The Manufacture
of Nitroguanidine
at Waltham Abbey

①

RGPF Report.

THE MANUFACTURE OF NITROGUANIDINE

AT

WALTHAM ABBEY.

---

by

H A Phillips

3/3/33.

Submitted by Lt Col P H Evans
Superintendent RGPF
to
DOF

THE MANUFACTURE OF NITROGUANIDINE AT WALTHAM ABBEY.

Manufacture at Waltham Abbey was commenced in 1928 in accordance with the experience gained, by the Research Department, Woolwich, in the preparation of nitroguanidine from calcium cyanamide fertilizer.

The progressive steps were the preparation of cyanamide, the condensation of this with ammonium nitrate to form guanidine nitrate and the nitration or dehydration of this to nitroguanidine.

This may be represented graphically as follows ;-

$$CO_2 \qquad Ca \mid N \cdot C \vdots N \qquad H_2N \cdot C \vdots N \qquad H_2N \cdot C \vdots NH \qquad H_2N \cdot C \vdots NH$$

| (Carbon dioxide) | (Calcium cyanamide) | (Cyanamide) | $NH_2 \cdot HNO_3$ (guanidine nitrate) | $NH \cdot NO_2$ (nitroguanidine) |

$$O \vdots H_2 \qquad NH_4 \ NO_3$$

(water) (ammonium nitrate)
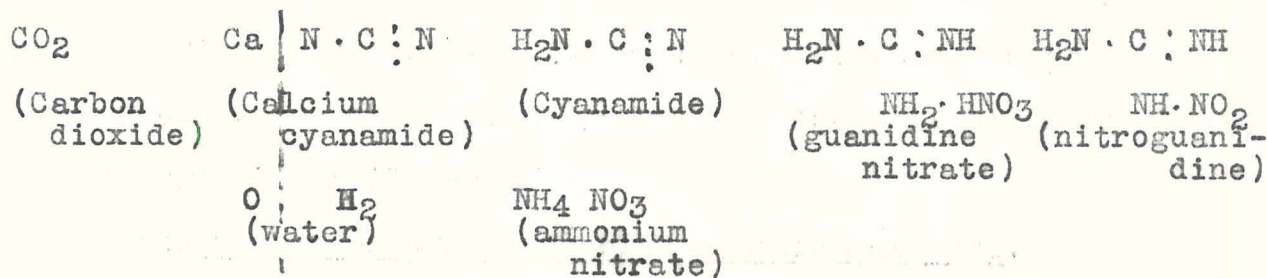
The fertilizer was treated with carbon dioxide and water under pressure, the resulting cyanamide solution was heated with ammonium nitrate under pressure and the resulting guanidine nitrate, after drying, converted to nitroguanidine by treatment with sulphuric acid.

Manufacture falls into the following main sections :-

I. Preparation of cyanamide.

II. Condensation of cyanamide with ammonium nitrate.

III. Conversion of guanidine nitrate to nitroguanidine.

IV. Purification and conditioning of nitroguanidine.

It is proposed, in the first place, to give a brief description of the processes and plant in operation at the commencement of manufacture at Waltham Abbey in 1928. The plant installed was required to be capable of an output of 500 lbs per week working day shift only.

I. Preparation of Cyanamide.

Reaction carried out at a temperature of 35°C. and under

a pressure of 80 lb per sq.inch. The plant consisted of a jacketed steel autoclave with stirring gear, capacity 60 gallons. 140 lb.of calcium cyanamide fertilizer and 40 gallons of water constituted a charge for the autoclave. Carbon dioxide supplied from cylinders of compressed gas. Pressure in the autoclave regulated by the rate of admission of the gas. Heat evolved during this reaction. Temperature controlled by the circulation of refrigerated brine in the jacket of the autoclave. Carbon dioxide passed in until the end of the reaction indicated by a drop in temperature, quantity required usually about 80 lb. Time occupied by the reaction about 3 hours. At its conclusion the precipitated chalk sludge separated from the cyanamide solution by means of a centrifuge. The cyanamide solution passed on to the next process; the chalk washings used in the extraction of the next charge of fertilizer.

II. Condensation of cyanamide with ammonium nitrate.

This reaction carried out at a temperature of 175°C. and under a pressure of 150 lb per sq.inch in a steel gas heated autoclave fitted with stirring gear, capacity 50 gallons. A charge consisted of the cyanamide solution from the previous process together with a total of 120 lb.of ammonium nitrate, made up partly of solid and partly of solution returned from the previous charge. The excess of ammonium nitrate over and above the theoretical requirement is 100%. Time occupied by the reaction about 2 hours. At its conclusion cooling to 110°C. before discharge effected by slowly releasing the pressure. This occupied about 45 minutes, when the contents of the autoclave were discharged through a filter to an enamelled cast iron jacketed evaporating pan, capacity 50 gallons. After evaporation to about one third the volume solution allowed to cool and crystallise, the guanidine nitrate separated by means of a centrifuge, dried and ground. The mother liquor returned to the autoclave for inclusion in the next cyanamide-ammonium nitrate charge. The evaporation plant was duplicated and capable of dealing with the product from two runs of each autoclave per shift. The guanidine nitrate yield from a single run was 70 lb.

III. **Conversion of guanidine nitrate to nitroguanidine.**

140 lbs of dried and ground guanidine nitrate added slowly to 238 lbs of sulphuric acid (96%) contained in 50 gallons lead lined jacketed cast iron vessel fitted with stirrer. Temperature regulated to 40°C. by circulation of refrigerated brine in the jacket. Time occupied in adding the nitrate about 1¼ hours. After adding the nitrate the charge was stirred for a further 2 hours, temperature falling to about 30°C. Charge then drowned in water contained in two stoneware guncotton nitrating pans. Sufficient water used to reduce acid concentration to about 20%. Nitroguanidine in suspension separated in two lead filter pans, packed with graded quartz chips as the filtering medium, and then washed free from acid.

IV. **Purification and conditioning of nitroguanidine.**

Nitroguanidine recrystallised in batches of 50-55 lb. This quantity dissolved in 75 gallons of boiling water contained in steam heated jacketed enamelled cast iron pan of 100 gallons capacity. Hot solution passed through steam heated filter and thence to similar jacketed pan where it was cooled by water circulation. Crystallised nitroguanidine separated by centrifuge, washed and dried. Mother liquor used in dilution of next nitration charge. The crystallisation plant was duplicated and capable of producing about 100 lb. per shift.

Finished nitroguanidine required to be ground to fineness of 200 mesh. Grinding carried out in cast iron end runner mill. 10 lb. charge milled for 30 minutes. Ground material sieved.

With the foregoing brief description as a basis it is proposed to review each section of manufacture in the light of present knowledge and to give an account of the various improvements and modifications introduced and of the difficulties encountered which led to these introductions.

I. **Preparation of cyanamide.**

Quite early in the manufacture certain irregularities

in the carbon dioxide consumption and the time of reaction indicated
that improvement in the conditions might be possible. It was found
subsequently that increase in the speed of the stirrer with the
consequent increase in the agitation of the mixture effected
considerable improvement. This led to the conclusion that quantita-
tive interaction between carbon dioxide and aqueous calcium cyana-
mide is not easily effected and it indicated further that an
increase in the scale of operations might possibly be attended with
still further trouble in this direction.

Subsequent experience confirmed this when the 60 gallon
extraction vessel was replaced by one of 360 gallons capacity. The
full charge for this vessel would be 8 cwt of fertilizer and 250
gallons of liquor but the behaviour with this charge was so unsatis-
factory that these quantities had to be halved. Under these
conditions the results were better but still not equal to those
obtained with the smaller vessel.

Leaving this matter for the moment another difficulty
encountered in this section of manufacture was the separation of
the precipitated chalk sludge from the cyanamide solution. This
precipitated chalk and the impurities in the fertilizer together
form a grey-black slimy sludge which is extremely difficult to
remove by any ordinary filtering process. The quantity to be dealt
with amounted to 300 lb per shift and it was necessary, for best
efficiency, that it should be washed as free as possible from
cyanamide before being discarded. The filtration and washing by
centrifuge was very slow on account of the difficultly penetrable
nature of the sludge and it became evident that a much improved
method would be necessary for really large scale production.
Separation of the sludge by means other than filtration was indicat-
ed. The use of settling tanks did not seem hopeful because of the
slowness of the process. It was decided therefore to try sediment-
ation of the sludge centrifugally. A centrifuge mounted in rigid
bearings is necessary for this purpose. A small machine was obtain-
ed in which the spindle is mounted in ball bearings horizontally i.e

the

the basket rotates in a vertical plane. The machine is charged
with the sludge mixture whilst in motion. A few minutes after
filling sedimentation is complete. With the machine still running
a dip pipe, provided for the purpose, is lowered into the clear
liquor which is thus removed. Washing the sludge with small
amounts of water is then carried out and finally the washed sludge
is removed by a cutting out device whilst the machine is still in
motion. This type of machine is capable of running continuously
without giving trouble. This small machine was so successful that
it has been replaced by a large one with a basket 1.6 metres in
diameter. The output of this machine is sufficient for really
large scale production.

In August 1929 C.S.R.D. advised that the charge for the
autoclave in section II of manufacture could be greatly increased
by concentrating the cyanamide solution before its introduction
into the autoclave. In the process of concentration the cyanamide
is polymerised to dicyandiamide which is equally satisfactory for
use in the manufacture of guanidine nitrate.

This changed the outlook to some extent and directed attention
to other methods of preparing dicyandiamide. It is known that
dicyandiamide is obtained when calcium cyanamide fertilizer is
extracted with hot water. The reaction proceeds in two stages,
first calcium bicyanamide is produced and this further reacts with
water to produce dicyandiamide.

$$2\ CaCN_2 \qquad + 2\ H_2O = Ca(CN.NH)_2 \ + \ Ca(OH)_2$$

    (Calcium cyanamide)   (Calcium   (Lime)
                                             bicyanamide)

$$Ca(CN.NH)_2 \quad + 2\ H_2O \ = \ (C\ N.NH_2)_2 \quad + \ Ca(OH)_2$$

                                     (Dicyandiamide)

These reactions occur in alkaline solution the base present
being lime. Under certain other conditions the bicyanamide
hydrolyses to urea, small quantities of other bodies being formed
at the same time. The chief factors controlling the reactions of

bicyanamide in alkaline solution are the nature and concentration
of the alkali.

A process for the manufacture of dicyandiamide from calcium
bicyanamide has been patented (German Patent 279,133. 1913). In
this process the lime concentration is controlled by the addition
of sulphuric acid at varying time intervals.

The American Cyanamid Co.(Buchanan & Barsky. J.Amer.Chem.Soc.
1930. 195) realising thatbthe reactions are controlled, evidently
by hydrogen-ion concentration have investigated the matter from
this point of view and working with cyanamide solutions at 50°C.
and within the range P$_H$6 to P$_H$ 13 have found (a) that the velocity
of dicyandiamide formation reaches a maximum at P$_H$ 9.6 and decreases
rapidly at hydrogen-ion concentrations above or below this value,
(b) that dicyandiamide formation is quantitative in alkaline
solution up to P$_H$ 10. Above P$_H$ 10 there is some destruction of
dicyandiamide and above P$_H$ 12 the cyanamide is hydrolised quantita-
tively to urea, (c) that the optimum hydrogen-ion concentration for
dicyandiamide formation is within the given limits for a temperature
range of 0 to 100°C.

From a consideration of all the facts it was decided to
investigate, on a laboratory scale, the preparation of dicyandiamide
by simple hot water extraction of calcium cyanamide fertlizer.

Quantitative experiments were carried out in which the fertili-
zer(1 part) was added to water (3 parts) heated to 90°C. and kept
vigorously stirred. Samples were withdrawn at intervals of 5, 10,
15, 20, 30, 45 and 60 minutes. The samples were filtered and the
filtrates allowed to cool. The quantity of dicyandiamide separating
increased up to the 30 minutes sample. In each case the amount of
lime remaining in solution was determined as a measure of the
completeness of the reaction and here again there was little change
after the 30 minutes sample.

It was then decided to make a series of extractions at 90°C.
for 30 minutes, using the mother liquor in each case for the next
extraction. In each extraction the residue, after hot filtration,

was washed with sufficient hot water to restore the mother
liquor to the volume necessary for the next extraction. The
highest yield of dicyandiamide was 23.5% of the fertilizer used.
The nitrogen content of the fertilizer is about 21% corresponding
to 60% calcium cyanamide. There was in each case about 2.1% of
nitrogen remaining in the residue. Assuming all the nitrogen in
the fertilizer is present as calcium cyanamide then the efficiency
of the process is as follows :-

Original cyanamide recovered as dicyandiamide			74.6 %
"	"	left in residue	6.0 %
"	"	lost (decomposition)	19.4 %
			100.0

The dicyandiamide produced was of high grade quality. It
contained 0.25% of mineral matter and melted at 203 - 209°C.
After one recrystallisation it was obtained practically pure with
a nitrogen content of 66.57, 66.63% (calculated for dicyandiamide
66.67%) and melted at 206 - 210°C. Recrystallisation would not
be necessary in manufacture.

It is not possible to compare directly the efficiencies of
hot water extraction on the one hand with carbon dioxide extraction
on the other at this stage of manufacture as the carbon dioxide
product is not isolated and weighed but by reference to the
efficiency tables at the end of this report it can be deduced that
for water extraction to equal carbon dioxide extraction, at its
best, and operated in the small extractor, the yield of dicyandi-
amide must be 23%.

The hot water extraction method of producing dicyandiamide
was introduced into the factory. Here it was found inconvenient
to add the fertilizer to water at 90°C.on account of the excessive
frothing which occurred. The procedure adopted was to add the
fertilizer (2 cwt) to well stirred cold water (66 gallons),
quickly to raise the temperature to 95°C., maintain at this for
a few minutes and then filter, the total time of heating being
about 40 minutes. The residual lime etc., which by this process

is

is quite granular and presents no filtering difficulties, is separated and washed by centrifuge, the dicyandiamide solution is cooled and after removal of the crystals the mother liquor is used for the next extraction.

In view of the work of the American Cyanamid Co., on the effect of hydrogen-ion concentration on the formation of dicyandiamide by similar methods the hydrogen-ion concentrations in the solution throughout an extraction on these lines was determined with the following results :-

Temperature °C.	PH
15	12.7
30	12.1
40	11.7
50	11.2
60	10.5
70	10.2
80	9.9
85	9.8
90	9.6
95	9.5

The progressive lowering of the P value throughout the heating may be caused partly by the decreasing solubility of lime with increasing temperature.

In the early stages of heating the solution is probably too alkaline for best results. At 80°C. and above the conditions appear to be good.

At the end of an extraction the reaction seems to be complete as there is very little soluble lime in the filtrate.

The yield of dicyandiamide under these conditions is 19%. The discrepancy, when compared with the laboratory results, may be due partly to the unfavourable P_H conditions, in the early stages of heating, resulting in decomposition. In addition to this the jacketed extractor is unsuitable for the process. It is impossible to control the temperature accurately when heating by steam circulated in the jacket and there is reason to believe that decomposition occurs at the high temperatures which are sometimes reached.

It has further been found in the laboratory that extraction of the fertilizer at 80°C. for a period of .5-1 hour gives results slightly superior to those obtained at the higher temperature of 90°C

The

The American Cyanamid Cos quantitative polymerisation of cyanamide was effected at $50^{\circ}C.$, occupying a considerable period of time, and it is not known to what extent it is affected by a considerable temperature rise.

The yield from fertilizer by efficient carbon dioxide extraction may be taken as a standard of the best obtainable, and the fact that it falls short of what would be expected from the nitrogen content of the fertilizer points to the possibility of the nitrogen not being present entirely as calcium cyanamide. This standard has been equalled by water extraction in the laboratory and there seems to be no reason why it should not also be equalled in the factory provided the necessary conditions are provided.

With this object in view the complicated carbon dioxide extraction vessel is being replaced by a cylindrical tank provided with a stirrer. The heating will be by "live" steam in order to provide accurate temperature control. The plant will be taken into use shortly when laboratory conditions will be imitated exactly i.e. the fertilizer will be added at $80^{\circ}C.$ and the temperature will be maintained at this throughout. It is expected that a "standard" yield will then be obtained.

There are many advantages in using water instead of carbon dioxide extraction. At present the carbon dioxide is purchased in cylinders and accounts for just over 4^d in a total of 10.7^d for materials consumed per pound of nitroguanidine manufactured. The extra fertilizer required on account of the present low yield of dicyandiamide by water extraction amounts to .6 lb per pound of nitroguanidine and costs $.45^d$. The nett saving by water extraction at present therefore is about $3\frac{1}{2}^d$ per pound of nitroguanidine. Other advantages are that simpler plant may be used as pressure is not necessary, the residue is granular and easily filterable thus effecting a saving in filtering machinery and labour and evaporation is entirely eliminated. This evaporation amounts to 70 gallons per shift on a 500 lb per week output and would necessitate a multieffect evaporator on full scale production.

It has been suggested that by-product carbon dioxide from some other manufacture could be utilised at very low cost. The carbon dioxide required amounts to about 1.5 lb. per lb. of nitroguanidine. When it is considered that the money available for its purchase is .45^d less the saving, by water extraction, on plant, labour and steam it would seem that the carbon dioxide would have to be supplied at a minus value for the scheme to be practicable. In addition it must be remembered firstly that it was the inefficiency of carbon dioxide extraction on large scale production that initiated the search for other methods and secondly that there is every reason to believe that the efficiency of water extraction will be improved.

II. Condensation of cyanamide with ammonium nitrate.

The first trouble to occur in this section of manufacture was corrosion of the steel autoclave. The vessel was in use for some time before corrosion was perceptible as a few small pittings. From this stage the deterioration was rapid. From the position of the corrosions there were some grounds for thinking that the localised direct gas heating might be responsible to some extent. It was arranged, therefore, that the new replacement pan should be oil jacketed in order to provide uniform heating. No benefit resulted from this, however, similar corrosions occurring in about the same time. Samples of various acid resisting steels were tested under similar conditions without discovering anything quite satisfactory. Corrosion trouble had been experienced in concentrating the liquor from the autoclave reaction and this had been overcome by the use of aluminium pans for this operation. It was decided, therefore, to try an aluminium liner in the autoclave. An autogenously welded liner was fitted and proved very successful. After about a year it was cut out and submitted to very careful examination. There was no evidence of corrosion and the aluminium generally had suffered no loss in thickness. An aluminium liner has therefore been adopted as standard practice. Trouble has been experienced through a liner cracking but this was due not to

corrosion

corrosion but to heavy strains set up when the liner expands
under pressure to adapt itself to the contours of the autoclave.
This can be overcome by careful design so as to avoid, as far
as possible, the strain being taken by a welded joint.

In working the autoclave in its present condition it has
been found that the rate of heating has been retarded consider-
ably. In the first place heating through an oil jacket is much
slower than the original direct gas heating and the rate is still
further retarded by the aluminium liner not being in perfect
thermal contact with the steel autoclave. The slow rate of
heating not only reduced the output but increases the amount
of an undesirable amorphous by-product. It is not considered
advisable to abolish the oil jacket and revert to direct gas
heating because of the risk of dangerous local overheating of
the steel due to poor thermal contact between the steel and
aluminium. The heating would be better carried out by an
internal aluminium coil supplied with superheated steam or
heated oil.

Recently (October 1931) an account has appeared in
"Industrial & Engineering Chemistry" of a "Quantitative Study
of the Preparations of Guanidine Nitrate and Nitroguanidine"
and in this it is shewn that guanidine nitrate may be prepared
very satisfactorily by the fusion together, in the dry condition,
of dicyandiamide and ammonium nitrate. Under suitable conditions
there is a 90% conversion to guanidine nitrate and in addition
to this the formation of undesirable amorphous by-product,
previously mentioned, is reduced to a minimum.   In the auto-
clave process as running at present this by-product is produced
to the extent of 15% of the total product whereas in the fusion
process this can be reduced to the neighbourhood of one or two
per cent. This reduction is understandable when it is realised
that the by-product, which is composed of ammelide, ammeline and
melamine, is very largely the result of the action of water on
dicyandiamide. If, therefore, water is excluded, as in the
fusion process, by-product formation is reduced to a minimum.

In

In the case of the autoclave process this side reaction takes place so long as there is dicyandiamide free to be attacked but ceases when all the dicyandiamide is combined with ammonium nitrate. The quicker, therefore, the temperature of the autoclave is raised to the optimum (about 165°C.) for the primary reaction the sooner will it be completed and the less time will there be for the side reaction to take place.

When the autoclave was directly gas heated the by-product formation was 8%. When the time of heating was lengthened by the necessary introduction of oil jacket and aluminium liner the by-product formation increased to 15%.

It is, therefore, very necessary to raise the temperature of the autoclave as rapidly as possible but, for the reasons given, it seems improbable, even under the best possible conditions, that the autoclave process can be as efficient as the fusion process.

Apart from efficiency another reason for reducing the formation of amorphous by-product to a minimum is that it has been found that the presence of more than a certain amount of by-product causes trouble in the subsequent nitration process. This matter has been fully investigated and is dealt with in the next section of manufacture.

From a consideration of all the facts it was decided to carry out a laboratory investigation of the fusion process.

In the account of a "Quantitative Study of the Preparation of Guanidine Nitrate and Nitroguanidine" previously mentioned the following method for the preparation of guanidine nitrate is evolved as the result of the investigation of the mechanism of the reaction.

264 grams (3.3 moles) of dried ammonium nitrate are mixed with 63 grams (0.75 mole) of dried dicyandiamide in a beaker and rapidly heated to 162-165°C. in an oil bath. A further 63 grams of dicyandiamide are slowly added, temperature not exceeding 165°C. Heating continued for total of 1 hour.

In this method the amount of ammonium nitrate over and above the theoretical requirement is 10%. The temperature is the optimum for the primary reaction and reduces by-product formation to a minimum.

Experimental

Experimental fusions on these lines have been carried out in the laboratory. In a series of six fusions, in which the fusion product was recrystallised, an average yield of 89% of recrystallised guanidine nitrate was obtained. Prepared by the autoclave process the yield is about 76%. It has been ascertained by experiment that equally good nitroguanidine can be prepared from the unrecrystallised fusion product as from the recrystallised. As recrystallisation involves expense and some loss of product it was decided to omit recrystallisation in future experiments. Under these circumstances it is not possible to directly determine the yield of guanidine nitrate as the fusion product is contaminated with ammonium nitrate. It is possible only to indirectly determine the yield by nitration to nitroguanidine and weighing the yield of this product.

Experiments in which the fusion product was nitrated without recrystallisation gave a yield of 77.5% of very good quality nitroguanidine. The yield is calculated as the percentage of the theoretical yield from the dicyandiamide used. The yield by the autoclave process is 67%.

All the above experiments were carried out with quite small quantities (about 100 grams) in beakers heated in an oil bath.

After ascertaining that aluminium and mild steel were not attacked by the fused mass it was decided to experiment with larger quantities in an aluminium vessel fitted with a mild steel stirrer, the vessel being made of aluminium because of the good heat conductivity of that metal. The dimensions of the vessel were 10 inches diameter and 7 inches deep. It was heated directly by gas and it was possible to fuse in it a charge of 18 lbs. Working with this amount of material some difficulty was experienced in discharging the contents of the vessel at the end of the reaction. At a temperature of $165^{o}C$.the fused mass is extremely viscous. In large scale operation it would be convenient if the mass could be poured , while molten, from the vessel and allowed

to solidify in thin layers. The viscosity of the fused mass is decreased considerably by raising the temperature and at 185°C. the mass is sufficiently fluid to flow readily. It is not harmful to raise the temperature to this extent provided the reaction has been completed at the optimum temperature of about 165°C. The following is the procedure finally evolved for the satisfactory fusion of 15 lb.(approx.) charges.

1125 grams of dicyandiamide are mixed with 4725 grams of ammonium nitrate. About a quarter of this mixture is placed in the fusion vessel and melted. This occurs at a temperature of about 125°C. The remainder of the mixture is added in suitable quantities and the temperature raised to 165°C. The heating is carried out carefully so as not to exceed 165°C. A further 1125 grams of dicyandiamide are now added, the rate of addition and the gas heating being regulated to maintain the temperature at 165°C. This addition occupies about 20 minutes. The temperature is then allowed to rise at such a rate that it reaches 185°C. in 30 minutes. It is maintained at this for a short time and the molten mass is then poured out on an aluminium tray where it sets as a cake on cooling.

A large number of fusions on this scale has been carried out. In every case the reaction proceeded smoothly and satisfactorily. No difficulty was experienced in controlling the temperature and the addition to the molten mass of such substances as charcoal, wood, paper etc., failed to cause an ignition.

A 446 lb. charge of the ground product was nitrated on the large scale in the factory. The nitration product was satisfactory in every way. The nitration and subsequent operations were carried out in the newly washed plant in order to avoid contamination with material produced by the autoclave process. The yield, reduced by the use of "clean" plant, amounted to 77.5% from the dicyandiamide used. This yield value is the same as that obtained from laboratory nitrations of 100 gram laboratory fusions. Laboratory nitrations of the product of 15 lb. fusions gave yields of well over 80% and there is no reason why similar yields should not be obtained from

regular

regular factory nitrations of fusion product. This is a considerable increase on the 67% yield by the autoclave process.

It has been mentioned that 10% excess of ammonium nitrate has been employed in the fusions. This excess is useful in lowering the melting point of the mixture. It is, of course, economically advantageous to reduce this excess as much as possible and it has been found that heating to a final temperature of $185^{\circ}C$. enables 5% excess only to be used quite successfully. By this means the loss of ammonium nitrate is reduced to about the same as in the autoclave process.

A plant capable of fusing charges of 1 cwt is now being erected. It consists of an aluminium vessel heated directly by gas. A mild steel stirrer is fitted and it is arranged that, at the end of the reaction, the molten mass can be discharged into aluminium trays by tipping the plant by means of suitable gear.

The advantages of the fusion over the autoclave process include not only the increased yield but also the cheaper plant required and the elimination of the need to separate and dry the guanidine nitrate produced.

III. <u>Conversion of guanidine nitrate to nitroguanidine</u>.

The first trouble experienced in this process was, on one occasion, the violent decomposition of the charge during the stirring period which follows the last addition of guanidine nitrate. All the mixture was ejected from the nitrator by the violence of the decomposition.

Towards the end of the normal process the nitroguanidine crystallises rapidly from the more or less supersaturated solution in sulphuric acid with considerable heat evolution and the thickening of the mass makes it the more difficult to disperse the heat.

To guard against a repetition of this the working of the process was modified slightly. Near the time when separation of the nitroguanidine was due to occur the temperature was allowed to fall so as to increase the margin between the working and decomposition temperatures.

(a)   The next important step in this section of manufacture was the
provision of a much larger nitration plant. This has been erected
as a separate unit and is capable of manufacture on the largest
scale. It consists of a lead lined jacketed cast iron nitrator
of 300 gallons capacity. This discharges into a lead lined drown-
ing vat provided with stirrer and cooling coils. The contents of
the drowning vat are fed by pump or air lift to a centrifuge where
the separated nitroguanidine is washed free from acid.

This plant was designed to deal with a 1000 lb. charge of
guanidine nitrate and has been worked with this load. Cooling and
stirring are efficient and no difficulty has been experienced in
controlling the reaction but the product is not uniform in quality
and generally is not so good as the small scale product..

The quality of the nitroguanidine may be assessed fairly
accurately from the form of the crystal after recrystallisation
from water. Long lustrous needles indicate satisfactory quality
while small powdery crystals indicate inferior quality and contamin-
ation with impurity. Nitrogen, as estimated in the Lungé nitrometer,
is also an indication of quality. Good quality nitroguanidine
gives a value of about 13.25% or higher.   With material of inferior
quality a lower value is obtained.

Not only was the inferior quality indicated by analysis
and characteristic appearance but also it is probable that trouble
in the cordite press through aggregates choking the straining gauze
was attributable to this.

It seemed evident that the deterioration in quality was a
direct result of the disturbance of the nitration conditions by the
sevenfold increase in the charge and further it was found that a
satisfactory product was obtained when the charge was reduced from
1000 lb to 400 lb.

Reduction of the nitration charge from 1000 lb. to 400 lb.
reduces considerably the time occupied in nitration and in drowning
and filtering. It seemed likely that the time factor was of
considerable importance.

Factors which are likely to influence nitration are

(a) The quality of the guanidine nitrate.

(b) The time occupied in nitration and in the subsequent drowning, filtering and washing processes.

(c) The temperature of nitration.

(d) The proportion of sulphuric acid used.

The effect of variations in these factors has been investigated.

In the first instance good quality guanidine nitrate was selected and used for studying the effect of variations in factors (b) (c) and (d).

The guanidine nitrate selected was a high grade factory product containing a minimum of the amorphous by-product to which reference has already been made. This standard of quality is not reached regularly in manufacture by the autoclave process.

In the first series of experiments six nitrations were carried out in each of which 50 grams of guanidine nitrate were nitrated with 100 grams of sulphuric acid at a temperature of 30° C. In each case the addition of the guanidine nitrate occupied 10 minutes. The time of standing in contact with the strong acid varied from 1 to 6 hours. The results were :-

1 hour contact	Yield 80%	Nitrogen (Lungé) 13.33%	Quality good.
2 " "	" 79	" " 13.31	"
3 " "	" 77.5	" " 13.28	"
4 " "	" 77.5	" " 13.32	"
5 " "	" 77.5	" " 13.30	"
6 " "	" 80	" " 13.29	"

In this first series variations in yield were cause by fluctuations in the temperature of the mother liquors and wash waters at the time of filtering. Subsequently standard conditions were adopted.

In a further series of experiments the nitrations were carried out with similar quantities but the addition of the guanidine nitrate occupied 30 minutes and the subsequent times of standing in contact with the strong acid ranged from 0 to 60 minutes. The results were :-

Immediate

High temperatures seem to have no adverse effect on the

Immediate drowning Yield 84.5 % Nitrogen(Lunge) 13.27% Quality
                                                                     good.
5 minutes contact   "   86.75   "   "   13.33   "

  "   "   "   "   87.25   "   "   13.27 30°C."

15 "   "   "   87.25   "   "   13.26 and "

30 "   "   "   88.00   "   "   13.25   "

  "   "   "   "   87.25   "   "   P

60 "   "   "   86.75   "   "   13.25   "

The results indicate that a very short time is necessary, after
the addition of the guanidine nitrate, to complete the reaction
and further that prolongation of the time in contact with the
strong acid up to 6 hours has no very marked effect on the yield
or quality of the nitroguanidine.

In the next series of experiments three nitrations were carried
out with similar quantities, guanidine nitrate addition 10 mins.,
subsequent contact with strong acid 30 mins., but the respective
times of contact with the dilute acid after drowning were 1 day,
2 days and 4½ days. The results were -

1 day contact with dilute acid. Yield 82 %

2 "   "   "   "   "   "   82

4½ "   "   "   "   "   "   82   Nitrogen 13.24 Quality
                                                                     good.

This indicates that long standing in contact with dilute
sulphuric acid has no marked effect on the quality of the nitro-
guanidine.

In the next series of experiments four nitrations were carried
out with similar quantities, guanidine nitrate addition 10 mins.,
subsequent contact with strong acid 30 mins., immediate filtration
after drowning but the respective temperatures of nitration were
10, 30, 40 & 50°C. instead of the usual 30°C. employed previously.
The results were :-

10°C.   Yield 89.25% Nitrogen 13.26% Quality good.

30°C.   "   87.25   "   13.27   "   "

40°C.   "   86.25   "   13.27   "   "

50°C.   "   84.00   "   13.27   "   "

High

High temperatures seem to have no adverse effect on the quality but there is a definite decrease in the yield caused, probably, by decomposition into innocuous products.

In the next series the nitartions were carried out at 30°C., nitrate addition 10 mins., subsequent contact with strong *acid* 30 mins., immediate filtration, but in addition to the usual nitrate : acid ratio of 1 : 2 other ratios were employed. The results were :-

Nitrate : acid ratio				Yield		Nitrogen		Quality	
Nitrate :	acid	ratio	1:3	Yield	84.5%	Nitrogen	13.28%	Quality	good
"	"	"	1:2	"	87.5	"	13.27	"	"
"	"	"	1:1.5	"	89.75	"	13.26	"	"
"	"	"	1:1.25	"	69.25	"	13.12	"	poor
"	"	"	1:1.25	"	72.75				

In a further series the ratio 1 : 1.25 was investigated with the object of ascertaining whether an increase in the temperature of nitration and in the time of contact with the strong acid would improve the quality of the product. The results were :-

						Yield		Nitrogen		Quality
Temp.30°C.,	Contact	2 hours,	Yield	76.75%	Nitrogen	13.10%	Quality
"	"	"	6	"	"	84.00	"	13.10		poor "
"	40°C.	"	1½	"	"	78.00	"	13.15		"
"	50°C.	"	1	"	"	75.75	"	13.11		"
"	"	"	2	"	"	79.25	"	13.08		"

It seems evident that it is not practicable to reduce the acid below the 1 : 1.5 ratio. With the 1 : 1.25 ratio the water content of the acid at the finish of the reaction would be over 10% which is probably too dilute an acid to complete the reaction.

With the 1 : 1.5 ratio the yield is higher than when more acid is used and the quality of the nitroguanidine is quite satisfactory but the mixture is so viscous that it is doubtful whether it could be handled satisfactorily in the factory.

Up to this point the investigations had shewn that, within fairly wide limits, variations in the time occupied by the processes, in the temperature at which the processes were carried out and in the quantity of acid used, have no deleterious effect on the quality of the product provided good quality guanidine

nitrate

nitrate is used. It seemed, therefore, that the explanation of the unsatisfactory quality of the product from the 1000 lb. nitrations must be connected in some way with the use of inferior guanidine nitrate.

It has been mentioned that the chief impurity in guanidine nitrate produced by the autoclave process is an amorphous by-product consisting of a mixture of ammeline, ammelide, and melamine. This by-product is in a very finely divided condition and under factory conditions of manufacture it is difficult to separate completely from the hot solution of guanidine nitrate produced in the autoclave. The result is that factory guanidine nitrate is always more or less contaminated with the by-product.

The effect of this contamination was now investigated by repeating some of the previous experiments but using contaminated guanidine nitrate instead of the fairly pure product. The contaminated guanidine nitrate was prepared by the addition of known quantities of by-product to guanidine nitrate from the batch used for the previous experiments. The effects of additions of 1, 2 & 5% have been investigated.

Nitration of 1% contaminated material.

Temperature 30°C., nitrate : acid ratio 1 : 2, contact 1 hour, dilute acid contact 30 minutes.

Yield 86.75% Nitrogen 13.20% Quality poor, small needles.

Temperature 50°C., nitrate : acid ratio 1 : 2, contact 1 hour, dilute acid contact 30 minutes.

Yield 83.25% Nitrogen 13.24% Quality poor, small needles.

Nitration of 2% contaminated material.

Temperature 30°C., nitrate : acid ratio 1 : 2, contact 1 hour, immediate filtration after drowning.

Yield 88.00% Nitrogen 13.19% Quality poor, powdery.

Temperature 30°C., nitrate : acid ratio 1 : 2, contact 1 hour, dilute acid contact 24 hours.

Yield 86.25% Nitrogen 13.23% Quality poor, small needles.

Nitration of 5% contaminated material.

Temperature 30°C., nitrate : acid ratio 1 : 2, contact 1 hour

immediate filtration after drowning.

Yield 84.25% Nitrogen 13.19% Quality poor, powdery.
Temperature 30°C., nitrate : acid ratio 1 : 2, contact 1 hour
dilute acid contact 24 hours.

Yield 86.75% Nitrogen 12.95% Quality poor, powdery.
Temperature 50°C., nitrate : acid ratio 1 : 2, contact 1 hour
immediate filtration after drowning.

Yield 80% Nitrogen 13,16% Quality poor, powdery.
Temperature 50°C., nitrate : acid ratio 1 : 2, contact 1 hour
dilute acid contact 24 hours.

Yield 84.5% Nitrogen 13.01% Quality poor, powdery.

It appears from these results that contamination to the extent
of 1 or 2% has a distinctly adverse effect on the quality of the
nitroguanidine. The Lungé nitrogen is to some extent affected and
the crystalline form is inferior.

With 5% contamination these effects are more apparent and the
effect on the Lungé nitrogen of prolonged contact with dilute acid
is remarkable.

A probable explanation of this effect is that the amorphous
material passes into solution in the sulphuric acid during nitration.
On drowning it is not immediately precipitated from the dilute acid
and therefore if the precipitated nitroguanidine is separated
immediately a product of satisfactory quality is obtained but if,
on the other hand, a long time elapses between drowning and separat-
ion then the amorphous material is precipitated and contaminates
the nitroguanidine from which it is not separated by subsequent
recrystallisation.

That this contamination has a deleterious effect on the
crystalline form is shewn also by the fact that recrystallisation
of the nitroguanidine to which so little as 1% of amorphous material
has been added invariably produces small powdery crystals.

In the 1000 lb.nitrations it was not possible to separate all
the nitroguanidine immediately after drowning, because if the

insufficient

insufficient capacity of the centrifuging plant, with the result
that the later fractions of a batch were sometimes inferior in
quality.

It may be assumed, in the light of present knowledge, that
in those instances where the quality was satisfactory throughout
the batch the contamination of the guanidine nitrate was slight
but in those instances where the quality of the later fractions
was inferior then the contamination was considerable.

The ideal remedy for the trouble is to produce guanidine
nitrate practically free from amorphous by-product. The best
method of accomplishing this is to avoid, as far as possible, the
formation of by-product by using a process in which its formation
is at a minimum, i.e. the dry fusion process. The next best method
is to endeavour to free completely the contaminated guanidine
nitrate from the by-product. Failing these methods the only remedy
is to so arrange the plant capacity that a nitration batch can be
dealt with completely immediately after drowning.

It has been mentioned previously that steps are being taken
to try out the first method, not only from this point of view but
also with a view to increasing the yield. In the meantime, so that
the production of satisfactory nitroguanidine should not be
interrupted the alternative methods have been employed.

These investigations have also given useful information as
to the optimum nitration conditions so far as temperature and
quantity of acid are concerned.

Low temperature is an advantage and the quantity of acid
may be reduced to 1.5 parts to 1 part of nitrate with benefit but
the combination of these optima is rendered impracticable by the
extreme viscosity of the mixture. Although nitration at 10°C. has
been shewn to be advantageous it is not practicable, on account of
viscosity, with less than 2 parts of acid and although nitration
with 1.5 parts of acid has been carried out at 30°C. in the
laboratory the mixture produced is too viscous to be manipulated
satisfactorily in the factory. The following experimental results

enable

enable conclusions to be drawn as to the best practicable
nitration conditions.

Nitration at 10°C. with 2 parts of acid   Yield 89.25%

     "   "   30°C.   "   1.5   "   "   "   "   89.75%

As it is not practicable to nitrate with 1.5 parts of acid
at so low a temperature as 30°C., the higher temperature necessary
would make the method inferior to nitration at 10°C. with 2 parts
of acid.

Actually these selected conditions must await large scale
application until such time as uniformly satisfactory guanidine
nitrate is available. Under present conditions it is necessary
to nitrate at 30°C. in order to save time so that drowning,
separation and washing may be completed in one shift.

Recovery of the waste sulphuric acid from the nitration process.

In the nitration process the sulphuric acid acts as a
dehydrating agent. It would seem an attractive proposition,
therefore, to concentrate the waste acid and use it again.

In the nitration process 200 parts of 98% sulphuric acid
are used for every 100 parts of guanidine nitrate. The yield of
nitroguanidine is 87% of the theoretical i.e. 13 parts of guanidine
nitrate remain in some form in the dilute sulphuric acid, either
as nitroguanidine or a decomposition product. When nitroguanidine
is heated with concentrated sulphuric acid it decomposes and one
half its nitrogen is converted into ammonium sulphate. In this
way 13 parts of guanidine nitrate are equivalent to 14 parts of
ammonium sulphate therefore the recovered sulphuric acid may be
expected to consist of 98% acid 200 parts, ammonium sulphate 14
parts. Its percentage composition, calculated water free, would
be sulphuric acid 93.3, ammonium sulphate 6.7 . An actual
analysis of the recovered waste acid has given a result of sulphur-
ic acid 88.5, ammonium sulphate 11.5. A small amount of the ammon-
ium sulphate in excess of what would have been expected from
decomposed nitroguanidine or guanidine nitrate is accounted for
by the presence of a small amount of ammonium nitrate in the

guanidine nitrate but the large excess appears to indicate that
the decomposition does not proceed quite in the way expected.
The fact remains that the recovered acid is always contaminated
with a considerable quantity of ammonium sulphate and is unsuitable
to use again in the process. At the present time it is being sold
to a gas works for use in ammonium sulphate production.

IV. Purification and conditioning of nitroguanidine.

Cordite is entirely colloidal but in R.D.N. there is a very
large proportion of crystalline mixture. It is necessary to over-
come this disadvantage, as far as possible, by reducing the
crystalline material to as fine a state of division as possible.

Nitroguanidine crystallises in long fine needles which prove
difficult to pulverise. It was required that the finished material
should be passed through a 200 mesh sieve. It was found that
although the product of the end runner mill was known to be of the
requisite fineness yet was it very difficult to pass through the
200 mesh centrifugal dressing machine. Under these circumstances
it was decided that the product of the mill passed through a 60
mesh gauze was acceptable.

It was found subsequently that the difficulty in sieving
the ground material was due to electrification. The use of silk
gauze (aperture .002 - ,003") as the sieving medium tended to
increase the trouble. In very dry weather the difficulty increased
but when the atmosphere of the sieving room was conditioned by the
admission of a small jet of steam a great improvement resulted.

Substitution of phosphor bronze for sik also helped matters
by facilitating the "earthing" of the gauze. These improvements
solved completely the sieving difficulties.

Other improvements introduced into this section of manufac-
ture were the use of air agitation during crystallisation thereby
producing a smaller and more easily grindable crystal and the
substitution of a ball mill for the end runner mill. These alter-
ations were very beneficial.

It

It has already been mentioned that contamination of nitro-guanidine with the amorphous by-product of the autoclave guanidine nitrate process has a marked effect on the crystalline form, the nitroguanidine being then produced in small powdery crystals.

An attempt to use small crystals produced in this way was not successful. On drying the crystals formed very hard aggregates which proved difficult to grind.

At a later date a spray crystalliser designed by the Research Department was introduced.

If, in the process of recrystallisation, the hot concentrated solution is atomised and cooled suddenly the dissolved substance will be deposited in very fine crystals.

In the crystalliser designed by the Research Department the filtered hot concentrated solution is sprayed through atomising jets on to the inside surface of a revolving cylindrical metal drum cooled by the circulation of refrigerated brine through an outer jacket. Stationary scrapers remove the crystals from the surface and the mother liquor, with the crystals in suspension, flows as a sludge from the bottom of the apparatus.

The crystals are separated from the mother liquor by means of a centrifuge, washed and dried. The product is in the form of lumps which consist of aggregates of very fine crystals. Disinte-gration of the aggregates is effected by means of a Schutz O'Neill disintegrator. The product is more finely divided than the material produced by grinding, the predominating crystals measuring .002 mm or less in width and .03 mm or less in length. These dimensions compare favourably with the .063 mm.aperture of a 200 mesh gauze.

The crystalliser itself gave rather a lot of trouble. In the first place the roller bearings supporting the very heavy revolving cast metal drum required constant attention. It was considered that a very much lighter sheet metal drum would probably be more effective from the cooling point of view and would be more economic-al in power consumption and maintenance charges.

The fixed scrapers also were not altogether successful. After

a long period of continuous operation incrustations of crystals formed on parts of the drum thereby interfering with the efficiency of the process.

Another defect was the need to feed the refrigerating brine to moving plant. With such an open brine system any choking of the outlet resulted in an overflow of brine which found its way into the product of the crystalliser. This resulted, on one occasion, in the production of a quantity of R.D.N. containing a perceptible amount of calcium chloride. After the danger was appreciated the brine system was, to some extent, modified so as to render a recurrence of the trouble less likely but the possibility was there still and a 100% system of testing the product had to be instituted in order to prevent the possibility of contaminated material being used in R.D.N. production.

Endeavours to remedy these defects and to simplify the process have resulted in the production of a new type of crystalliser in which -

(1) the only moving mechanism is a simple stirrer

(2) scrapers are abolished, crystal removal being effected by the mother liquor.

(3) the brine system is closed and cannot overflow into the product.

The crystalliser consists of a sheet aluminium truncated cone of 50 inches length of side, 43 inches diameter at the top or larger end and 32 inches diameter at the bottom or smaller end. This is supported in a cooling jacket by a flanged joint near the top. The vertical stirrer shaft is suspended from a double bearing carried by cross supports just above the vessel. The stirrer blades, mounted opposite each other, are close to the bottom of the vessel and are fashioned also to extend upwards for some distance close to the sides of the vessel. The stirrer revolves at 140 revolutions per minute. At this rate liquid entering the vessel is swirled immediately to the top where an overflow is

provided.

provided. The atomised hot spray is directed to the side of the vessel from jets at the top. It is cooled immediately and the mother liquor with the crystals in suspension is swirled to the overflow. After long periods of continuous working there is no sign of incrustation. The cooling is very effective, hot spray delivered at a rate of 60 gallons per hour is cooled to 5 to $10^{\circ}C$. when the cooling brine circulating in the jacket is at a temperature of -5 to $-10^{\circ}C$. Under similar flow and temperature conditions in the original crystalliser the finishing temperature would have been over $20^{\circ}C$.

The new type has considerable advantages in capital and maintenance costs and has superseded the original machine.

Efficiences of the processes.

For reasons which have already been stated it may be assumed that 23% is a reasonable figure to adopt at present as a satisfactory yield of dicyandiamide from fertilizer.

In separate columns below are given (1) the yields by the original processes i.e. carbon dioxide extraction of fertilizer and autoclave production of guanidine nitrate (2) the yields by water extraction of fertilizer and autoclave production of guanidine nitrate, and (3) the yields expected when improved water extraction of fertilizer and dry fusion production of guanidine nitrate have been installed.

Yields from 100 parts of fertilizer.

	(1)	(2)	(3)
Dicyandiamide	23 (estimated)	19	23
Guanidine nitrate	51	42	
Nitroguanidine	38	31.5	45.5

The yields of 38 parts of nitroguanidine in column (1) and 31.5 parts in column (2) are 67% of the theoretical yield from the dicyandiamide. The yield of 45.5 parts of nitroguanidine in column (3) is 80% of the theoretical yield and is arrived at from the experimental work recorded.

Deduced

Deduced from these yields and tabulated below are the quantities of chief raw materials required for the production of 1 lb. of nitroguanidine by systems (1) & (3).

	System (1)	System (3)
Fertilizer	2.6 lb.	2.2 lb.
Carbon dioxide	1.3 "	----
Ammonium nitrate	1.1 "	1.0 "
Sulphuric acid	2.2 "	2.2 "

Manufacture on a larger scale.

Assuming the dry fusion process is successful it is possible to visualise requirements for manufacture on the largest scale. With present knowledge there would be no difficulty in designing plant for any output.

The plant required for the processes is simple consisting largely of cylindrical tanks fitted with stirrers, cooling tanks, centrifuges drying stoves, lead lined jacketed pans, sheet aluminium crystallisers, disintegrators etc. - all plant which is easily procurable.

3rd March, 1933.