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The Preparation and Properties of Diethylene Glycol Dinitrate

PART V

Acid Recovery in the Manufacture of D.E.G.N.

S. E. Smith

INCLOSURE 3 TO REPORT No. R-1814-50

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EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

THE PREPARATION AND PROPERTIES OF DIETHYLENE  
GLYCOL DINITRATE

Parts I and II. E.R.D.E. Report No. 18/R/48 - Ref. C.R.Temp. 7/11/2/1

By

S. Masterman  
S.E. Smith  
W.E. Turner

Parts III.	E.R.D.E. Report	2/R/49	-	Ref. X.R. 510/1.
" IV.	" "	3/R/49	-	" X.R. 510/2
" V.	" "	4/R/49	-	" X.R. 510/3
" VI.	" "	21/R/49	-	" X.R. 510/5

by

S.E. Smith

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## SUMMARY

I. Objects of the investigation

To examine the properties of diethylene glycol dinitrate, and to develop a method for its manufacture from diethylene glycol.

II. Scope of the investigation

The requirements of commercial diethylene glycol for nitration to the dinitrate for Service use have been investigated. The optimum conditions for the nitration, and for the stabilisation of diethylene glycol dinitrate, have been determined by laboratory and semi-technical scale investigations, and batch and continuous pilot plants for these operations have been developed.

The manufacture of D.E.G.N. and recovery of the spent acid have been established on the semi-manufacturing scale and quantities of the product supplied for experimental propellant manufacture.

The chemistry of D.E.G.N., the mechanism of its nitration and the reactions of the spent acid have been given some fundamental study.

No difficulty has been met in obtaining D.E.G.N. of acceptable purity and chemical stability by these processes.

The maximum overall manufacturing yield of D.E.G.N. so far obtained is 90 per cent theory as against 94 per cent for nitroglycerine. This is a disadvantage of D.E.G.N.

The spent acid from D.E.G.N. nitration retains some D.E.G.N. in solution and fumes off at ordinary temperatures after a 'life' depending on the composition of the acid. An acid composition for continuous nitration has been devised to give a spent acid with a safe life around 12 hours at 20°C. A procedure has been developed in which the spent acid from the continuous process is run directly down a dinitration tower in which the dissolved organic matter is destroyed. This involves the recovery of NO<sub>2</sub> as 50 per cent nitric acid and some additional nitric acid concentration.

The physical, chemical, explosive and physiological properties of diethylene glycol dinitrate so obtained have been determined.

Conclusions

1. D.E.G.N. can be safely manufactured in the same types of plant, batch or continuous, as are used for nitroglycerine. The continuous process is more suitable for operation with a continuous waste acid denitration. In both batch and continuous nitration the safety of D.E.G.N. enables simplifications to be made. The yield of D.E.G.N. is less and the consumption of nitric acid is somewhat higher than for nitroglycerine.
2. The spent acid from D.E.G.N. nitration is unstable and needs to be decomposed directly and continuously. Denitration tower practice has been found suitable for this purpose and can be safely linked up with continuous nitration.
3. D.E.G.N. is superior to nitroglycerine in safety in handling.
4. D.E.G.N. appears to have no disadvantageous physiological effects during the short manufacture to date; the long term effect on health of the workers is yet to be determined.



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The Preparation and Properties of Diethylene  
Glycol Dinitrate.

Part V. Acid Recovery in the Manufacture  
of D.E.G.N.

by

S.E. Smith.

This report does not contain any information of  
overseas origin.

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CONTENTS.

- I. Introduction.
- II. Denitration of DEGN Waste Acid.
- III. Recovery of Prewash Liquors.
- IV. Acid Recovery as a Continuous Process.



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Reference: X.R.510/3.

## I. Introduction.

The recovery of spent acid in DEGN manufacture is less straight-forward than the recovery of N.G. waste acid, for the following reasons :-

(1) Nitric acid has a much greater solubility in DEGN than in N.G., owing to the ether link, and must be recovered from the acid-ester, as well as from the waste acid, if the process is not to become uneconomic with respect to nitric acid consumption.

(2) DLGN waste acids contain more dissolved ester than does N.G. waste acid, and are markedly less stable. Spontaneous decomposition of the DEGN, accompanied by much heat evolution, becomes rapid within a few hours. This makes it necessary either to destroy the ester content under controlled conditions (as in a denitration column) before the spontaneous decomposition occurs, or to reduce the water content of the acid by fortifying it with more strong acid, since this has the effect of prolonging the 'life' of the acid, and permits longer storage.

(3) The waste acid contains insufficient nitric acid to oxidise all the dissolved DEGN and more must be added to ensure the complete elimination of organic matter.

With regard to (1), the bulk of the nitric acid in the DEGN can be extracted in the first water prewash. This yields a solution of nitric acid which also contains some dissolved DEGN, and is somewhat unstable; a spontaneous oxidation occurs on storage. The 'safe' life, and the violence of the oxidation, depend on the concentration of the solution, but the decomposition is in any case much less violent than the waste acid fume-off. For example, a 54% nitric acid solution containing DEGN (but probably not saturated with it) had a life in a Dewar flask of 24-30 hours, after which it heated up to 60°C., while a 37% solution containing DEGN had a life of 40 hours, and rose to 33°C.

Obviously, from the point of view of recovery, the aim must be to produce the maximum concentration of nitric acid from the pre-washing; the practical limit is governed, not so much by the rising instability of the solutions, as by the increasing loss of DEGN in the solution, with consequently lower yield of product, and the incomplete removal of acid (partition of acid between DEGN and water). The experimental work shows that 40-45% nitric acid is the maximum strength permissible, and this is confirmed by German manufacturing practise. It is not practicable to mix directly a prewash solution of this strength with the waste acid for recovery, owing to the unsuitability of such a mixture for treatment in the usual types of denitration equipment available, and also because of its instability.

In the recovery of DEGN spent acids at Krummel, a proportion of the prewash liquor was blended with the waste acid for denitration, but only weak nitric acid was obtained from this mixture, and from the remaining prewash liquor, the principal object being to destroy the DEGN under controlled conditions.

/strong



Strong nitric acid could then be recovered in a subsequent operation.

We have taken the view that it is more desirable to aim at adjusting the composition of the solutions before denitration so that only one passage through the recovery plant is required, to recover strong nitric acid.

In the course of batch manufacture with the pilot plant described in Part III, some experiments on the denitration of the spent acid produced, were made.

As stated earlier, this plant is less suitable for obtaining prewash liquors of recoverable strength than the Schmid continuous plant, and when the latter came into operation, the acid recovery work with the batch plant was discontinued.

In conjunction with the Schmid process, plant has been installed for the continuous recovery of both the spent acid and the prewash liquor.

In the following sections, the requirements for the recovery of spent acid and of prewash liquors are first considered separately, and the experimental work with the batch plant acid is reported. Later, the methods adopted for the treatment of the spent acid and the prewash liquor from the Schmid plant, are described. These are applicable to batch manufacture but the conditions are, in this case, less favorable.

## II. Denitration of DEGN Waste Acid.

The composition of the waste acid is predetermined by the proportion and composition of mixed acid used for nitration. The waste acid aimed at is chosen to have a minimum solubility for the ester, consistent with maximum yield of product. In the case of DEGN the choice is modified by the necessity to produce a waste acid of adequate stability.

From the point of view of recovery, the aim must be to produce a waste acid from which the nitric acid can be most conveniently recovered at maximum concentration.

German practise was to pass the waste acid first through a destructor tower, to eliminate the organic matter, and render the acid safe, and then to reconcentrate the resulting nitric acid in a subsequent operation. For batch operation at Krummel 2.90 parts mixed acid per part DEG nitrated, containing 65%  $\text{HNO}_3$ , 35%  $\text{H}_2\text{SO}_4$ , was used, which was stated to give 1.52 parts waste acid of composition 64-66%  $\text{H}_2\text{SO}_4$ , 9%  $\text{HNO}_3$ , 4-5% DEGN, 20-23%  $\text{H}_2\text{O}$ . For continuous operation, at Bomlitz, 3.18 parts mixed acid, containing 62%  $\text{HNO}_3$ , 35%  $\text{H}_2\text{SO}_4$  and 3%  $\text{H}_2\text{O}$  was used, and this gave 1.78 parts waste acid, composition 60.1%  $\text{H}_2\text{SO}_4$ , 12.8%  $\text{HNO}_3$ , 4.5% DEGN., 22.6%  $\text{H}_2\text{O}$ .

As a result of the investigational work undertaken in this department the batch pilot plant was operated with an acid ratio of 2.57 parts mixed acid, 72%  $\text{HNO}_3$ , 28%  $\text{H}_2\text{SO}_4$ , which yields 1.26 parts waste acid, 54.6%  $\text{H}_2\text{SO}_4$ , 13.5%  $\text{HNO}_3$ , 5.4% DEGN, 26.5%  $\text{H}_2\text{O}$ . The same waste acid is obtained if less

/anhydrous



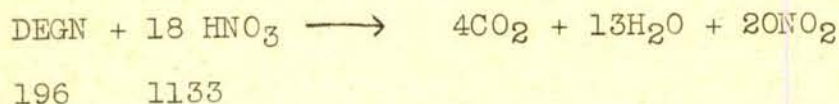
anhydrous mixed acid is available, by increasing the quantity of mixed acid and slightly modifying the proportions; for instance, 2.61 parts mixed acid, 71.0% HNO<sub>3</sub>, 28.5% H<sub>2</sub>SO<sub>4</sub>, 0.5% H<sub>2</sub>O, produce the same waste acid, in slightly greater amount.

All of the nitration acids mentioned have been used for comparative nitrations on the 20 lb. scale, and as far as yield was concerned, the Woolwich process was slightly superior. It is seen to be much superior, however, in respect of acid usage. Against this, the waste acid was less stable than the German waste acids, because of its higher water content, comparative figures obtained from the same series of experiments being :-

	<u>Life of Waste Acid before</u> <u>spontaneous fume-off.</u>
Woolwich Process Acid	4 - 6 hours.
Bomlitz " "	6 - 12 "
Krummel " "	12 - 18 "

However, at some stage before destructive distillation, additional nitric acid must be added and it was at first found convenient to add this in the form of mixed acid immediately after separation. This not only provides the additional oxidising acid required, but reduces the water content considerably and permits a period of storage of up to 24 hours if this should be necessary; it also eliminates any possibility of after-separation.

According to the combustion equation,



1 part DEGN requires 5.8 parts HNO<sub>3</sub>, so that 0.755 parts waste acid (basis 1 part DEGN produced, Part III, Table 5(b)), containing 0.041 parts DEGN and 0.102 parts HNO<sub>3</sub>, requires an extra 0.136 parts HNO<sub>3</sub>, or 0.189 parts 72/28 mixed acid.

Varying additions of mixed acid and also of 96% sulphuric acid were made to the waste acid separated from the 125 lb. batch nitrator in order to determine the minimum additions necessary in practise to

- (1) guarantee complete elimination of DEGN
- (2) give complete denitration of the sulphuric acid
- (3) produce nitric acid at as high a concentration as possible.

These experimental denitrations were made with a quartz-packed silica tower, of a type previously used at Waltham for the denitration of N.G. waste acid, from which it produced 65% H<sub>2</sub>SO<sub>4</sub>, free of nitric acid, and 60% nitric acid, this being later reconcentrated by distillation in a Pauling tower. It was

/found



found that a minimum HNO<sub>3</sub>/DEGN ratio of about 6.0/1 was required, to eliminate the organic matter from the acid; the effect of the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O ratio on the strength of the weak sulphuric acid produced was also apparent. The results obtained are given in Table 1.

This obsolete type of tower was later abandoned and a new silicon-iron tower was built, with the object of producing concentrated nitric acid in one operation, from a suitable waste acid feed. This is in essential features a replica of a Pauling Tower, to a scale of about 1/8th full size, having a throughput rate of about 100 lb/hr. feed acid.

This will satisfactorily denitrate DLGN waste acid, providing the HNO<sub>3</sub>/DLGN ratio is not less than about 6.0/1 and the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O ratio not less than about 2.5/1, the products being 65% H<sub>2</sub>SO<sub>4</sub>, free from HNO<sub>3</sub> and organic matter, and 90-95% HNO<sub>3</sub>, which however is liable to contain up to 1-2% HNO<sub>2</sub>.

From the foregoing work it was concluded that the minimum additions that must be made to 0.755 parts separated waste acid (basis, 1 part DLGN produced, Part III, Table 5(b)), are

- (1) Addition of 0.20 parts mixed acid immediately after separation. This will stabilise the waste acid sufficiently for 18-24 hours storage, and provide the additional nitric acid needed.
- (2) Addition of a further 0.375 parts 96% sulphuric acid, prior to, or at the time of, denitration.

The heat evolution from the mixed acid addition is relatively small and can be easily controlled with cooling in the spent acid tank at the nitrating house, whereas the heat evolved on adding the 96% H<sub>2</sub>SO<sub>4</sub> is much greater and could be profitably used in the denitration process. The changes in composition of the acid are as shown :-

	Waste Acid		Mixed Acid		Fortified Waste Acid		96% H <sub>2</sub> SO <sub>4</sub>		Denitration Acid	
	%	pts.	%	pts.	%	pts.	%	pts.	%	pts.
H <sub>2</sub> SO <sub>4</sub>	54.6	41.2	28	5.6	49.0	46.8	96	36	62.25	82.8
HNO <sub>3</sub>	13.5	10.2	72	14.4	25.75	24.6	-	-	18.5	24.
DEGN	5.4	4.1	-	-	4.3	4.1	-	-	3.1	4.1
H <sub>2</sub> O	26.5	20.0	-	-	20.95	20.0	4	1.5	16.15	21.5

$$0.755 + 0.20 = 0.955 + 0.375 = 1.33.$$

/TABLE I



TABLE I

## DENITRATION OF DE

Expt.	Origin	WASTE ACID FEED						% H <sub>2</sub> SO <sub>4</sub>	% HNO <sub>3</sub>
		H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	DEGN	H <sub>2</sub> O	$\frac{\text{HNO}_3}{\text{DEGN}}$	$\frac{\text{H}_2\text{SO}_4}{\text{H}_2\text{O}}$		
1	W.A. .755 pts. H.A. .245 pts.	48.1	27.8	4.1	20.0	6.8	2.4	56.5	Nil
2	W.A. .755 pts. COV. .419 pts.	54.6	13.5	5.4	26.5	2.5	3.75	70.0	Nil
3	W.A. .755 pts. COV. .419 pts.	69.3	8.7	3.5	18.5	2.5	3.75	66.5	Nil
4	W.A. .755 pts.	54.6	13.8	5.4	26.5	2.5	2.05	58	Nil
5	Synthetic	61.5	11.0	4.5	23.0	2.45	2.7	62.5	Nil
6	Synthetic	65.5	12.05	3.6	18.8	3.35	3.5	65.5	Nil
7	Synthetic	62.9	15.0	3.35	18.55	4.25	3.4	65.0	Nil
8	Synthetic	62.0	18.5	3.1	16.4	6.0	3.8	66.4	Nil



TABLE I

## NITRATION OF DEGN WASTE ACIDS

DENITRATED H <sub>2</sub> SO <sub>4</sub> PRODUCED				
O <sub>2</sub>	% HNO <sub>3</sub>	Organic matter		Effect of Further Heating
		Total	K <sub>2</sub> O	
	Nil	Traces present	Traces present	-
	Nil	1.75%	1.3%	Blackening and formaldehyde evolved at 200 - 210°C.
	Nil	1.6%	1.2%	Blackening, CO <sub>2</sub> & HCHO at 185 - 200°C.
	Nil	2.3%	1.6%	Blackening with HCHO at 210 - 220°C.
	Nil	3.0%	2.0%	Blackening, CO <sub>2</sub> , etc. at 175 - 180°C.
	Nil	2.0%	1.45%	Blackening
	Nil	2.15%	1.95%	Blackening
	Nil	1.75%	1.6%	Mild charring at 230°C. with CO <sub>2</sub> and HCHO



The total quantity of denitration acid is 1.33 parts per part DEGN produced, compared with 1.71 parts W.G. waste acid; the Bomlitz process for DEGN produced 1.05 parts separated waste acid which was processed twice to recover concentrated acid. The present waste acid scheme, outlined above, is preferred because of the lower ratio of mixed acid used for nitration, resulting in a larger output of DEGN from nitrators of a given size, and because the waste acid separated is closer in composition to that having the minimum solubility for DEGN, so that the losses from this cause are less. Furthermore, strong nitric acid can be obtained in one denitration, after adding strong acid as indicated.

### III. Recovery of Prewash Liquors.

The acid ester after separation, contains 21.2%  $\text{HNO}_3$  and 1.4%  $\text{H}_2\text{SO}_4$ . In parts per part of DEGN produced, this amounts to 0.274 parts  $\text{HNO}_3$ , i.e. much more than in the waste acid (0.102 parts  $\text{HNO}_3$ ). When acid DEGN is shaken or agitated with water, the bulk of the acid is rapidly transferred to the aqueous layer, although complete equilibrium is not reached for some time. The composition of the two phases at equilibrium depends principally on (a) the partition of  $\text{HNO}_3$  between water and DEGN and (b) the solubility of DEGN in the nitric acid solution, the small amount of  $\text{H}_2\text{SO}_4$  present being almost completely transferred to the aqueous phase.

The partition of  $\text{HNO}_3$  between DEGN and water, at 25°C., is as shown:-

<u>% <math>\text{HNO}_3</math> in aqueous phase.</u>	<u>% <math>\text{HNO}_3</math> in DEGN.</u>
0.2	0.0008
0.7	0.0011
1.4	0.0015
5.1	0.01
10.4	0.05
19.7	0.25
29.0	1.0
37.0	2.9
37.75	3.8
42.5	10.0
45.0	13.5

The solubility of DEGN in nitric acid solutions, is as follows:-

<u>% Nitric Acid.*</u>	<u>% DEGN.*</u>
0	0.4
5.7	0.6
10.0	0.8
15.1	1.06
20	1.5
25	2.05
30	2.9
35	3.35
40	5.0
45	6.7
50	9.0

\* The figures quoted, in the range 20-50%  $\text{HNO}_3$ , neglect the hydrolysis effect which sets up an equilibrium between DEGN, DEG mononitrate and  $\text{HNO}_3$ , in the solution.

/The



The following are the final equilibrium concentrations resulting from the extraction of 133.3 parts acid DEGN, as separated (see Flow Sheet Part III, Table 5(b)), with quantities of water calculated to produce 30, 35, 40 and 45% HNO<sub>3</sub> solutions respectively :-

(1) 30% HNO<sub>3</sub> solution produced :-

	<u>Acid Layer.</u>		<u>DEGN Layer.</u>	
	%	parts.	%	parts.
H <sub>2</sub> SO <sub>4</sub>	2.0	1.9	-	-
HNO <sub>3</sub>	30.0	23.3	1.1	1.1
DEGN	3.0	2.8	98.9	103.8
H <sub>2</sub> O	65.0	61.4	-	-
		<u>94.4</u>		

(2) 35% HNO<sub>3</sub> solution produced :-

	<u>Acid Layer.</u>		<u>DEGN Layer.</u>	
	%	parts.	%	parts.
H <sub>2</sub> SO <sub>4</sub>	2.4	1.9	-	-
HNO <sub>3</sub>	35.0	27.3	2.1	2.1
DEGN	3.9	3.0	97.9	103.6
H <sub>2</sub> O	58.7	45.8	-	-
		<u>78.0</u>		

(3) 40% HNO<sub>3</sub> solution produced :-

	<u>Acid Layer.</u>		<u>DEGN Layer.</u>	
	%	parts.	%	parts.
H <sub>2</sub> SO <sub>4</sub>	2.8	1.6	0.3	0.3
HNO <sub>3</sub>	40.0	22.5	6.3	6.9
DEGN	5.0	2.8	93.4	103.8
H <sub>2</sub> O	52.2	29.4	-	-
		<u>56.3</u>		

/(4)



(4) 45% HNO<sub>3</sub> solution produced :-

	<u>Acid Layer.</u>		<u>DEGN Layer.</u>	
	%	parts.	%	parts.
H <sub>2</sub> SO <sub>4</sub>	3.0	0.9	0.3	1.0
HNO <sub>3</sub>	45.0	13.5	13.5	15.9
DEGN	6.7	2.0	85.7	104.6
H <sub>2</sub> O	45.3	13.6	-	-
		<u>30.0</u>		

These figures show that batch washing is not very suitable for obtaining prewash liquors of recoverable strength, because although the equilibrium state is approached, if not actually attained, with a reasonable time of washing, the remaining DEGN still retains an appreciable proportion of the original acid, owing to the rapid deterioration in the partition coefficient in this region.

On the other hand, a continuous counter-current washing system, equivalent to a number of equilibrium stages, permits virtually complete removal of acidity at one end, and an aqueous extract of maximum strength, at the other end. The number of 'theoretical stages' required for these desirable end conditions can be calculated, and is found to be quite small. Assuming acid free DEGN and 45% prewash solution to be the end products from such a washing system, then the quantity of prewash solution produced would be approximately 0.65 parts per part DEGN produced :-

	%	parts.
H <sub>2</sub> SO <sub>4</sub>	3.0	1.9
HNO <sub>3</sub>	45.0	29.4
DEGN	6.7	4.4
H <sub>2</sub> O	45.3	<u>29.7</u>
		<u>65.4</u>

The final strength in this case is limited by the loss of DEGN in the acid solution and by its rising instability, but not by the amount of acid retained by the DEGN.

For these reasons, the strongest prewash solution that can be tolerated from batch washing is between 35-40% HNO<sub>3</sub>, while with continuous counter-current washing, 45% is quite permissible. At this strength the small difference in density between acid (1.33) and ester (1.39) becomes an added source of inconvenience.

/The



The stabilities of nitric acid solutions, saturated with DEGN, of concentrations ranging from 57% to 52%  $\text{HNO}_3$ , have been investigated by following the temperature rise of samples stored in glass and stainless steel beakers. They all had a 'life' of from 6 to 18 hours and the maximum temperature reached with the 52% solution was  $40^\circ\text{C}$ . Greenish solutions were left after fuming off, due to dissolved  $\text{NO}_2$ ; this could be removed by aeration when the solutions regained the appearance of normal weak nitric acid. After several days the solutions still contained some organic matter, showing that oxidation under these conditions was incomplete. Little danger is, however, to be expected from the spontaneous fuming off of the prewash solutions, and it is not considered essential to take the precautionary measure of passing the solution through a denitration column, as was the German practise.

The prewash liquor can be reworked by mixing it with 96% sulphuric acid, and denitrating in a Pauling type tower. The total nitric acid content, including recoverable  $\text{HNO}_3$  present, initially as DEGN, is approximately 50%, so that mixing 0.65 parts with approximately 1.00 parts 96% sulphuric acid will produce about 1.65 parts of a feed acid containing 60%  $\text{H}_2\text{SO}_4$ , 20%  $\text{HNO}_3$  and 20%  $\text{H}_2\text{O}$ , plus residual organic matter which will be oxidised away in the final denitration.

The batch plant described in Part III is unsuitable for producing recoverable prewash liquors for another reason. This is, that skimmer separation is not suitable for separating off the first prewash liquor; an alternative arrangement to enable a sharp separation to be made is required.

With the schemes outlined above it is seen that the total acid to be recovered amounts to 1.33 parts from the original waste acid, and 1.65 parts from the prewash solution. To keep the total amount of acid to be reworked in this way below 3.0 parts per part of DEGN produced, with a nitration acid usage of 1.54 parts, is probably the best that can be achieved. The corresponding figures for N.G. manufacture (Waltham) are (a) waste acid produced, 1.71 parts, (b) mixed acid usage, 2.485 parts per part N.G. produced.

The flow sheet for batch manufacture (Table 2) shows the recovery of a 35% prewash solution with batch washing; in this case the acid reworked is approximately 3.7 parts/part.

#### IV. Acid Recovery as a Continuous Process.

The waste acids, etc., from a continuous nitration plant may themselves be more conveniently stabilised and reworked on a continuous basis, with a quite small time interval between the operations, when the instability risks diminish accordingly.

Given the appropriate layout of plant, it could be arranged to fume off (a) separated waste acid (with added nitric acid), and (b) prewash liquors, as produced from a continuous plant, in destructor towers located fairly near to the nitrating house.

The resulting weak acids could then be stored and subsequently reconcentrated in the usual way.

/However,



However, if the prewash liquor is fortified with COV and the resulting acid combined with the waste acid, a blend is obtained whose composition meets the requirements for denitration fairly satisfactorily. In the flowsheets, Tables 3, 4, 5 and 6, the waste acids and prewash liquors from the four nitration procedures previously mentioned, are combined in this way, the amount of COV used being calculated to produce a denitration acid containing 20% water. It is assumed that the prewash liquor is obtained by counter-current washing and contains 43%  $\text{HNO}_3$ .

It is seen that with the 72/28 mixed acid, the quantity of denitration acid produced is only 2.82 parts, per part of DLGN produced, and somewhat more with the other mixed acids. The  $\text{HNO}_3/\text{DEGN}$  ratio lies between 4.5 and 5.0, which is sufficient to oxidise the DEGN at least to the oxalic acid stage (4.5).

This scheme has been adopted in connection with the Schmid pilot plant and acid handling equipment for this purpose has been installed.

The waste acid from the Schmid plant is transferred from the Nitrating House, by air lift, direct to a feed tank above the miniature Pauling denitration tower.

The prewash liquor is also withdrawn from the Nitrating House by air lift and sent to the Egg House, where it is run into COV in a 100 gallon mixing vessel, provided with a stirrer and water cooling, from there it can be elevated to a second feed tank at the denitration site.

The denitration of the waste acid is thus continuous; the denitration of the prewash liquor is semi-continuous since this is added to the COV until a 100 gallon mix has been produced, which is then sent for denitration and the mixing vessel recharged with COV.

At present the tower is being fed with waste acid, but no results with the dual feed are available.

/Table 2.



TABLE 2

FLOW SHEET FOR THE MANUFACTURE OF DEGN BY

DEG Used	M.A. Used	W.A. Produced	Acid Ester Produced	1st Prewash Liquors Produced	Ester after 1st Prewash
59.9 pts.	153.9 pts.	75.5 pts.	138.3 pts.	78.0 pts.	105.7
	pts.	pts.	pts.	pts.	p
Recovered as DEGN 90.2	H <sub>2</sub> SO <sub>4</sub> 28 43.1	H <sub>2</sub> SO <sub>4</sub> 54.6 41.2	1.5 1.9	2.4 1.9	-
Lost in W.A. 3.7	HNO <sub>3</sub> 72 110.8	HNO <sub>3</sub> 13.5 10.2	21.2 29.4	35.0 27.3	2.1 2
Lost in Prewash liquor 2.7		DEGN 5.4 4.1	77.0 106.6	3.9 3.0	97.9 10
Lost in later washes 2.1		H <sub>2</sub> O 26.5 20.0	0.3 0.4	58.7 45.8	-
Mechanical etc. losses 1.3				Wash water used 45.4 pts.	
100.				add 156 pts. 96% H <sub>2</sub> SO <sub>4</sub>	
		133 pts. denitration acid		238 pts. denitration acid	
			3.71 pts./pt. DEGN		



TABLE 2

YIELD OF DEGN BY THE BATCH PROCESS (DEGN BASIS)

1st Prewash Liquors Produced	Ester after 1st Prewash	2nd Prewash Liquors Produced	Ester after 2nd Prewash	Wash waters	DEGN Produced
3.0 pts.	105.7 pts.	107.1 pts.	103.2 pts.	418.4 pts.	100 pts.
0 pts.	0 pts.	0 pts.	0 pts.	pts.	pts.
4 1.9	- -	- -		Soda wash 104.6	From Prewashing 103.2
0 27.3	2.1 2.1	2.0 2.1	DEGN 103.2	Soda/sulphite wash 104.6	Losses in final washing 1.7
				Soft water 104.6	
9 3.0	97.9 103.6	0.4 0.4		Soft water 104.6	Transport losses 0.2
7 45.8	- -	97.6 104.6		Soda ash 8.4	Mechanical and volatility losses 1.3
				Sodium sulphite 2.1	Net yield 100 pts.
Wash water used 4 pts.		Wash water used 104.6 pts.			= 90.27
pts. H <sub>2</sub> SO <sub>4</sub>					
pts. Nitration					
DEGN					

2



TABLE 3

Flow Sheet for the Manufacture of DEGN by the Continuous (Schmid) Process

A. 2.57 parts 72/28 Mixed Acid

(Basis: 100 pts. DEGN produced)

DEG Used	M.A. Used	W.A. Produced	Acid Ester Produced	Prewash Liquors Produced	Ester after Prewash	Denitration acid Produced	HNO <sub>3</sub> Consumed
59.6 pts.	153.0 pts.	75.0 pts.	137.6 pts.	67.9 pts.	102 pts.	281.9 pts.	65.4 pts.
Recovered as DEGN	90.8 % H <sub>2</sub> SO <sub>4</sub> 28 42.9 pts.	54.6 % H <sub>2</sub> SO <sub>4</sub> 41.0 1.9 pts.	1.5 % 1.9 pts.	2.8 % 1.9 pts.	-	63.1 % 177.7 pts.	Total usage 110.1 pts.
Lost in W.A.	3.7 % HNO <sub>3</sub> 72 110.1 pts.	13.5 % HNO <sub>3</sub> 10.1 29.2 pts.	21.2 % 29.2 pts.	43.0 % 29.2 pts.	-	13.9 % 39.3 pts.	Recoverable from W.A. 10.1
Lost in P.W. Liquor	3.7 %	5.4 % DEGN 4.1 106.1 pts.	77.0 % 106.1 pts.	6.0 % 4.1 100	102	2.9 % 8.2 pts.	Recoverable from DEGN in W.A. 2.7
Lost in later washing and Transport	0.9 %	26.5 % H <sub>2</sub> O 19.8 0.3	0.3 % 0.4 pts.	48.2 % 32.7 pts.	-	20.1 % 56.7 pts.	Recoverable from P.W. 29.2
Mechanical etc. losses	0.9 %			Wash water used 32.3 pts.		97 % COV 139.0 pts.	Recoverable from DEGN in P.W. 2.7
						Total recoverable	44.7 #
						H <sub>2</sub> SO <sub>4</sub> usage (100 % H <sub>2</sub> SO <sub>4</sub> )	
						Mixed Acid Fortification	42.9
							134.8
							177.7

# Not including concentration losses







TABLE 5

Flow Sheet for the Manufacture of DEGN by the Continuous (Schmid) Process

C. 2.90 parts 65/35 Mixed Acid

(Basis: 100 pts. DEGN produced)

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IEG used	M.A. used	W.A. Produced	Acid Ester Produced	Prewash Liquors Produced	Ester after Prewash	Denitration acid Produced	HNO <sub>3</sub> Consumed
60.4 pts.	191.7 pts.	107.1 pts.	145.0 pts.	78.4 pts.	102 pts.	329.0 pts.	65.4 pts.
Recovered as DEGN	88.8 % H <sub>2</sub> SO <sub>4</sub> 35 pts. 61.7	H <sub>2</sub> SO <sub>4</sub> 62.9 pts. 59.4	1.6 pts. 2.3	3.0 pts. 2.3	-	62.4 pts. 187.8	Total usage 114.8 pts.
Lost in W.A.	5.4 % HNO <sub>3</sub> 65 pts. 114.8	HNO <sub>3</sub> 10.1 pts. 9.5	23.0 pts. 32.9	43.0 pts. 32.9	-	14.1 pts. 42.4	Recoverable from W.A. 9.5
Lost in P.W. Liquor	4.0 % 4.0	DEGN 6.5 pts. 6.1	74.5 pts. 106.5	6.0 pts. 4.5	100 pts. 102	3.5 pts. 10.6	Recoverable from DEGN in W.A. 3.9
Lost in later washing and Transport	0.9 % 0.9	H <sub>2</sub> O 20.5 pts. 19.4	0.9 pts. 1.3	48.0 pts. 36.8	-	20.0 pts. 60.1	Recoverable from P.W. 32.9
Mechanical etc. losses	0.9 % 0.9			Wash water used 35.5 pts.		97% COV 130.0 pts.	Recoverable from DEGN in P.W. 2.9
							Total recoverable 49.2
							H <sub>2</sub> SO <sub>4</sub> usage (100% H <sub>2</sub> SO <sub>4</sub> )
							Mixed Acid 61.7
							Fortification 126.1
							187.8

≠ Not including concentration losses

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August 4, 87

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