constant,
- T = the exposure temperature, i.e. the dryer solid exit temperature.

Integration of this relation between corresponding limits for urea concentration and time, and transformation to logarithms to the base 10 for the sake of convenience, shows that for the mechanism

to be valid

$$\log \frac{\Delta U}{t} \text{ should be proportional to } \frac{1}{T}$$

where ΔU = urea loss,
 t = effective retention time in the dryer
 $= \frac{H}{G} \times 100$

where H = single pass retention time in the dryer
 G = granulation efficiency.

Using data obtained from seven full-scale runs on two different plants, we may then plot figure 2. Statistical tests applied to these data show that the relation is highly significant.

It is possible to advance other mechanisms to explain the urea hydrolysis, and both a first order process (with respect to urea concentration) and a second order process (with respect to urea and water concentrations) are conceivable. These give plots analogous to that shown in figure 2, and do not explain the observed data more effectively. In addition they suffer from theoretical objections in that they introduce concentration terms into the differential equation which seem difficult to justify, as the hydrolysis process presumably takes place in a solution saturated with respect to urea, concentration then being dependant on temperature alone.

The regression equation derived from figure 2 may be used to predict urea hydrolysis, after manipulation into the form

$$\Delta U = \frac{2.601 \times 10^{12}}{10^{4853/T}} \times t \dots\dots\dots (2)$$

where ΔU = urea hydrolysed (%)

The slope of the regression line gives an estimate of the activation energy for the hydrolysis process of 22.2 kcal/mole, compared with the value of 28.2 kcal/mole found for hydrolysis in dilute solution.

The ammonia formed hydrolytically does not necessarily escape from the system, as there is the possibility of reaction with the superphosphate present. As is well known this gives rise to the reversion of water-soluble phosphate to citric-soluble form. The actual extent of the reversion is determined by several factors, chief among which are ammoniation level and drying temperature. At an ammoniation level of 1.5% about 65% of the citric-soluble P_2O_5 remains water-soluble at a dryer solids exit temperature of $100^\circ C$, whereas only about 45% remains in water-soluble form at an ammoniation level of 3.5%. Virtually no reversion to citric-insoluble form has been observed, even at ammoniation levels of the order of 6%. For the experimental conditions prevailing in this investigation some 12-15% of the urea can, on average, be hydrolysed before actual nitrogen losses are incurred. Nitrogen loss is strongly correlated with urea hydrolysis, the relation being of the form

$$\Delta N = 0.876 \Delta U - 11.9 \dots\dots\dots (3)$$

where ΔN = nitrogen loss (%).

As an example let us consider a granulation plant operating at a granulation efficiency of 67%. Let the solids exit temperature from the dryer be $100^\circ C$ and let the single pass retention time in the dryer be 10 minutes.

Then the effective retention time is given by

$$t = \frac{10}{67} \times 100$$
$$= 15 \text{ minutes.}$$

Substituting in equation (2), (or using figure 3):

$$\Delta U = \frac{2.601 \times 10^{12}}{\frac{4853}{373}}$$
$$10$$
$$= 3.8\%$$

Insertion of this value in equation (3) shows that this small amount of urea hydrolysis is not likely to lead to nitrogen loss.

The nitrogen content of these mixtures is comparatively low and no caking troubles have been experienced on storage, even with moisture contents as high as 2%.

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APPENDIX

The average retention time in a recycle process

Consider a quantity of material passing through the dryer in time H . Then, if f is the recycle ratio, the quantity of material making a single traverse is $A(1 - f)$. Now the quantity Af is, by definition, recycled, and passes through the dryer twice. Of this Af^2 is recycled, so that the quantity of material which is resident in the dryer for time $2H$ is $Af(1 - f)$. In the same way we find that $Af^2(1 - f)$ is present for period $3H$, $Af^3(1 - f)$ for period $4H$, and so on.

The weighted average of all these gives an expression for average retention time, i.o.

$$\begin{aligned}
 t &= \frac{A(1 - f)H + Af(1 - f)2H + Af^2(1 - f)3H + \dots}{A(1 - f) + Af(1 - f) + Af^2(1 - f) + \dots} \\
 &= \frac{H(1 + 2f + 3f^2 + 4f^3 + \dots)}{(1 + f + f^2 + f^3 + \dots)} \\
 &= H \frac{\sum_{r=1}^{\infty} r f^{r-1}}{\sum_{r=0}^{\infty} f^r}
 \end{aligned}$$

Now $\sum_{r=0}^{\infty} f^r = \frac{1}{1 - f}$ and the numerator, which results from the

denominator series by differentiation term by term, can be summed simply by differentiation of the sum of the denominator series with respect to f , to give $\frac{1}{(1 - f)^2}$

$$\begin{aligned}
 \text{whereupon } t &= \frac{H}{(1 - f)^2} \bigg/ \frac{1}{1 - f} = \frac{H}{1 - f} \\
 &= \frac{H}{G} \times 100,
 \end{aligned}$$

where $G =$ the granulation efficiency.

FIG 1

A TYPICAL A.F. & C.I. PLANT.

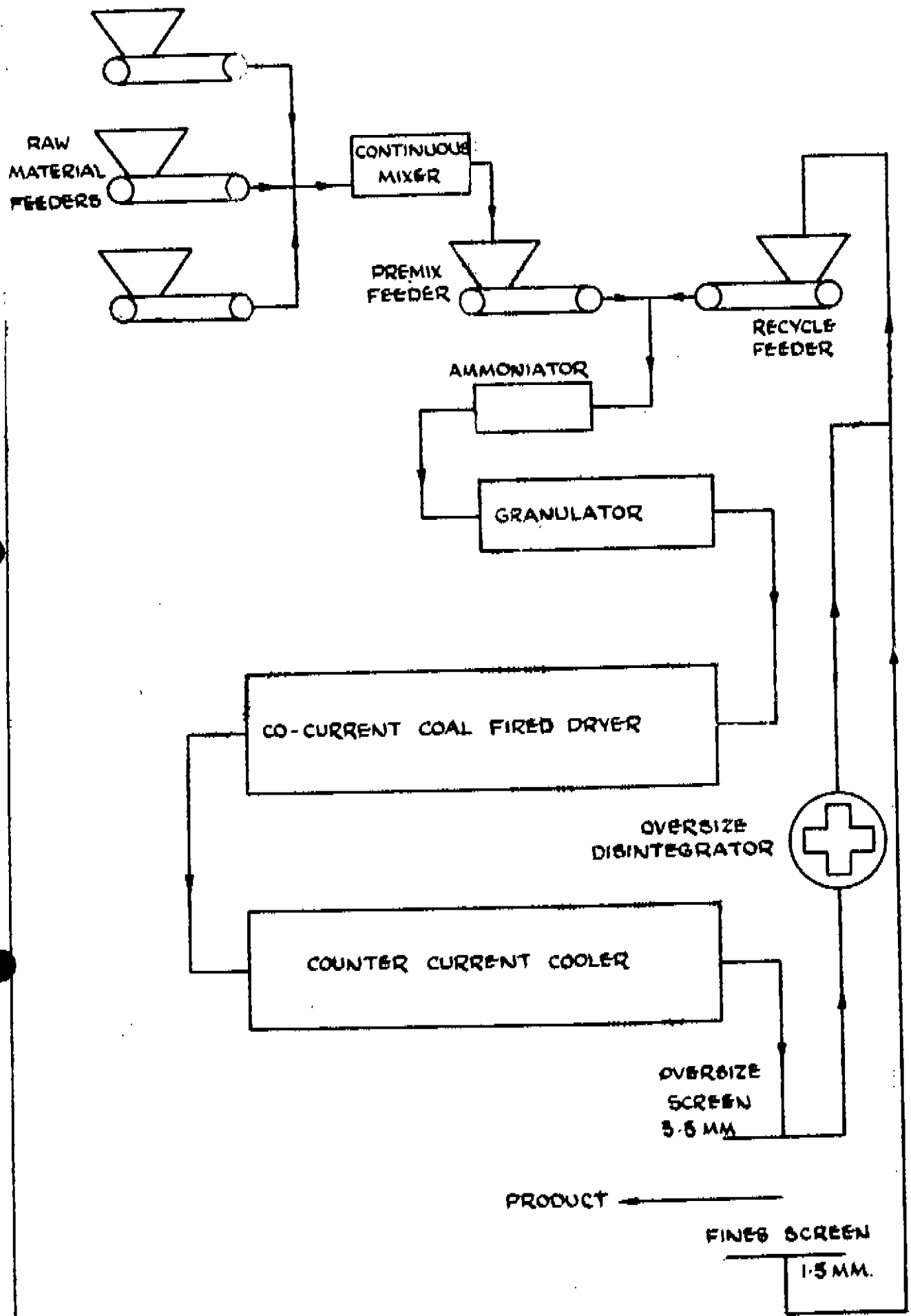


FIGURE 2

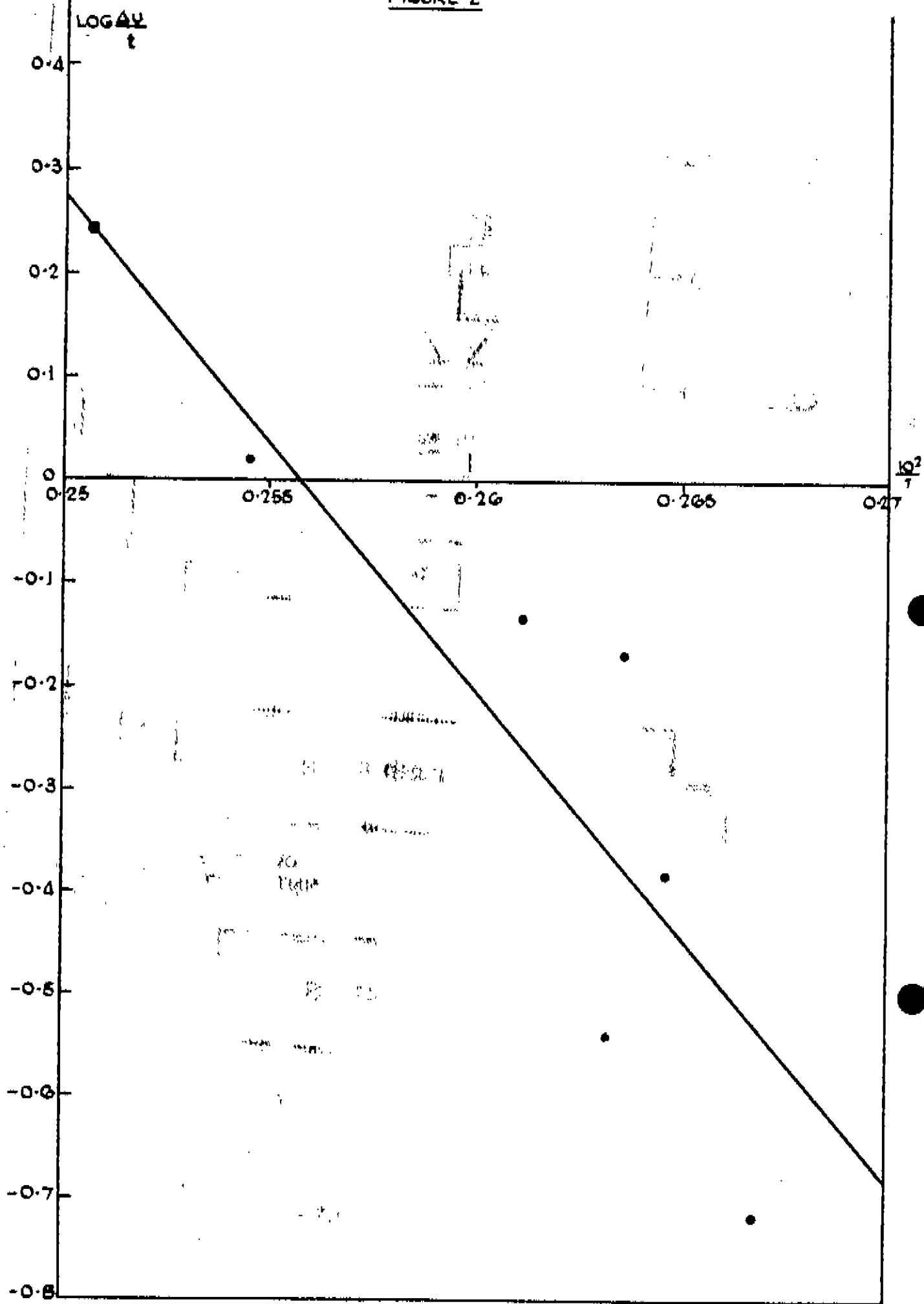


FIGURE 8

