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The Preparation and Properties of Diethylene Glycol Dinitrate

PART VI

Conclusions and Recommendation

S. E. Smith

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MINISTRY OF SUPPLY

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

WALTHAM ABBEY
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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_2 as 60 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 niti 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 VI. Conclusions and Recommendation.

by

S.E. Smith.

This report does not contain information of overseas origin.

Submitted by A Foster
S.E.I.

Approved by C. H. Johnson
A/C.S., E.R.D.E.

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CONCLUSIONS.

1. Diethylene Glycol.

DEG used for the manufacture of DEGN must be of high purity, otherwise the stability of the waste acid and the colour and stability of the ester itself, will be adversely affected.

The DEG used in the semi-technical and pilot plant scale manufacture was of adequate purity for large scale manufacture.

It is recommended that DEG supplied for nitration should conform to the specification attached to Part II of this report.

2. Nitration of DEG.

The nitration of DEG is very similar to that of glycerine; the mechanism of the reaction is the same, and the heat evolved is almost the same.

The chief differences between the two nitrations are :-

(1) The best yield of DEGN obtainable is less than that of N.G., owing to the greater solubility of DEGN in its waste acid and in the wash liquors.

(2) The waste acids produced in nitrations which give good yields of DEGN are unstable and decompose violently within a few hours of separation. On no account may water be added to the waste acid, since this accelerated the decomposition.

(3) The separated DEGN contains considerably more dissolved acid than does N.G. (22-23% compared with 5-7%), and this acid must be recovered, otherwise the consumption of nitric acid would make the process uneconomic.

3. Properties of DEGN.

The most important differences between the properties of DEGN and N.G. are :-

(1) DEGN is more volatile than N.G.

(2) It is less sensitive than N.G.

(3) It is more soluble in water and acid solutions than N.G.; and acids are more soluble in DEGN than in N.G. These enhanced solubilities in the case of DEGN are no doubt due to the ether link in its chemical structure.

(4) DEGN freezes at a lower temperature than N.G.

/4. Plant Design.

4. Plant Design.

DEGN can be made in the same types of plant as are used for N.G.

The lower sensitivity of DEGN permits simplifications in the design, compared with N.G. practise. For example, in the batch pilot plant, gravity separation with a sight glass and plug cock was used instead of a cockless system with displacement separation.

The lower freezing point of DEGN also largely eliminates the need for precautions against the freezing of the ester during manufacture and storage.

Batch manufacture of DEGN suffers from the following disadvantages :-

(1) The spent acid cannot be stored for longer than a few hours, owing to its instability, except by fortifying it with additional strong acid.

(2) Batch washing is less suitable for recovering acid from the separated DEGN than continuous countercurrent washing. A solution of 43% HNO_3 can be recovered by continuous countercurrent washing, whereas by batch washing, 30% HNO_3 is the maximum that can be obtained without undue loss of DEGN. In addition the need for sharp separation of the acid wash liquor requires a more complicated arrangement of plant, since the skimming method usually used in N.G. batch washing tanks is unsatisfactory in this case.

Hence, although a relatively simple batch nitrator can be used for DEGN, the batch process as a whole is unsuitable, and is not recommended.

On the other hand, a continuous process of nitration, separation, and washing, in which the waste acid and acid wash liquors are also continuously removed and denitrated, is especially suitable for DEGN manufacture, and this arrangement is recommended. The Schmid plant is suitable for this purpose, if means are provided for removing and denitrating the acids produced, without delay.

5. Yield and Nitrating Conditions.

As with N.G., the yield depends largely on fixing the nitrating conditions so as to produce a waste acid in which the loss of DEGN is as small as possible. Owing to the instability of acids having a minimum solvent power for DEGN, it is necessary to compromise between adequate stability and minimum solubility (i.e. maximum yield).

In the continuous pilot plant, the throughput time for the waste acid, from the time of nitration to the time of denitration, was 3 hours; allowing for a factor of safety, it is considered that the safe life of the waste acid, for this throughput time, should be 12 hours. The optimum nitration conditions arrived at in Part II of this report on the basis of laboratory investigations, produced a spent acid having a life of only four hours, and this is not thought good enough for safe working.

/A

A waste acid with a safe life of approximately 12 hours, has a water content of 24% and this may be produced by nitrating with 2.76 parts of a mixed acid containing 69% nitric acid, 31% sulphuric acid.

A flow sheet for this recommended procedure is attached, from which it may be seen that the overall yield of DEGN is 90%.

This composition of mixed acid assumes that an anhydrous acid can be obtained from the nitric and sulphuric acids available. It is also necessary that the initial nitrous acid content of the mixed acid should not exceed 0.05%, otherwise the stability of the waste acid will be lessened.

RECOMMENDATION.

That for DEGN manufacture, DEG be nitrated in a continuous Schmidt or similar nitrator with 2.76 parts of a mixed acid containing 69% nitric acid and 31% sulphuric acid and not more than 0.05% nitrous acid, to give a spent acid with a safe life of approximately 12 hours, and an overall yield of DEGN of 90% theory.

The nitration procedure, spent acid treatment and recovery and the washing of the DEGN should be as described in parts IV and V of this Report.

/Flow Sheet

FLOW SHEET FOR THE MANUFACTURE OF D

2.76 PARTS OF 69/

(BASIS: 100 PARTS O

D.E.G. used		M.A. used			W.A. Produced			Acid ester produced		Prewas liquor produc	
60.0 parts	%	165.6 parts	%	pts.	85.3 parts	%	pts.	140.3 parts %	pts.	74.9 pa %	pt
Recovered as DEGN	90.0	H_2SO_4	31	51.4	H_2SO_4	58.0	49.5	1.3	1.9	2.4	1.
Lost in W.A.	4.2	HNO_3	69	114.2	HNO_3	12.6	10.7	22.9	32.1	43.0	32.
Lost in Prewash	4.0				DEGN	5.5	4.7	75.8	106.3	6.0	4.
Lost in later washing	0.9				H_2O	23.9	20.4	-	-	48.6	36.
Mechanical, etc. losses	0.9				H						
										Wash wate used 36.4	

CTURE OF DEGN BY THE CONTINUOUS PROCESS

RTS OF 69/31 MIXED ACID

DO PARTS OF DEGN PRODUCED)

Prewash liquors produced		Ester after prewash		Denitration acid produced		Nitric acid consumed (as 100%)		Sulphuric acid consumed (as 100%)	
74.9 parts		101.8 pts.		306.0 parts		66.7 parts		2.9 parts	
%	pts.	%	pts.	%	pts.		pts.		Pts.
						Total usage	114.2	M.A. usage	51.4
2.4	1.9	-	-	63.0	192.8	Recoverable		Fortification	141.4
43.0	32.1	-	-	14.0	42.8	From W.A.	10.7	Total usage	192.8
						" DEGN in WA	3.0		
6.0	4.5	100	101.8	3.0	9.2	" Prewash	32.1	Recovery losses ($1\frac{1}{2}$%)	2.9
48.6	36.4	-	-	20.0	61.2	" DEGN in P.W.	2.9		
						Total recoverable	48.7		
Wash water used 36.4pts				97% COV used 145.8 pts.		Consumed in nitration	65.5		
						Recovery losses ($2\frac{1}{2}$%)	1.2		
						Total consumed	66.7		

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