UNCLASSIFIED

AD NUMBER

AD888965

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Foreign Government Information; SEP 1971. Other requests shall be referred to British Embassy, 3100 Massachusetts Ave., nW, Washington, DC 20008.

AUTHORITY

RARDE list no 61, 31 Mar 1973

THIS PAGE IS UNCLASSIFIED

BR26539

22/71

COPY No 74

AD888965

MINISTRY OF DEFENCE

ROYAL

ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT

EXPLOSIVES DIVISION

R.A.R.D.E. MEMORANDUM 22/71

Explosibility hazard of unpigmented industrial nitrocellulose

Part I. Commercial samples

DDC
RECEIVED
NOV 17 1971
C

A. J. Taylor

FOR CONDITIONS OF RELEASE SEE INSIDE COVER

The information given in this document is not to be communicated either directly or indirectly to the Press or to any person not authorised to receive it.

R.A.R.D.E.
Fort Halstead.

September,
1971

This Document was Graded
UNCLASSIFIED
at the 260th meeting of the R.A.R.D.E.
Security Classification Committee

RELEASE CONDITIONS FOR OVERSEAS DISTRIBUTION

A

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.

2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.

3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT AND TO ITS DEFENCE CONTRACTORS WITHIN ITS OWN TERRITORY EXCEPT AS OTHERWISE AUTHORISED BY THE MINISTRY OF DEFENCE. SUCH RECIPIENTS SHALL BE REQUIRED TO ACCEPT THE INFORMATION ON THE SAME CONDITIONS AS THE RECIPIENT GOVERNMENT.

4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

B

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.

2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.

3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT AND TO THOSE NOTED IN THE ATTACHED LIST, EXCEPT AS OTHERWISE AUTHORISED BY THE MINISTRY OF DEFENCE. SUCH RECIPIENTS SHALL BE REQUIRED TO ACCEPT THE INFORMATION ON THE SAME CONDITIONS AS THE RECIPIENT GOVERNMENT.

4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

C

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.

2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.

3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT, EXCEPT AS OTHERWISE AUTHORISED BY THE MINISTRY OF DEFENCE.

4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

D

5. THIS INFORMATION IS RELEASED FOR INFORMATION ONLY AND IS TO BE TREATED AS DISCLOSED IN CONFIDENCE. THE RECIPIENT GOVERNMENT SHALL USE ITS BEST ENDEAVOURS TO ENSURE THAT THIS INFORMATION IS NOT DEALT WITH IN ANY MANNER LIKELY TO PREJUDICE THE RIGHTS OF ANY OWNER THEREOF TO OBTAIN PATENT OR OTHER STATUTORY PROTECTION THEREFOR.

6. BEFORE ANY USE IS MADE OF THIS INFORMATION FOR THE PURPOSE OF MANUFACTURE THE AUTHORISATION OF THE MINISTRY OF DEFENCE, D SALES (SALES 5a (~)), ST. CHRISTOPHER HOUSE, SOUTHWARK STREET, LONDON S.E.1 MUST BE OBTAINED.

R.A.R.D.E.
Printing Section

MINISTRY OF DEFENCE

ROYAL ARMAMENT RESEARCH & DEVELOPMENT ESTABLISHMENT

R.A.R.D.E. MEMORANDUM 22/71

Explosibility hazard of unpigmented industrial nitrocellulose

Part I. Commercial samples

A.J. Taylor (E2)

Summary

The unpigmented nitrocellulose which is used in various non-explosive industrial applications is exempted from all the current explosive regulations. A review has been made of these regulations and their present application. Over the period 1965 to 1967, 23 samples of powder were received from industry by E2 (Home Office) Branch, R.A.R.D.E. and examined. All samples were considered to possess explosive properties to varying degrees, although some were known to be unrepresentative of normal commercial production.

Some of the factors thought to control hazard risk in these materials are discussed and recommendations are made for further work.

Approved for issue:

D.F. Runnicles, Principal Superintendent, 'E' Division

CONTENTS

		Page
1.	Introduction	1
	1.1 Historical	1
	1.2 Transportation regulations	2
	1.3 Current problems	3
2.	Samples	3
3.	Tests	4
	3.1 Analysis	4
	3.1.1 Desensitiser content	4
	3.1.2 Nitrogen content	5
	3.2 Sensitiveness	5
	3.2.1 Sensitiveness to impact	5
	3.2.2 Sensitiveness to ignition	5
	3.3 Response to detonative shock	5
	3.4 Response to ignition when confined	5
	3.5 Other tests	5
4.	Test data	6
	4.1 Routine explosibility test results	6
	4.2 Measurements of grain	6
	4.2.1 Gas flow permeability	6
	4.2.2 Gas adsorption (BET)	7
	4.2.3 Heat of wetting	7
	4.2.4 Microscopy	7
	4.2.5 Effects of added phthalate	7
	4.2.6 Tests in 12-bore shotgun	8
5.	Discussion	9
	5.1 Factors influencing the explosive combustion of commercial nitrocellulose	9
	5.2 Effect of nitrogen content	10
	5.2.1 Nitrogen content of constituent nitrocellulose	10
	5.2.2 Total nitrogen in sample	10
	5.3 Effect of plasticiser content	11
	5.4 Effect of grain structure	11
	5.4.1 Microscopy studies	12
	5.4.2 Heat of wetting	12
	5.4.3 Gas flow permeability	13

CONTENTS

		Page
5.5	Effect of damping liquid - isopropyl alcohol	14
5.6	Assessment of fire hazard and philosophy of tests	14
5.6.1	Hazard from direct ignition	14
5.6.2	Hazard from impact shock	15
5.6.3	Hazard from friction	15
5.7	Assessment of explosion hazard and philosophy of tests	16
5.7.1	Time/Pressure test	17
5.7.2	Other tests	18
6.	Conclusions	19
7.	Recommendations	20
8.	Acknowledgments	20
9.	References	20
	Appendix - Test methods	23
	Table 1	27
	Table 2	29
	Figures 1 to 20	

IMPORTANT

This document should be returned to the Reports Officer Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks Kent when no longer required

INITIAL DISTRIBUTION

Internal

No.1	Director
2	Deputy Director (1)
3	Deputy Director (2)
4	SMO
5	PS/E
6	PS/A
7	PS/B
8	PS/C
9	PS/D
10	Dr C K Thornhill
11	S/E1
12	S/E2
13–17	E2 (Att Mr E R Camplin, Mr A J Taylor, Mr A R Martin, Mr B C Turner, Mr B G P Freeder)
18–19	E2 Registry

External (UK)

20	Chief Scientist (Army)
21	Deputy Chief Scientist (Army)
22	DGW(A) (Wpns Coord (A))
23	DW(A) (2)
24	CSO, MOD (Av Supply), St Mary Cray
25	QAD (Mats), Royal Arsenal East, London, SE18 6TE
26	D Safety (AD), Lansdowne House, Berkeley Square, W1
27	Secretary OB
28	MOD Library (C&A), Old War Office Bldg
29–33	HM Chief Inspector of Explosives, Home Office Explosives Branch, Ruskin Avenue, Kew, Richmond, Surrey
34	Chief Scientist and Director of Research, Home Office, Whitehall, SW1
35	D/ERDE, MOD (Av Supply), Powdermill Lane, Waltham Abbey, Essex
36–38	HM Inspector of Factories, Department of Employment & Productivity, Baynards House, 1-13 Chepstow Place, Westbourne Grove, W2 (Att Mr J Nixon, Mr E W Langley, Mr R Walpole)
39	Laboratory of the Government Chemist, Cornwall House, Stamford Street, SE1 (Att Dr R Wood)
40	Secretary Dangerous Goods Committee, D of Transport, St Christopher House, Southwark Street, SE1
41	British Railways Board, Research Dept, Traffic & Dangerous Goods Section, Blandford House, Melbury Terrace, NW1
42	Port of London Authority, Claims Assessment Branch, PO Box No.242, Trinity Square, London EC3 3BX

External (UK) (continued)

43	Director, Fire Research Station, Boreham Wood, Herts (Att Mr P C Bowes)
44	Dept of Trade & Undustry, Marine Division, Dangercus Goods Section, Sunley House, 90-93 High Holborn, WC2 (Att Mr C L Jackson)
45	Inter Governmental Maritime Consultative Organisation (IMCO), 22 Berners Street, W1 (Att Dr A J Gross)
46	TRC - for retention

Overseas (through TRC)

47	BDSW (R&D) (Att Director of Munitions)
48	British Defence Liaison Staff (Army), Ottawa (Att Lt Col P Camp)
49-51	Canada - CFHQ for DCENG Technical Library
52-55	- Def Res Board
56	- CDLS
57	- Chief Inspector of Explosives, 555 Booth Street, Ottawa 1, Ontario
58-59	- Director, Explosives Research Laboratory, RR No.5, Ottawa, Ontario (Att Mr J A Darling)
60	Australia - AAS (UK)
61-65	- Dept of Supply
66	- RAAF Overseas HQ, London
67	- Postmaster General's Department (Research Laboratories), Planning & Research Division, 59 Little Collins Street, Melbourne, C1, Vic (Att Senior Librarian)
68	- Chief Inspector of Explosives, Dept of Chemistry, Kintore Avenue, Adelaide, S Australia
69	- Chief Inspector of Explosives, Central Government Buildings, Perth, W Australia
70	- Chief Inspector of Explosives for Victoria, 22-32 William Street, Melbourne
71	- Chief Inspector of Explosives, Government Chemical Laboratory, Brisbane, Queensland
72	USA - Assist Sec of Def (Dep DDR&E)
73-87	- ONR (London)
88	- Defense Documentation Center, Cameron Station, Alexandria, Va 22314
89-93	- US Army Standardization Group, UK
94-95	- Bureau of Mines, Department of Interior, 4500 Forbes Avenue, Pittsburg 13, Pa (Att Dr R Van Dolah)
96	Ceylon - Government Analyst, Colombo (Att Mr Humzah)

Overseas (through TRC) (continued)

97	India - Chief Inspector of Explosives, Department of Explosives, Delhi
98	Pakistan - High Commissioner, Controller Defence Services, Stores Division, 2 Palace Gate, London W8
99	New Zealand - Chief Inspector of Explosives, Department of Internal Affairs, Wellington C1
100	Tasmania - The Director of Mines, Box 124B, Hobart
101	S Africa - Chief Inspector of Explosives, PO Box 4570, Johannesburg
102	Singapore - Chief Inspector of Dangerous Materials, Department of Chemistry, Outram Road, Singapore 3
103	Hong Kong - Senior Explosives Officer, Mines Dept, Buckingham Building, Nathan Road, Kowloon
104-105	Belgium - Centre de Recherches Scientifiques et Techniques pour l'Industrie des Produits Explosifs, Val du Bois, Sterrebeek, Brabant (Att Dr L Deffet, Dr C Fosse)
106-107	France - Laboratoire de la Commission des Substances Explosives, Pouderies de Sevran, Sevran, Seine et Oise, Boite Postale No.4 (Att M. G Angerand, M. A Calzia)
108-112	Germany - Bundesanstalt fur Materialprufung (BAM), Unter den Eichen 87, Dahlem, Berlin (Att Professor J Zehr, Dr Swart, Dr Treumann, Dr E V Zahn, Dr P Wandrey)
113	Italy - Ministero dei Transporti, Instituto Sperimentale, Piassa Ippolito Nievo 46, Roma (Att Dr L Savi)
114	Japan - Nippon Kaiji, Kental Kyokai, Kaiji Building No.5, 1-Chome, Nishi-Latyoboyi, Chno-Ku, Tokyo (Att Capt N Matsuzawa)
115-116	Netherlands - Director, Technical Laboratory RVO-TNO, Lange Kleiweg 137, Rijswijk ZH (Att Dr E W Lindeijer, Mr Van de Putte)
117	Norway - Sjofarsdirectoratet, Fernbanetorget, 2 Oslo-Dept, Oslo 1 (Att Mr G Stubberud)

Overseas (through TRC) (continued)

118 Spain - Centre de Estudios de Materiales Especiales, General Aranaz 38, Guidad Lineal, Madrid (Att Senor J Zubizarreta)

119 Sweden - Director General, Statens Provningsanstalt, Drottning Kristinas, vag 31, Stockholm O, (Att Mr H L Simonsson)

120 - Forsvarets Forskningsanstalt, Fack Stockholm, 80, (Att Ir S Ek)

121 Switzerland - Chef de Division des Combustibles, Station Federale d'Essai des Materiaux, Dubendorf, Ueberlandstrasse 129 (Att Dr B Bieri)

122 OECD - Organisation for Economic Co-operation and Development (OECD), Directorate for Scientific Affairs, 2 Rue Andre-Pascal, Paris-16^{e} (Att Mlle L de Lamajorie)

Stock

123-150

1. INTRODUCTION

1.1 Historical

Nitrocellulose has for the past hundred years formed an active constituent of military and civil explosives. It is normally prepared by the nitration of cellulose such as cotton linters, wood pulp or straw. By controlling the nitration process it is possible to produce a range of materials whose nitrogen content varies from a fully nitrated cellulose (13.2 to 13.4% nitrogen) to a partially nitrated cellulose with nitrogen content less than 11%. Nitrocellulose finds uses in industry other than for explosives manufacture and in general this type of material, corresponding to the partially nitrated material, is loosely termed "collodion cotton". Collodion cotton is still a nitrocellulose and as such is subject to all restrictions of the Explosives Acts of 1875 and 1923 where it is listed as an explosive in Division 2 of Class 3. This Class refers to the Nitro-compound type of explosive and is subdivided into Division 1 - liquid nitro-compounds - and Division 2 - solid nitro-compounds. In the Notes to Section 3 of the Guide to the Act (1) collodion cotton is defined as a nitrocellulose which contains less than 12.3% nitrogen; additionally not less than 85% of collodion cotton must be soluble in ether and alcohol. Since the "non-explosive" application of nitrocellulose reached considerable proportions, the Notes to the Act referred to above state that under certain circumstances, collodion cotton may be regarded as being exempted from the explosives restrictions. These conditions are provided when the collodion cotton has been desensitised as follows:-

"... (a) In solution

(b) Uniformly mixed with not less than one-third of its weight of one of the following liquids:

(i) Calcium chloride solution
(ii) Water
(iii) Benzene
(iv) Butyl alcohol
(v) Iso-propyl-alcohol
(vi) Methylated spirit
(vii) Methylated spirit and Xylol in equal parts
(viii) Naphtha, heavy solvent
(ix) Toluol
(x) Xylol free from pyridine.

Provided that in the case of liquids (iii) to (x) inclusive the containers are air-tight and weak enough to open at or below a pressure of 200 psi or alternatively fitted with a bursting disc or other device which will act at or below a pressure of 200 psi.

(c) Gelatinised, the product consisting of 82 parts collodion cotton and not less than 18 parts of di-butyl phthalate, tricresyl phosphate or mixtures of these substances with and without castor oil.

If other substances are required for either (b) or (c), reference should be made to Her Majesty's Inspectors of Explosives ...."

All these limits which at present define the conditions under which collodion cotton or industrial nitrocellulose as it is normally termed, may be exempted from explosives restrictions, appear to have been determined largely by the industrial requirements of the day rather than on the basis of experimentally evaluating hazard.

Incidentally although for very many years after the passage of the Explosives Acts, the major proportion of industrial nitrocellulose was processed into celluloid or nitrate film, neither of these materials are mentioned in the Notes to the Explosives Acts (1), and camphor, which was the main desensitising and gelatinising agent, is not named as an approved plasticiser.

Following a series of disastrous fires involving nitrocellulose and its products, some controls were established through the mechanism of the Factories Acts. Over the period 1928 to 1939 a series of Statutory Regulations were effected which empowered HM Inspectors of Factories or Local Authority Inspectors to exercise control over premises where nitrocellulose products were stored or processed.

1.2 Transportation regulations

On the European Continent the transportation of nitrocellulose and its products are subjecteto control on an international basis. Road transport is covered by the "European Agreement concerning the international carriage of dangerous goods by road (ADR)" (2). Rail transport is covered by the "International Convention concerning the carriage of goods by rail (RID)" (3). Highly nitrated cellulose (gun cotton) and weakly nitrated cellulose (collodion cotton) are classified as explosives and placed in Class 1a of the respective regulations. Collodion cotton is defined both by ADR and RID as being nitrocellulose whose nitrogen content does not exceed 12.6%. There is also a general requirement on all nitrocellulose which is subject to these regulations, that it must be stable. A minimum level of "stability" is assured by subjecting the nitrocellulose to a specified heat test. Provided collodion cotton is suitably desensitised it may be categorised in Class III of ADR and RID, ie the highly inflammable substances class. If the nitrocellulose is in solution of an inflammable solvent, it is categorised in Class IIIa, the hazard rating of the inflammable liquid. If the nitrocellulose is damped with water or other specified liquids (eg methylated spirit, ethyl alcohol, xylol) or plasticised with a non-volatile material (eg dimethyl, dibutyl or dicyclochexyl phthalate) it is categorised as an inflammable solid, ie Class IIIb of ADR and RID.

Within the United Kingdom carriage of dangerous goods by rail and handling in docks and harbour is regulated by the British Transport Commission. In a similar manner, transport of dangerous goods by sea and air is controlled by the Board of Trade. Both of these bodies treat the hazard categorisation of industrial nitrocellulose and its products in a similar but not identical manner to that shown by ADR and RID. There are differences in detail for example the Board of Trade define collodion cotton in terms of ADR and RID, ie maximum nitrogen 12.6%; British Transport Commission fix the nitrogen content at 12.3% maximum. Further differences arise if the nitrocellulose is desensitised with an inflammable liquid; in some instances it is categorised for transportation purposes as a liquids hazard, sometimes as a solids hazard. At the present time there are no statutory regulations which control the carriage of "non-explosive" nitrocellulose by road within the United Kingdom.

The European transport regulations (ADR and RID) are now due for review. To assist in this, discussions and laboratory studies are being held between signatories to these Agreements and other interested countries including the United Kingdom.

1.3 Current problems

For the first 60 to 70 years following the Explosives Acts, a large proportion of industrial nitrocellulose went into the celluloid and nitrate film industry, but starting from the 1914-18 war, the aircraft industry began to consume large amounts in the form of adhesives for constructing air frames and cellulose "dopes" for coating the fabric covers of air frames. A further major industrial process involved the recovery of nitrocellulose from waste celluloid and nitrate film.

Generally the plasticiser content of the finished product was within the range 18 to 25% and the presence of pigment or other inorganic filler assisted in the reduction of the fire and explosion hazard. With the advent of relatively non-inflammable plastics in more recent years, there have been further changes in the main industrial applications of nitrocellulose, the greatest consumers now being the paint, lacquer and timber trades. Smaller quantities find their way into the plastics, packaging and footwear trades. These changes in the industrial usage of nitrocellulose have also been followed by decreasing use of pigmented material. The desensitising action of plasticiser and pigment are recognised in ADR and RID (4, 5) where certain nitrocellulose is classed as non-hazardous.

Although industrial nitrocellulose represents a partially nitrated cellulose and is required to be desensitised by inert materials, it remains a highly inflammable substance. There have been many records of accidents where industrial nitrocellulose has been involved in disastrous fires. In one case involving a celluloid and waste film store, severe scorching of vegetation demonstrated that the fire had "flashed" over 250 ft (75 m) from the source. In another more recent accident in Tooting, London, 1 cwt (50 Kg) of plasticised nitrocellulose became involved in a fire (6). The material was stored in a disused air-raid shelter, a substantial brick and concrete structure 10 x 8 x 7 ft (3.0 x 2.5 x 2.0 metres) built underground. An explosion followed which dislodged and split the concrete roof.

From time to time samples of industrial nitrocellulose are submitted to E2 (Home Office) Branch, RARDE for examination. Some samples have been received from industrial organisations in the United Kingdom via HM Inspectors of Factories; other samples have been received via HM Inspectors of Explosives following requests for specific importations of industrial nitrocellulose into this country. Test data from samples received over the 3 years 1965 to 1967 have been collated and with other associated investigations have formed the basis for this report.

2. SAMPLES

The samples of desensitised nitrocellulose examined in the report may be divided into two groups. The larger group (13 samples) represent plasticised material submitted to E2, RARDE for routine testing, either from HM Inspectors of Factories or HM Inspectors of Explosives. The samples originated from various manufacturers, both inside and outside the United Kingdom.

The remaining 10 samples were supplied by one manufacturer of industrial nitrocellulose. These samples were either especially prepared or selected from current production and may not have represented the average type of commercial product. Eight were plasticised with dibutyl phthalate and two damped with isopropyl alcohol.

All samples were alleged to comply with the current United Kingdom requirements by which the nitrocellulose was exempted from control under the Explosives Acts regulations. The physical nature varied considerably and photographs of typical specimens are given in Figures 1 to 5; these show the samples in the form of flat sheet, curled sheet or flake, chip, spherical grain or prill and crumb.

From discussions with industry and the Explosives Research and Development Establishment, Waltham Abbey, it has been learned that the manufacture of plasticised nitrocellulose is carried out by two processes, which by analogy with propellant production may be termed (i) solvent, and (ii) solventless methods. The solvent process is founded upon the Olin-Matheson or Dupont process for the manufacture of nitrocellulose ball powder. Nitrocellulose (wet with water) is dissolved in a suitable solvent; plasticiser is added and the solution dispersed in an aqueous phase. Control of droplet size is important. Finally the solvent is recovered by distillation leaving the spherical grain or prill of plasticised nitrocellulose.

In the solventless process, the charge of plasticiser is added to a water slurry of nitrocellulose. Following thorough agitation the solids are filtered, dried and then hot-rolled so that the plasticiser may gelatinise the nitrocellulose. The final form of the product, eg chip, flake, or sheet, depends upon subsequent treatment.

Of the 21 samples of plasticised material examined in this report, the 5 prilled samples were prepared by the solvent process; the remainder were prepared by the solventless or hot-rolling technique which is now generally adopted within the United Kingdom.

3. TESTS

Tests originally devised at E2 (Home Office) Branch, RARDE for industrial explosives (7) have been extended to a variety of hazardous materials. These include fertilisers based upon ammonium nitrate (8) and organic peroxides (9). Recently the Cartridge Case Test (10) was used to examine detonability of nitrocellulose samples. Routine tests which were applied to the nitrocellulose samples are listed in the following sub sections. Details of the tests are given in the Appendix.

3.1 Analysis

3.1.1 Desensitiser content

The amount of desensitiser in the plasticised samples was determined by extraction with boiling solvent. In the case of samples damped with isopropyl alcohol, the amount of desensitiser was determined by weight loss following oven drying.

3.1.2 Nitrogen content

Nitrogen estimations were carried out on the samples which had previously been extracted and dried, as in 3.1.1.

3.2 Sensitiveness

3.2.1 Sensitiveness to impact

This is the well-known fall-hammer or drop-weight test in which a small sample is struck an indirect blow when retained between an anvil and a striker.

3.2.2 Sensitiveness to ignition

The sparks from the end of a length of Bickford Fuze are directed onto the surface of the sample contained in a test tube.

3.3 Response to detonative shock

This test is carried out by firing 10 g charges in the Mk IIIc and the Mk I Ballistic Mortars.

3.4 Response to ignition when confined

5 g of the sample is decomposed by a match-head igniter in a closed vessel. This is the Time/Pressure test.

3.5 Other tests

Other techniques were used to test selected samples. Since physical factors appear to play an important role in defining the hazard properties of a material, the physical form of some samples was examined by the following techniques:-

(i) Gas flow permeability

(ii) Gas absorption (BET)

(iii) Heat of wetting

(iv) Microscopy

(v) Attempts were made to modify the surface characteristics of samples of plasticised nitrocellulose by treating them with phthalate solutions. The The sample was immersed at room temperature for 5 minutes in a solution of dibutyl phthalate in methylene chloride. The liquid was decanted and the sample dried at 60°C. The normal analyses were carried out and the treated material tested in the Time/Pressure apparatus.

(vi) Firing trials were carried out on a sample of plasticised nitrocellulose in a 12-bore gun. In these tests the ballistic performance of the nitrocellulose

was assessed in terms of propellants more usually fired in shot-guns. The assessment was obtained by comparing the pattern of shot distribution produced on a hardboard target set 30 ft (10 m) from the gun, when cartridges containing identical weights of shot and propellant were fired through the same gun barrel.

4. TEST DATA

4.1 Routine explosibility test results

All data are given in Tables 1 and 2 at the end of the report. Table 1 deals with the routine test samples covering the period 1965 to 1967. Table 2 contains the data obtained on the special samples A to J, which were supplied by one manufacturer.

4.2 Measurements of grain

4.2.1 Gas flow permeability

Results obtained from measurements carried out on plasticised nitrocellulose (15) are given in Table 3. Nitrocellulose in the form of chip, flake or crumb did not lend itself to this treatment due to the great variation between the shape and size of grains. All the samples in Table 3 were of prilled material.

Table 3. Surface area measurements on prilled nitrocellulose

Measurement	Sample number (Table 1)			
	2	5	12	13
Retained B.S. 10 mesh sieve) %	4.5	nil	3.3	4.5
Bulk density (g/cm^3)	-	0.86	-	0.42
Apparent density (g/cm^3)	1.05	1.36	0.69	0.70
Porosity ε	0.369	0.386	0.385	0.397

The porosity of the flow bed ε is given by $\frac{\text{pore volume}}{\text{bed volume}}$.

Attempts to measure internal surfaces of grains by liquid intrusion under vacuum were not successful since all values of density obtained came within the range 1.45 to 1.50 g/cm^3, which corresponds to the absolute density of plasticised nitrocellulose. Permeability measurements using

liquid flows were also unsuccessful as the fluids normally used for this technique were found to leach out plasticiser from the sample bed.

4.2.2 Gas adsorption (BET)

Attempts to measure internal surface of various types of plasticised nitrocellulose by BET at the Chemical Defence Establishment, Porton (16) proved unsuccessful due to slow vapourisation of plasticiser from the sample when the surfaces were being outgassed.

4.2.3 Heat of wetting

Results of measurements carried out on two samples of plasticised chip at Porton (16) are given in Table 4.

Table 4. Heats of wetting for plasticised NC chips

Sample No.	Heat of wetting Cal/g
3	2.2
7	3.7

The samples were dried over phosphorous pentoxide then wetted with methanol. In both samples there was initial rapid heat release which indicated that appreciable absorption had occurred; this was followed by a relatively slow heat release indicating that some solvent action was occurring.

4.2.4 Microscopy

Photomicrographs of plasticised nitrocellulose are shown in Figures 6 to 10. The grains have been fractured to show the nature of the internal structure at a magnification of X15. Figures 6 to 9 are of chip or flake and Figure 10 is of a prilled nitrocellulose.

4.2.5 Effects of added phthalate

A sample which was known to be a fast burner (sample 8 Table 1) was treated with various solutions of dibutyl phthalate in methylene chloride. Details of the treatment and of subsequent tests are given in Table 5 below.

Table 5. Effects of added phthalate

Expt No.	% phthalate in solution	Test data on treated sample		
		phthalate content %	Time/Pressure (m sec)	Impact (in)
1.	25%	31.1	52	21
2.	10%	20.0	7	-
3.	16%	18.9	8	-
4.	20%	20.0	9	-
5.	25%	23.5	15	-
6.	Untreated sample (No.8 Table 1)	16.0	4.5	15

4.2.6 Tests in 12-bore shotgun

Photographs of the targets showing shot pattern and penetration effects are given in Figures 11 to 15. The "a" series show the front of the targets and give the general pattern of shot spread; the "b" series show the rear face of the targets and provide a measure of shot penetration. The results are summarised in Table 6 below.

Table 6. Tests in 12-bore shotgun

Round	Details of propellant charge	Target effect and shot pattern
1.	2.4 g Sporting Powder (Reference Cartridge)	Penetration and heavy shot pattern over 4" dia. Irregular hole 1"-2" diam.
2.	2.4 g Gunpowder G.20	Penetration and shot pattern over 6" diam.
3.	2.4 g Nitrocellulose Sample E. Table 2.	No effective penetration - charge partially burned.
4.	0.3 g Gunpowder G.40	No effective penetration.
5.	2.1 g Sample E primed) 0.3 gm G.40)	Penetration and heavy shot pattern over 4" diam. Irregular hole 1"-2" diam.

Note: To obtain the necessary loading density, nitrocellulose Sample E was ground to pass a 12 mesh BS sieve.

5. DISCUSSION

5.1 Factors influencing the explosive combustion of commercial nitrocellulose

It has long been recognised in the United Kingdom and in Europe that the degree of explosiveness of commercial nitrocellulose was largely dependent upon the following factors:-

(i) nitrogen content of the constituent nitrocellulose

(ii) the amount of plasticiser in a plasticised nitrocellulose or the amount and type of damping fluid in a damped nitrocellulose.

In more recent years it has been thought that there were other factors which had a bearing upon the degree of fire and explosion hazard presented by such material. These include:-

(iii) the distribution of nitrogen in the cellulose, ie the degree of homogeneity of the nitration process

(iv) the type of plasticiser

(v) the degree of gelatinisation of the nitrocellulose by the plasticiser

(vi) the physical form of the plasticised nitrocellulose, ie chip, flake, prill, etc.

All these factors require a close examination in order that their relative importance may be assessed. Unlike the extensive investigations which have been carried out on the burning characteristics of propellants, where a high combustion performance is required, comparatively little work has been undertaken on commercial nitrocellulose where to minimise the risk of explosive deflagration a low combustion performance is to be preferred. In the following sections the results which have been obtained on commercial nitrocellulose samples are examined to find out if the factors listed above are significant.

5.2 Effect of nitrogen content

5.2.1 Nitrogen content of constituent nitrocellulose

In the plasticised samples the nitrogen content of the constituent nitrocellulose varied from 10.6 to 11.6%. The influence of this variation upon the "explosiveness" of the samples has been examined by considering those tests in Tables 1 and 2 for which there were a reasonable number of experimental data, ie Impact Sensitiveness, Ballistic Mortar Mk IIIc and Time/Pressure. There was considerable variation of test data but there was no trend discernible to link test performance with the nitrogen content of the constituent nitrocellulose. All samples were sensitive to impact. The values varied considerably.

Ballistic Mortar and Time/Pressure data exhibited more than a 10-fold variation in values, which by their random behaviour showed that factors other than nitrogen content appeared to be playing a great part in controlling the explosive and combustion performance of the samples.

5.2.2 Total nitrogen in sample

By considering total nitrogen in the sample in conjunction with its combustion and explosive characteristics, some discernible trends were apparent. In Figures 16, 17 and 18 the total nitrogen has been plotted against impact, ballistic mortar and time/pressure respectively. Figure 16 shows that in general a random variation appeared to exist between impact sensitiveness and the total nitrogen content of the sample. The samples from Table 1 gave values within the range 15 to 30 in, corresponding to the degree of sensitiveness shown by blasting gelatine containing 90% nitroglycerine. All samples from Table 2 gave values ranging from 30 to 43 in. The samples in Table 1 represented products from several manufacturers, while all those in Table 2 were produced by another single manufacturer. The difference in sensitiveness values between the two groups indicates that even though total nitrogen content of the sample may exert some influence upon impact sensitiveness, the differences in production technique between one manufacturer and another appear to exert an equal if not greater influence upon the impact sensitiveness.

Figure 17 shows that there is a discernible pattern linking ballistic mortar values with total nitrogen. This is not unexpected since within certain limits, explosion power as measured by the Ballistic Mortar Mk IIIc is known to be largely independent of the physical form of the sample and mainly dependent upon the total chemical energy available. With nitrocellulose samples, this corresponds to the amount of nitrate grouping present in the sample as tested, ie total nitrogen. Thus explosive power tends to increase with increasing total nitrogen.

In general there is no discernible pattern linking Time/Pressure results with total nitrogen (Fig 18). This is not unexpected in that a combustion process, eg such as occurs in the Time/Pressure test, is very dependent upon surface effects. Therefore with this type of test, the effects due to nitrogen content are masked by variations in the physical form of the nitrocellulose, since the samples consisted of flat sheet, curled flake, chip, prill and crumb. A limited correlation may be demonstrated by replotting some of the data from Figure 18 as shown in Figure 19. Only those samples made by the solventless process and containing less than 23% plasticiser were selected. The trend of the Time/Pressure data shows that with increasing nitrogen content, the rate of burning increases.

5.3 Effect of plasticiser content

Data from Table 5 has been plotted in Figure 20. The curve shows that for this particular sample, which was especially treated with various amounts of phthalate, the rate of burning was significantly reduced by increased phthalate content. However the general effect from all samples indicates that factors other than phthalate content have exerted great influence upon the explosibility characteristics of the material as measured by these tests. For example, data relating to Time/Pressure performances are given in Table 7 below.

Table 7

Sample	Analysis %		Time/Pressure (m sec)
	Nitrogen	Phthalate	
Expt 1 from Table 5	11.4	31.1	52
Ref B from Table 2	11.4	30.2	4.8

These demonstrate that for samples of plasticised nitrocellulose of almost identical composition, the rate of burning can be made to vary by a factor X10.

5.4 Effect of grain structure

From 5.2 and 5.3 above it is apparent that while total nitrogen and plasticiser content may exert some control over the explosion and combustion properties of plasticised nitrocellulose, there are other factors which appear to exert even more influence. (This conclusion is reached because the usual plasticised material contains between 18 and 20% phthalate and this is considered insufficient to effect complete gelatinisation unless a very extensive hot-rolling technique was applied. In this country it is common industrial practice for other reasons to restrict the degree of hot-rolling). Since all plasticised industrial nitrocellulose made in the United Kingdom is now produced by the solventless technique and since the bulk of such product contains less than 20% plasticiser, it may be assumed that a large proportion of all such material remains ungelatinised, ie fibrous in nature. This assumption was demonstrated by (i) the microscopy studies and (ii) the heat of wetting experiments.

5.4.1 Microscopy studies

In the photomicrographs 6, 7 and 9 all the samples of chip and flake exhibited an internal structure which was fibrous; externally the surface generally appeared smooth but at times a cellular pattern could be identified. The manner in which degree of 'fibrousness' or non-gelatinisation affects the burning rate of the nitrocellulose as shown by the Time/Pressure results, can be seen in Table 8, where the relevant data for samples 3 (MX 199) and F have been collated.

Table 8

Sample	Analysis %		Microscopy examinations assessment	Time/Pressure (m sec)
	Nitrogen	DBP		
3) MX 199)	11.0	20.6	Fibrous material; relatively coarse fibres, a high proportion partially gelatinised with DBP	28
F	11.1	20.6	Fibrous material; relatively fine, hair-like fibres	3.2

Figures 8 and 9 show the samples previously mentioned in Table 7. Despite the very high level of phthalate in both samples (i.e. 30-31%), Fig 9 is largely ungelatinised when compared with the material shown in Fig 8. Comparison of Fig 6 with Fig 7 and of Fig 8 with Fig 9, shows that the degree of gelatinisation has a very profound effect upon the burning characteristics of the plasticised nitrocellulose.

In the case of the plasticised material in prill form, the grains which were examined showed no traces of ungelatinised nitrocellulose fibres. Fig 10 shows however that the sample is not a homogeneous spheroid but is full of a large number of small voids which vary from 1 mm to 0.01 mm in diameter. This may be termed a form of "porosity" and control of the degree of grain porosity could be a significant feature in controlling the combustion characteristics of prilled nitrocellulose. Once the outer, relatively impervious skin of the prill had been penetrated the large internal surfaces would be exposed to the decomposition process, which could result in an increase in the mass rate of burning.

5.4.2 Heat of wetting

Measurements of surface outlined in 4.2.3 showed that some types of nitrocellulose samples exhibited considerable surface area. The measurements at Porton (16) quoted values of 10 to 40 m^2g^{-1}. Effects produced by variations in the surface structure upon the burning of the nitrocellulose grain are shown in Table 9 where data displayed previously have been rearranged.

Table 9

Sample	Analysis %		Heat of wetting (cal g^{-1})	Time/Pressure (m sec)
	Nitrogen	DBP		
MX 199) 3)	11.0	20.6	2.2	28
OECD 1965) 7)	11.1	22.4	3.7	13.5

The values for heat of wetting may be related directly to the total surface area of the sample. The significant feature from Table 9 is that the sample with the larger surface area burned faster.

5.4.3 Gas flow permeability

Assuming that the form of the nitrocellulose prills was a solid spheroid, the critical physical parameter for the combustion performance of a given composition would be surface mean diameter. By further examination of the data obtained in 4.2.1, it appears that surface mean diameter does not appear to be the controlling factor in determining the burning of the nitrocellulose. In Table 10 the specific surface (S_a) and the surface mean diameter (SMD) have been calculated for samples 2 and 12, and the values collated with the relevant Time/Pressure data.

Table 10

Sample	Analysis %		SMD μm	Sa cm^2g^{-1}	Time/Pressure (m sec)
	Nitrogen	Plasticiser			
2	10.7	19.9	1.7	33	26
12	10.6	18.6	1.5	57	8.5

Samples 2 and 12 had virtually identical chemical analysis, were produced by the same type of process (solvent process), but the rate of burning as shown by the Time/Pressure are different. With this material surface mean diameter does not appear to be as important as specific surface, since the sample with the greater specific surface gave the faster burning time.

5.5 Effect of damping liquid - isopropyl alcohol

Both samples I and J contained sufficient isopropyl alcohol to warrant exemption from the Explosives Act and from the explosives classes under RID and ADR. Both samples burned rather rapidly in the Time/Pressure test. This result indicated that the proportions of damping fluid used were not sufficient to render the nitrocellulose free from an explosive deflagration risk. However considering the remaining explosive test data - ballistic mortar and ignitability tests - the two wetted samples were considered to present less hazard than any plasticised sample.

5.6 Assessment of fire hazard and philosophy of tests

Nitrocellulose with low nitrogen content (collodion cotton grade) has been commonly accepted as an inflammable liquid or solid hazard for most purposes of transportation by the various national authorities.

The feature which distinguishes nitrocellulose from the majority of other hazardous substances which occupy the inflammable goods class, is that nitrocellulose contains its own supply of fueld and oxygen. Thus it is possible to initiate a decomposition within a sealed container of nitrocellulose by application of the appropriate stimuli. The commonest and one of the most effective in causing decomposition in nitrocellulose is heat, which itself may arise from a variety of external factors, eg

(i) Direct ignition of loose powder by sparks or flame

(ii) Ignition by impact

(iii) Ignition by friction

(iv) Ignition following application of heat from any other external source.

5 6.1 Hazard from direct ignition

Under conditions of normal transportations, the hazard of nitrocellulose being ignited directly from a source of ignition is extremely unlikely, provided the container remains sealed. If a container has been damaged so that powder has escaped then there exists a serious ignition hazard. If the material has been desensitised by a volatile liquid (eg water, alcohols, hydrocarbons etc) then the spilled or exposed powder will soon dry out due to local evaporation of desensitising liquid and this will result in a dangerous situation. The dried-out powder possesses all the properties and potential commonly attributed to explosive grade nitrocellulose. In addition, if the damping fluid is inflammable then there arises an additional hazard due to the threat of a vapour phase ignition which could ignite the sensitised nitrocellulose. In a recent accident at the Port of London Authority Docks, Tilbury (17) which involved two 40 gallon drums containing 343 lb of nitrocellulose wetted with isopropanol, there were grounds for believing that the drums were not properly sealed and thus liquid and/or powder could have escaped.

The laboratory test which provides a measure of the "ignitability" of a sample from a spark source is the Bickford Fuze Test listed in the Appendix. From the limited data in Tables 1 and 2, samples 8, 10, 11 and E, which in other tests produced vigorous deflagration or explosive effects, all ignited and burned

in the Ignition Test. Thus this test proves a guide to indicating those samples which are likely to present serious hazard risk.

5.6.2 Hazard from impact shock

In the course of transport and handling on dock-sides or loading bays, it is possible for a container of nitrocellulose to be dropped, or to fall from a stack. Also if the vehicle on which the container is being carried was involved in an accident, then the container could be subjected to violent mechanical shocks or blows between hard surfaces. If the mechanical shock was severe enough or if powder was trapped between hard surfaces, eg at the corners of a container, then a local ignition could occur in the nitrocellulose. Several industrial accidents involving fires with nitrocellulose have been reported from German sources (18), due to initiation by impact. The ease with which such decomposition takes place can be measured by the Impact Sensitiveness Test. This test should be used only as an indication since quantitative interpretation of test results is only possible when uniformity of sample and precise control of sample size can be assured. With industrial nitrocellulose neither of these conditions may be met due to variation in physical form of the grain and variations within the grain structure. However all the samples of plasticised material examined in this test proved sensitive or very sensitive to initiation by impact.

This feature is thought to be linked to the generally fibrous nature of the commercial plasticised nitrocellulose, since a fibrous powder (ie ungelatinised or partially gelatinised) contains a mass of gas space and free solid surface; following a violent shock, such as impact, adiabatic compression of the entrapped gas will cause local ignitions of the solid. This hypothesis finds confirmation in the Cartridge Case Tests (10) mentioned previously. This test provides a measure of the ease with which a substance may be decomposed explosive sively, and a measure of the degree of explosive decomposition following such initiation. The method of decomposition in this test is to apply a detonative shock to a lightly contained charge. In all experiments where plasticised samples were tested, those which were more fibrous proved easier to initiate and produced a much greater "explosion" effect.

5.6.3 Hazard from friction

Under normal conditions of transport, accidents have happened where a drum or container of nitrocellulose has ignited as the result of frictional heating, eg where a drum has been allowed to stand in contact with the road wheel on a trolley or vehicle. Following movement of the vehicle an ignition has occurred within the sealed drum. Several accidents have been reported in which the evidence points to frictional effects providing the prime source of decomposition (18) (19) (20). It has been established that the threshold temperature at which nitrocellulose begins to decompose exothermically is in the region 140-160°C. Within a metal container a relatively small degree of local heating would be sufficient to cause the decomposition of material which was in intimate contact with the unlined metal, since the nitrocellulose is such a poor heat conductor.

It is doubtful if the existing tests for frictional sensitivity have any significance for industrial nitrocellulose. The test as carried out under ADR (21) and RID (22), also the tests as practised within the United Kingdom, all depend for quantitative data upon precise control of sample quantity and quality.

As discussed in the previous sub-section, it is impossible to achieve this degree of control with an average sample of commercial nitrocellulose.

At international meetings it has been suggested that frictional heating may arise within a container of nitrocellulose gfains due to vibration during transport. This could arise by movement of the grain in relation to the container or in relation to neighbouring grains. To date there has been no experimental evidencepput forward to support this suggestion.

5.7 Assessment of explosion hazard and philosophy of tests

In the explosives application of nitrocellulose, the main use has been in the role of appropellant either on its own ("single base propellants") or in admixture with other explosives. When fired in a weapon the propellant burns in an accelerating manner to produce a maximum pressure in the breech or chamber before the projectile has moved appreciably down the barrel. The total charge must be consumed before the projectile is ejected. Control of the internal ballistics of a weapon system depend upon the evaluation of many chemical and physical parameters associated with the propellant and the gun. One of these related to the physical nature of the propellant is termed the Form Function (23).

A similar treatment has been given in a more simplified manner for the ballistic performance of shotguns (24). In this case differences obtained by varying the physical form of the propellant have been explained in terms of (i) a fibrous powder, (ii) a non-fibrous powder, (iii) a fully gelatinised powder. Briefly, the rate of charge consumption - ie the rate of pressure development - depends basically upon the rate of heat transfer in the state:

Unreacted Solid ⟶ Reacting Material ⟶ Combustion Products.

Higher chamber pressures force the flame front nearer to the surface of the unreacted powder grain, which if it has an "open" structure, allows more efficient penetration by hot combustion products so that the entire heat transfer process is increased.

The chief hazard, which is presented by certain samples of industrial nitrocellulose, stems from the combustion parameters of the material being sufficiently vigorous so that if an accidental ignition occurred within an appropriate "chamber" or "container", the resulting combustion would proceed in an accelerative manner and produce a deflagration as in the manner of a propellant. Once again, the dependance of burning rate upon pressure means that there is an interelationship between the powder and the "container". In the present context, "container" may refer to either the individual pack, the complete store unit, or the self-confinement due to the inertial resistance of unreacted nitrocellulose such as in a 300 Kg drum. In the incident quoted previously (6) the rate of pressure development was rapid enough to produce an explosion which caused major damage to the concrete roof of the building.

Summarising, the main factors which decide whether a nitrocellulose fire would transform into a violent deflagration effect are:

(a) the rate of burning of the material under the operating pressures

(b) the pressure/time characteristics of the "container".

Adequate hazard evaluation of the product depends upon a solution of these factors and no single laboratory test as now practiced by the various international testing authorities seems to afford anadequate solution. Such a range of variables is involved, eg the significance of the initial ignition on the subsequent combustion, the parameter equivalent to Form Function (23) for the combustion of the powder, the size and nature of individual packages, the size and nature of the complete shipment or storehouse, that development of a single laboratory test capable of being operated by the usual competent testing authority, would appear to be impracticable. At E2 (Home Office) Branch, RARDE, the main emphasis for evaluating the explosion hazard presented by industrial nitrocellulose has been placed on the Time/Pressure Test. Explosive characteristics of selected samples were confirmed by a series of additional tests.

5.7.1 Time/Pressure Test

In the field of testing dangerous goods, it is common practice among test laboratories that where explosion hazard has to be assessed, the laboratory test conditions should correspond to the most severe that could conceivably occur in normal conditions of transport. In respect to industrial nitrocellulose the sample must be made to ignite and burn under moderately severe conditions of confinement. These conditions are fulfilled in the Time/Pressure Test.

In this test the charge of 5 g is brought to a self-sustaining decomposition by applying a relatively small amount of heat very locally for a relatively short time. This test is of special significance in respect of substances which may burn or decompose exothermically producing a deflagration and not a detonation, eg gunpowder type of substances. The standard ignition system when fired in an empty bomb produces a pressure of approximately 50 psi (3.5 Kgf/cm^2). Further, there are often irregularities in the behaviour of the initial stages of the ignition before a stable propagation is developed in the test sample. For these reasons it is generally impossible to ascribe any precise interpretation to the initial stages of the pressure/time relationship. Attention is concentrated upon the rate of pressure rise after it has reached 100 psi (7 Kgf/cm^2) until either it reaches 300 psi (21 Kgf/cm^2) or it reaches a maximum which is less than this.

If the time taken for the pressure to rise from 100 to 300 psi is less than 30 m secs (or an equivalent rate of pressure rise if the peak pressure of 300 psi is not recorded) the sample is considered as presenting an explosion hazard. This value has been reached as a result of many years testing dangerous materials which could not be categorised in the Explosives Class, yet were known to possess the potential of producing an explosive deflagration affect when decomposed under confinement. These substances have included industrial nitrocellulose, boiler cleaning compounds, fumigant smoke compounds and very many other solids (other than conventional explosives) which can be brought to a self-propagating decomposition by a transient local ignition in the absence of atmospheric oxygen. The plasticised nitrocellulose involved in the Tooting accident (6) gave burning times of 5-10 m secs in this test.

While the above criteria define the region whereby the sample exhibits an "explosive" behaviour, there is an area of doubt when the rate of pressure rise is a little lower than these figures. This arises from two causes, (i) it has

been found that substances which give a slower pressure rise may behave irregularly under the test conditions, and (ii) the substances may be subjected during transport to special conditions of more vigorous initiation and/or confinement which could increase the hazard. For this reason a zone of uncertainty has been laid down and this has been found to vary slightly with the type of hazardous material tested. For example, for those substances which ignite readily so that there is normally a regular and predictable propagation of the charge in the bomb, and which possess a fairly powerful explosion potential in the Ballistic Mortar Mk IIIc, (eg industrial nitrocellulose) the zone of uncertainty is defined in terms of a pressure rise from 100 to 300 psi in 30 to 100 m secs, or the equivalent rate of pressure rise if the maximum pressure does not reach 300 psi. For substances which give results in this range it is necessary to carry out repeat tests and to give due consideration to any special circumstances which might arise.

Samples of nitrocellulose which give a pressure rise slower than any of the above may be judged to behave in a non-explosive manner, since if they were involved in a fire the rate of combustion and of pressure rise would ensure that combustion products would be vented by the "container" before the bulk of the decomposing material was consumed.

In the Time/Pressure test, the charge of 5 g industrial nitrocellulose is not totally consumed when the bursting disc vents. Most of the charge is ejected unburned. Only in the case of materials which deflagrate violently, such as a fine grain gunpowder, would the charge be burned either before the bomb could vent or during the venting process.

If during transport conditions, a "container" of industrial nitrocellulose became ignited, then by virtue of being a fast burner, and/or the "container" being unduly restrictive to free venting, the pressure rise could proceed exponentially; a large proportion of the total charge would be consumed before the container would allow the products to vent freely. Thus an explosive effect would be produced.

5.7.2 Other tests

Most samples tested in the Ballistic Mortar Mk IIIc showed very strong explosive power; for the plasticised samples this varied between 56 and 16% of the value given by a standard charge of picric acid. The explosive power of the two samples damped with isopropanol was considerably reduced, being between 17 and 1.3% of picric acid. Although this test has significance in deciding the degree of explosive hazard shown by many types of dangerous goods, in the context of the degree of explosive hazard presented by industrial nitrocellulose it does not warrant the weighting which the Time/Pressure test attracts. In the previous section the mechanism whereby an ignition in this material may give rise to explosions has been discussed. It is thought that explosive decomposition of industrial nitrocellulose is achieved by a deflagration-burning mechanism and not by a shock-propagation. Therefore any laboratory test which is based upon a detonative type of ignition is considered of secondary importance when assessing the explosive hazard of this material.

In the firing trials carried out with the 12-bore shotgun (Table 6) the sample of plasticised nitrocellulose produced a similar propulsive effect to that provided by corresponding charge weights of gunpowder or a normal sporting powder. The significant difference between the combustion properties of the recognised explosives and that exhibited by sample E was that the

relatively weak flash from the cap alone did not provide adequate ignition for the latter. In order to boost the initial combustion of sample E in the gun chambers, it was necessary to add a small amount (0.3 g) of fine gunpowder to the base of the cap. By this the weak flash from the cap was augmented by the flame and hot particles from the gunpowder, thus providing adequate ignition for the plasticised nitrocellulose. In itself, the small priming charge made a negligible contribution towards the ultimate ballistic performance of the charge, as may be noted in experiment 4 of Table 6.

Fired in the Cartridge Case Test (10) sample E could be made to produce the same or even more violent explosion effect than that given by gunpowder G12 or G20.

6. CONCLUSIONS

6.1 Samples of industrial nitrocellulose received at F2 (Home Office) Branch, RARDE, Woolwich, over the period 1965-1967 have been examined by various tests. The effects of common industrial hazards upon material as offered for transport have been discussed with reference to its properties and the role played by the container. The test behaviour of samples which comply with current British and European transport regulations, leads to the conclusion that these regulations may have originated from the convenience of established industrial practices, rather than from an evaluation of controlled hazard testing.

6.2 With particular reference to plasticised nitrocellulose, the present regulations are incapable of preventing the transport of material which is considered, as a result of the present examination, to offer a serious fire and explosion hazard. For example in some plasticised nitrocellulose which was considered to possess definite explosive properties, the constituent nitrocellulose had a nitrogen value of only 11%; other samples which contained up to 30% dibutyl phthalate as plasticiser could also display explosive properties.

6.3 The plasticised samples complied with the various national and international regulations for nitrocellulose which is exempted from explosive regulations, yet it is concluded that under limiting conditions of confinement, all the material could give rise to explosive effects if they were involved in a fire. Four samples (viz 8, 10, 11 and E) were considered to present a serious explosion hazard and this feature was demonstrated by special tests.

6.4 The selection of material for test did not form part of a controlled experiment, so the pattern of samples must be considered as random. Thus no one of the various factors thought to influence the hazardous behaviour of industrial nitrocellulose could be systematically varied and studied. The present work has shown that there are at least three factors which have been identified as exerting considerable influence upon the hazardous properties of the material:

(i) Total nitrogen in the sample

(ii) Total desensitiser in the sample

(iii) A complex factor relating to composition and structure of the powder grain; this is thought to have analogies with the Form Function which is used in the technology of propellant combustion.

The latter factor appears to have a greater significance than either (i) or (ii) in the case of plasticised nitrocellulose which has been made either by the hot-rolling method or by the "solvent" method.

6.5 There is a requirement for the development of tests which are more specific for determining the hazard characteristics of industrial nitrocellulose. It is considered that most reliance should be placed upon tests which can quantify:

(i) The ease with which a decomposition may be initiated in the powder.

(ii) The combustion behaviour of the powder-container assembly.

Of those routine tests used in the present work, the Spark Ignition and Impact tests provide a measure of (i) above and the Time/Pressure test provides a measure of (ii).

7. RECOMMENDATIONS

It is recommended that further work should be carried out to:-

1. Define the effect on ignition susceptibility and on explosion potential of:

   (i) various quantities of damping fluids

   (ii) various qualities of plasticiser

   (iii) varying degrees of gelatinisation

   (iv) varying total nitrogen content.

2. Improve test techniques so that definitions and regulations which may in future be used to control the hazard presented by industrial nitrocellulose, will be agreed by the various test authorities. This includes consideration of the properties of the powder and of the effect of the container.

8. ACKNOWLEDGEMENTS

The author wishes to thank Mr W G Perkins (BX Plastics Ltd), Mr V J Clancey (formerly of E2, RARDE), and Mr E G N Marsden, QAD (Mats), Woolwich).

9. REFERENCES

1. Guide to the Explosives Acts 1875 and 1923. HM Stationery Office (London 1941).

2. European Agreement concerning the international carriage of dangerous goods by road (ADR) Annex A - Provisions concerning dangerous substances and articles. HM Stationery Office (London 1967).

3. International Convention concerning the carriage of goods by rail (CIM) Annex 1 - International Regulations concerning the carriage of dangerous goods by rail (RID). HM Stationery Office (London 1968).

4. ADR (Ref 2) Marginal 2331 (c), page 89.

5. RID (Ref 3) Marginal 331 (c), page 102.

6. Report by HM Inspector of Factories on Dangerous Occurrence No.840 22 September 1964.

7. RARDE Memorandum X 18/63 - V J St Clancey.

8. RARDE Memorandum 16/67 - V J St Clancey, B C Turner.

9. RARDE Memorandum 21/70 - V J St Clancey, A J Owen.

10. RARDE Memorandum 15/69 - D P Lidstone.

11. Imperial Chemical Industries Ltd, Nobel Division, Ardeer - Unpublished document (1966).

12. BX Plastics Ltd, Manningtree, Essex - Unpublished document (1966).

13. Ind Eng Chem (1915) 7 - 766 - F C Bowman, W W Scott.

14. Unpublished RARDE Document (1968) - B G P Freeder, A J Taylor.

15. QAD (Mats), Woolwich - Private communication (1968) - E G N Marsden.

16. Chemistry Research Division, CDEE Porton - Private communication (1967) - F A P Maggs.

17. Fire at Port of London Authority, Tilbury Dock, 14 March 1970.

18. Wolff & Co, Walsrode, Hamburg (1969) - Private communication - Dr Ing K Schildt.

19. Fire at Container Base, Barton Dock, Urmston, Manchester, 7 May 1970.

20. Fire at Port of London Authority, Tilbury Dock, 11 September 1970.

21. ADR (Ref 2) Marginal 3156 (b), page 204.

22. RID (Ref 3) Marginal 1156 (b), page 258.

23. Internal Ballistics, Chapter 4 - HM Stationery Office (London 1951).

24. The Modern Shotgun II the Cartridge (London 1950) - G Burrard.

PRECEDING PAGE BLANK-NOT FILMED.

APPENDIX

TEST METHODS

1. Analysis

1.1 Determinations of plasticiser content

Determination of plasticiser content was carried out by solvent extraction methods which were currently used by the manufacturers of industrial nitrocellulose and by various testing agencies. The method normally used in the present work was based upon that adopted by Imperial Chemical Industries (11). This involves extraction of the sample, with chloroform in a Soxhlet apparatus for 5 hours. Previous to extraction the sample was dried in a vacuum dessicator, then ground with sodium chloride and acetone to a thick paste. This was allowed to dry then reground to a fine powder. After chloroform extraction, the residues were washed with boiling water to remove sodium chloride, then dried to constant weight. The loss in weight gives the plasticiser content.

This method is tedious and the repeatibility is not good due mainly to errors which occur in the grinding and the subsequent transfer stages. A simpler extraction method based upon that adopted by BX Plastics (12) was also used. This method gave values which correlated with the acetone-salt method for the samples which were under investigation.

1.2 Determination of nitrogen in the compound nitrocellulose

During the initial stages of this investigation, the nitrogen content of the constituent nitrocellulose was determined by a simple titrimetric method based upon the acid hydrolysis of the nitrocellulose as originally shown by Bowmann and Scott (13). As the test programme developed, other methods were tried and modified. Eventually a modified form of titrimetric technique was adopted using ferrous ammonium sulphate followed by either a "dead-stop" or a potentiometric technique (14).

2. Sensitiveness to impact

A standard sample is retained between a steel striker and a steel anvil; the striker is hit by a 1 lb steel ball (0.45 Kg) falling freely from a selected height. The height from which the weight drops to produce an audible explosion is a measure of the impact sensitiveness. The results are normally quoted as the height in inches at which ignition may be expected with a probability of 0.5. This is known as the 50% drop height.

3. Ignitability (ignition by sparks)

This test is laid down in the Manual of Explosives Safety Certificate Sensitiveness Tests, it is also very similar to the Ignition by Sparks test which is used by the German Authorities at BAM, Dahlem, Berlin. Sparks from the end of a length of Bickford fuze are directed onto the surface of the sample which is held in a test tube. The behaviour of the sample is noted as follows:-

(i) Ignition, followed by an explosion effect.

(ii) Ignition and smooth burning; time in seconds.

(iii) Ignition, followed by subsequent failure of combustion to propagate completely.

(iv) No ignition (NI.) in three tests.

4. Response to detonative shock

4.1 Ballistic Mortar Mk IIIc

In the BM Mk IIIc a 10 g charge is fired under very heavy confinement using a No.8 conical-base detonator. The energy released on detonative impulse is approximately proportional to the square of the length of the horizontal component of its swing. The result is expressed as a percentage of the recoil effect produced by 10 g of a standard picric acid fired under the same conditions.

4.2 Ballistic Mortar Mk I

In the BM Mk I a 10 g charge is fired with virtually no confinement using a No.6 flat-based detonator. The principles of measurement are very similar to those for the BM Mk IIIc but the mortar body is much lighter. The result is expressed as a percentage of the recoil effect produced by 10 g of a standard picric acid fired under the same conditions.

5. Time/pressure test

The apparatus consists of a small steel bomb capacity 18-20 ml fitted with an ignition device and connected to a pressure recorder. The bomb is a steel cylinder 3.5 in long by 0.8 in diam (89 x 20 mm ∅). One end is closed by a stout plug housing the ignition system and the other end by an aluminium disc which bursts at 300 psi (21 Kgf/cm^2). The bomb is supported by a tubular fitting screwed into the curved surface, which also serves to transmit the operating pressure to the gauge. A Dobbie McInnes Small Engine Indicator records bomb pressure directly by moving a pen arm against a revolving drum. The ignition system consists of an electrically fired match head, around which is wrapped a small square (0.1 g) of primed cambric*

When fired in an empty bomb the ignition system alone produces pressures up to 50 psi (3.5 Kgf/cm^2). To reduce variations which can occur during the initial stages of charge decomposition (due to the low-energy ignition source) only that portion of the record between the pressure limits

Footnote: *Primed cambric is used extensively for providing a controlled but hot source of ignition. It consists of a linen, coated on both sides with a potassium nitrate-silicon composition.

100-300 psi (7 to 21 Kgf/cm^2) is deemed useful. The combustion characteristic of the sample is taken as the time in milliseconds for the bomb pressure to rise from 100-300 psi, or if the disc burst below 300 psi, the time that it would have taken to reach 300 psi.

At E2 (Home Office) Branch, RARDE, the bomb is always fired with the ignition plug at the bottom so that the charge (5 g) is in intimate contact with the ignition device.

6. Surface (area) measurements on plasticised nitrocellulose prills

6.1 Method

After sieving out irregular particles on a 1.67 mm sieve (BS 10 mesh) 10 g was transferred to a precision bore glass tube 20 mm I.D. Supporting plugs of wire gauze were used at each end and the length of the particle-bed between the plugs was carefully measured. The tube containing the packed bed was then connected into an air flow system which included a rotameter calibrated in litres/minute air and a water filled manometer to measure the pressure drop across the bed.

To obtain the pore volume of each bed, a bung and stop-cock was fitted to one end of the bed tube, water pulled in to the lower surface of the bed and the weight recorded. After raising the water to the top of the bed the weight was again taken and the difference used to calculate the volume of the voids and a density figure.

Area per unit volume was calculated as follows:-

$$So = \left(\frac{A\varepsilon^3 \cdot \Delta p}{5\,(1-E)^2\,\eta L q e}\right)^{\frac{1}{2}} \text{cm}^2/\text{cm}^3$$

where A = area of cross section of bed tube in cms^2

ε = porosity of bed = $\frac{\text{pore volume}}{\text{bed volume}}$

Δp = pressure drop across bed in dynes

η = viscosity of air in poises

L = length of bed in cms

qo = rate of flow of air in cm^3/sec

S_o = surface area per unit volume

S_a = surface area per unit mass

PRECEDING PAGE BLANK-NOT FILMED.

Table 1. Commercial plasticised nitroc

Sample			Analysis %	
Reference	Type	Dimensions (mm)	Plasticiser	Nitrogen[1]
1. MX 197 HMIF 17/5/65	Flat sheet	0.48 to 0.63 thick	19.5	10.6
2. MX 198 HMIF 17/5/65	Spherical Grains	1¼ to 2 ø	19.9	10.7
3. MX 199 HMIF 17/5/65	Chip	3 x 3½ x 1¼	20.6	11.0
4. MX 200 HMIF 17/5/65	Chip	3 x 3½ x 1½	20.4	10.6
5. R.1507 Sample 1 HMIE 9/1/65	Spherical Grains	1¼ to 2 ø	-	-
6. R.1507 Sample 2 HMIE 1/10/65	Spherical Grains	1¼ to 2 ø	-	-
7. OECD Sample 1965	Chip	3 x 3½ x 1	22.4	11.1
8. R.1540 HMIF	Flat sheet	1.0 thick	16.0	11.4
9. Sample 15/6/65	Chip	3 x 3½ x 1¼	19.2	10.7
10. MX 224 HMIF 5/5/65 No.1	Curled flake	1 to 1½ thick	22.7	11.5
11. MX 224 HMIF 5/5/65 No.2	Curled flake	1 to 1½ thick	-	-
12. R.1590 HMIE 5/11/66	Spherical Grains	1¼ to 2 ø	18.6	10.6
13. R.1618 HMIE 16/11/67	Spherical Grains	1¼ ø (some larger)	18.8	10.6

Note: (1) Percent nitrogen in constituent

PRECEDING PAGE BLANK-NOT FILMED.

mercial plasticised nitrocellulose 1965-67

Analysis %		Ignitibility	Time-Pressure (m sec)	Impact height (ins)	Ballistic Mortar	
Plasticiser	Nitrogen[1]		100-300 psi		Mk IIIc	Mk I
19.5	10.6	Ignition-5 seconds	14	24	41	0.7
19.9	10.7	Ignition-10 seconds	26	26	20	0.6
20.6	11.0	Ignition-5 seconds	28	21	30	0.5
20.4	10.6	-	26	20	32.0	0.6
-	-	-	16	35	16	0.3
-	-	-	24	26	19	0.7
22.4	11.1	Ignition-3 seconds	13.5	23	46	1.0
16.0	11.4	-	4.5	15	54	5.0
19.2	10.7	-	18.5	26	-	-
22.7	11.5	Ignition-3 seconds	7.3	19	34	0.3
-	-	Ignition 2 seconds	5.7	33	33	1.4
18.6	10.6	-	8.5	25	20	0.6
18.8	10.6	-	18.0	-	-	-

ent nitrogen in constituent nitrocellulose

2

PRECEDING PAGE BLANK-NOT FILMED.

Table 2. Commercial nitrocellulose spe

Samples received 19

Sample			Analysis %		Ignitibi
Reference	Nominal comp^{n}	Type	Plasticiser	Nitrogen(1)	
A	30% DBP Medium nitrogen	Flake	31.1	11.0	No ignit
B	30% DBP High nitrogen	Flake	30.2	11.4	-
C	-	Flake	21.2	10.9	Ignition 2-3 seco
D	-	Flake	21.4	11.6	-
E	20% DBP Medium nitrogen	Flake	19.3	11.0	Ignition 2-3 seco
F	20% DBP Medium nitrogen	Chip	20.6	11.1	Ignition 2-3 seco
G	24% DBP Medium nitrogen	Crumb	22.5	10.7	No ignit
H	24% DBP Medium nitrogen	Crumb	22.4	10.6	-
I	30% IPA (2) High nitrogen	Cotton linters	40.1(3)	11.4	No ignit
J	30% IPA (2) High nitrogen	Wood pulp	31.3(3)	11.5	No ignit

Note: (1) Percent nitrogen in c
(2) Unplasticised NC wett
(3) IPA content

PRECEDING PAGE BLANK-NOT FILMED.

Commercial nitrocellulose special samples

Samples received 1966

Analysis %		Ignitibility	Time/Pressure (m sec)	Impact height (ins)	Ballistic Mortar Mk IIIc
ticiser	Nitrogen(1)		100–300 psi		
.1	11.0	No ignition	8.0	31	27
.2	11.4	-	4.8	37	30
.2	10.9	Ignition - 2-3 seconds	12.0	43	-
.4	11.6	-	6.4	31	-
.3	11.0	Ignition - 2-3 seconds	3.0	38	42
.6	11.1	Ignition - 2-3 seconds	3.2	37	-
.5	10.7	No ignition	16.0	32	19
.4	10.6	-	17.0	34	17
.1(3)	11.4	No ignition	5.2	-	1.3
.3(3)	11.5	No ignition	16.3	-	17

Note: (1) Percent nitrogen in constituent nitrocellulose
(2) Unplasticised NC wetted with isopropyl alcohol (IPA)
(3) IPA content

2

FIGS. 1&2

30mm

FIG. 1 PLASTICISED NITROCELLULOSE

30mm

FIG. 2 PLASTICISED NITROCELLULOSE

FIGS. 3&4

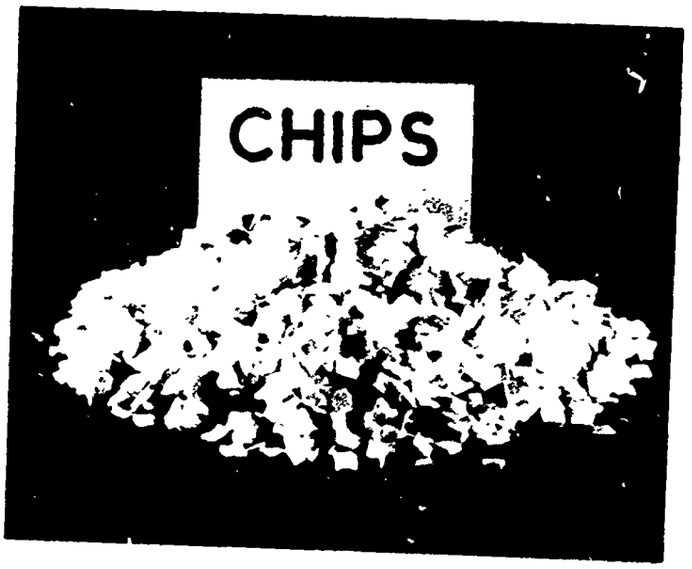


FIG. 3 PLASTICISED NITROCELLULOSE

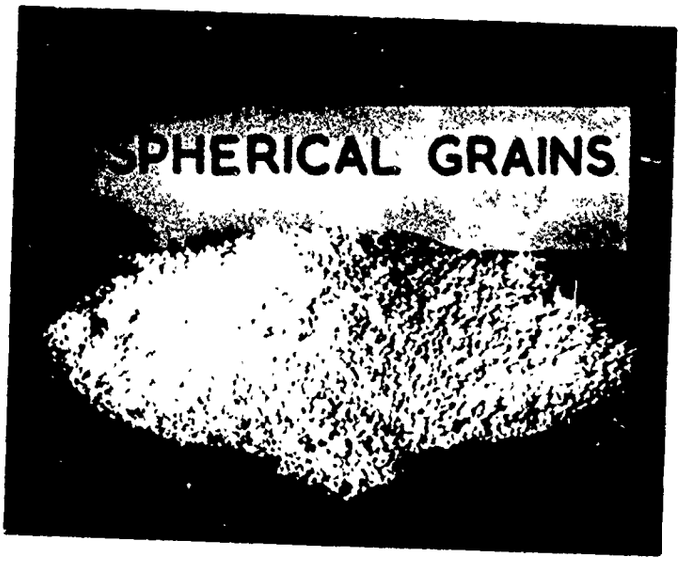


FIG. 4 PLASTICISED NITROCELLULOSE

FIGS. 5&6

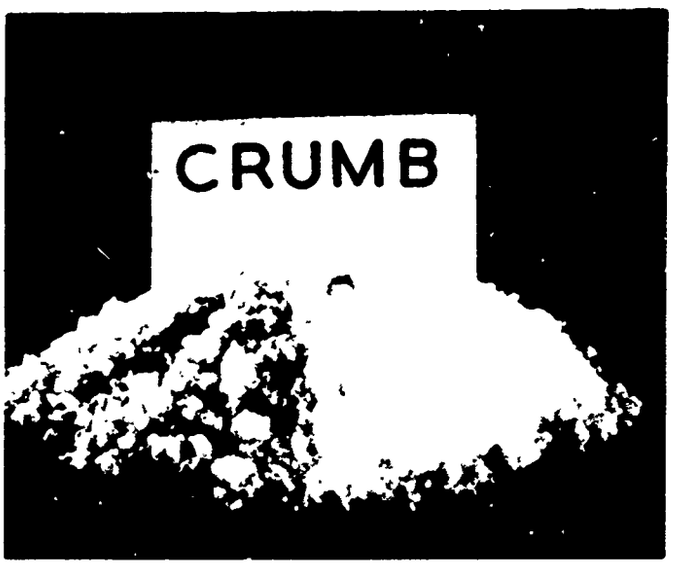


FIG. 5 PLASTICISED NITROCELLULOSE

FIG. 6 SAMPLE MX 199 NITROGEN 11·0%
PLASTICISER 20·6% T/P 26-30 m/s

FIGS. 7&8

FIG 7 SAMPLE F NITROGEN 11·1 %
PLASTICISER 20·6% T/P 3·2 m/s

FIG. 8 SAMPLE B NITROGEN 11·4 %
PLASTICISER 30·2% T/P 4·8m/s

FIGS. 9&10

FIG.9 CHIP NITROCELLULOSE DIPPED IN DIBUTYLPHTHALATE
NITROGEN 11·4% PLASTICISER 31·1% T/P 52 m/s

FIG.10 SAMPLE R1618 NITROGEN 10·6 %
PLASTICISER 18·8% T/P 18 m/s

FIGS.11a & 11b

3 in

FIG.11a FRONT OF TARGET CHARGE 2·4g SPORTING POWDER

3 in

FIG.11b REAR OF TARGET CHARGE 2·4g SPORTING POWDER

FIGS.12a & 12b

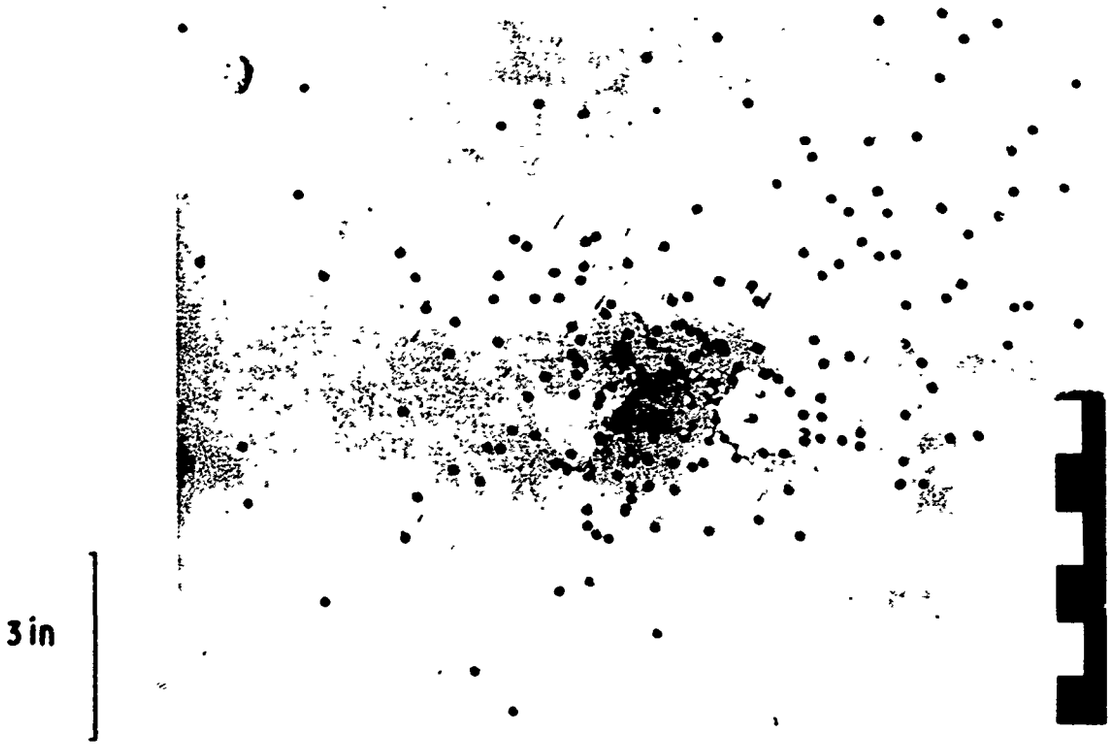


FIG.12a FRONT OF TARGET CHARGE 2·4g GUNPOWDER G20

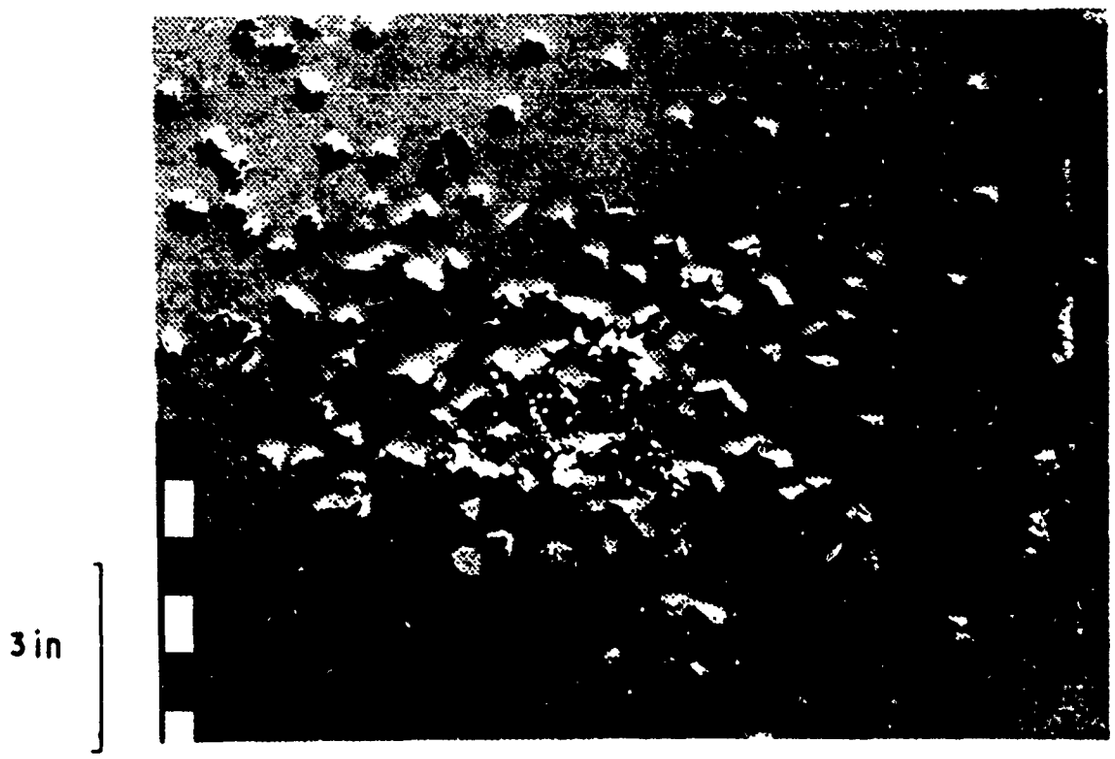
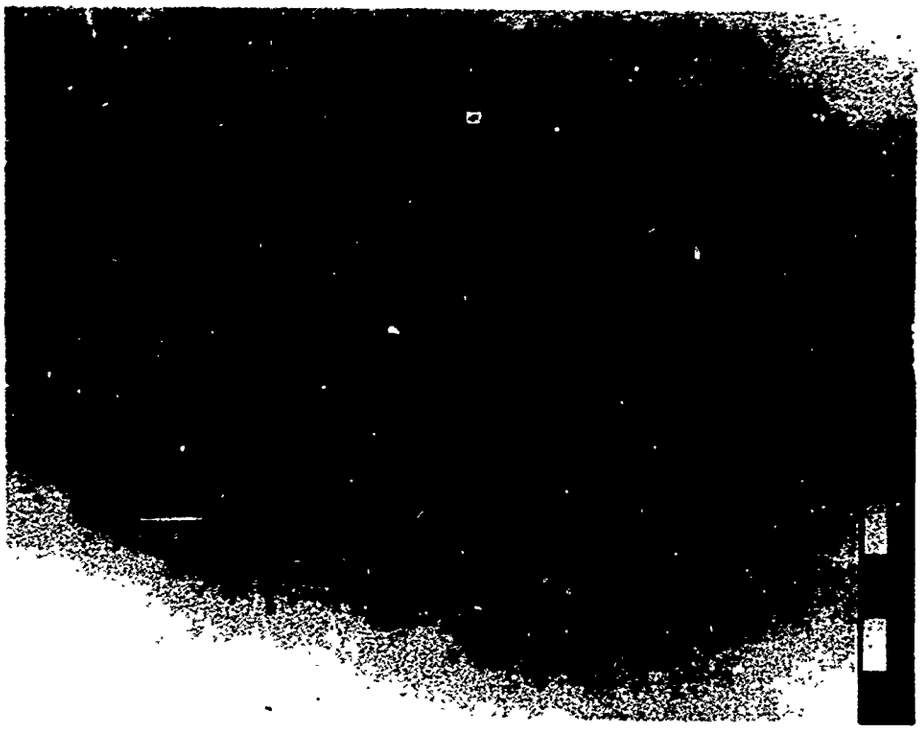


FIG.12b REAR OF TARGET CHARGE 2·4g GUNPOWDER G20

FIGS.13a&14a



3in

FIG.13a FRONT OF TARGET CHARGE 24g PLASTICISED NITROCELLULOSE SAMPLE E

3in

FIG.14a FRONT OF TARGET CHARGE 0·3g GUNPOWDER G40

FIGS.15a&15b

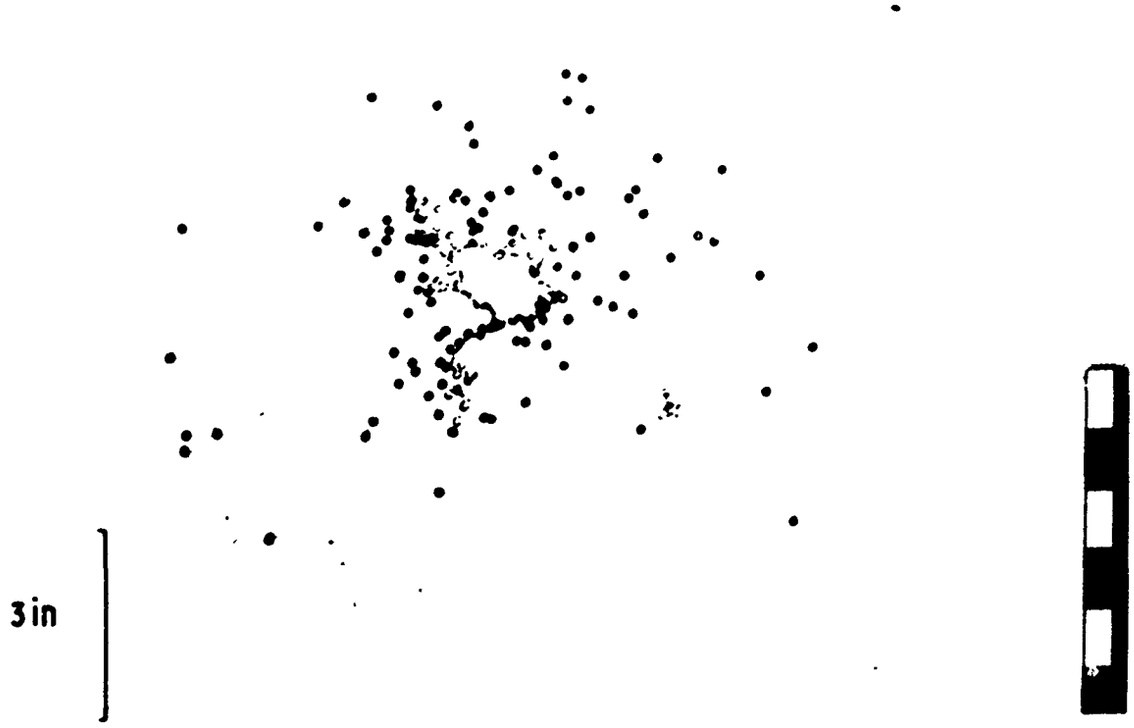


FIG 15a FRONT OF TARGET CHARGE 2·1g PLASTICISED NITROCELLULOSE SAMPLE E 0·3g GUNPOWDER G40

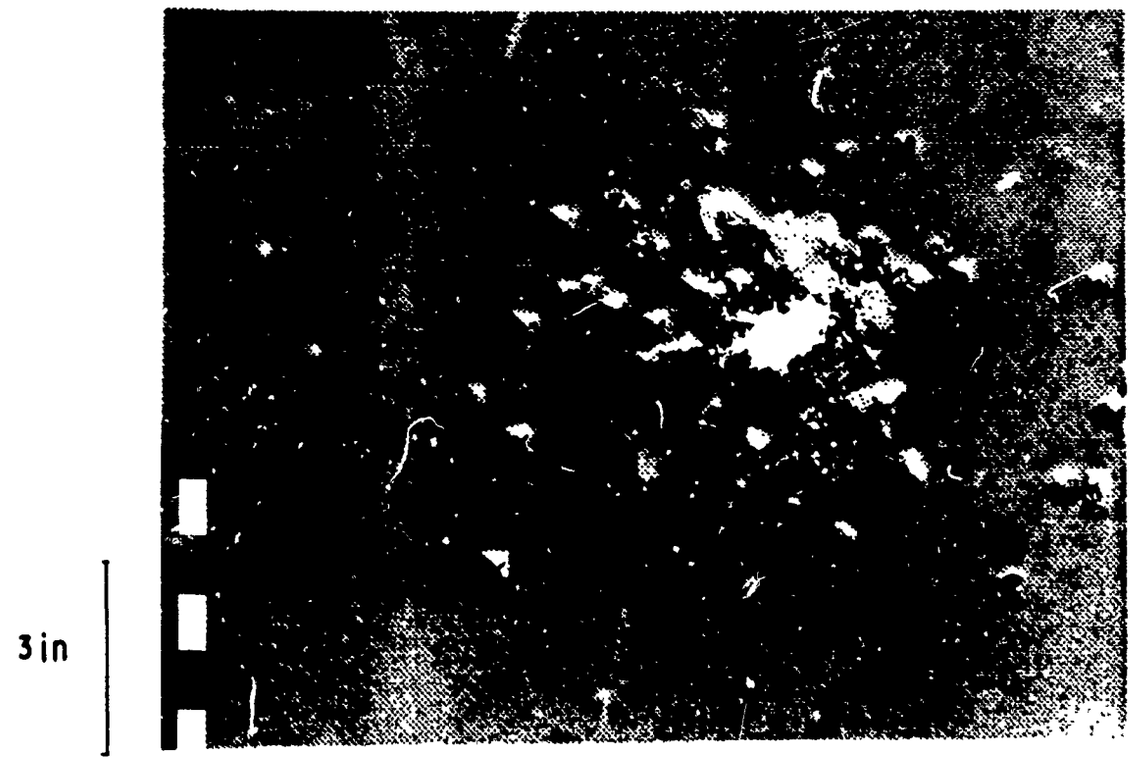


FIG 15 b REAR OF TARGET CHARGE 2·1g PLASTICISED NITROCELLULOSE SAMPLE E 0·3g GUNPOWDER G40

FIGS. 16 & 17

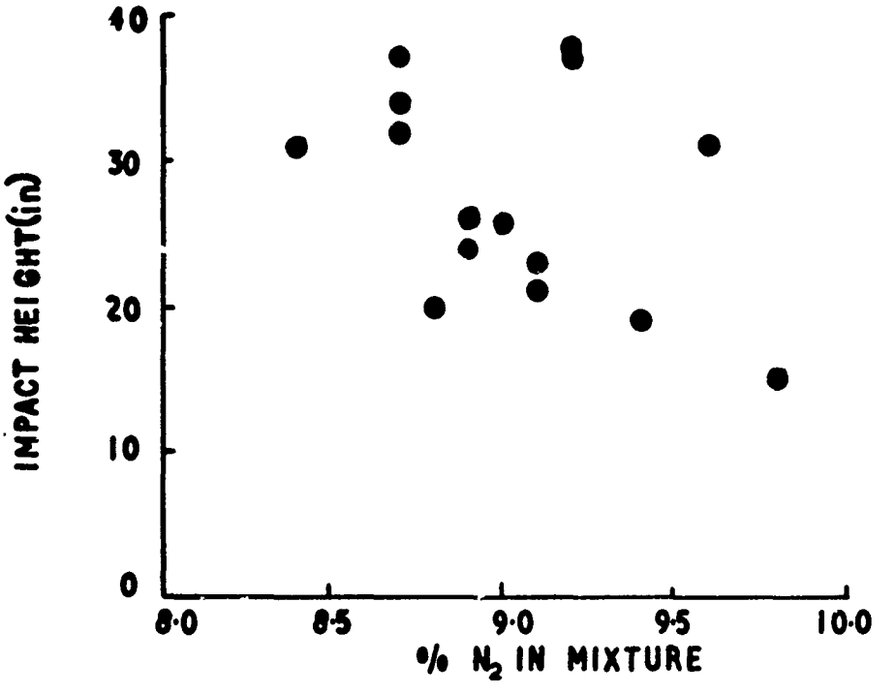


FIG. 16 % N_2 V IMPACT

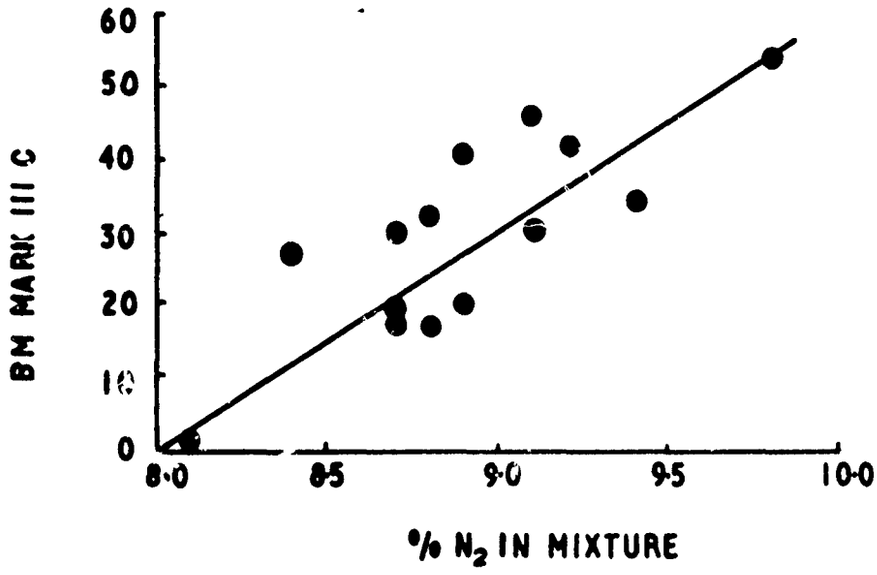


FIG. 17 % N_2 V BM MARK III C VALUES

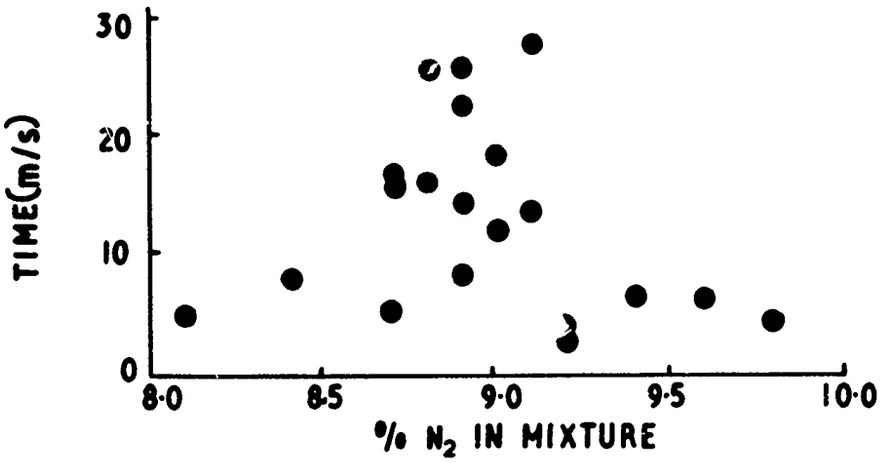


FIG. 18 % N_2 v TIME/PRESSURE

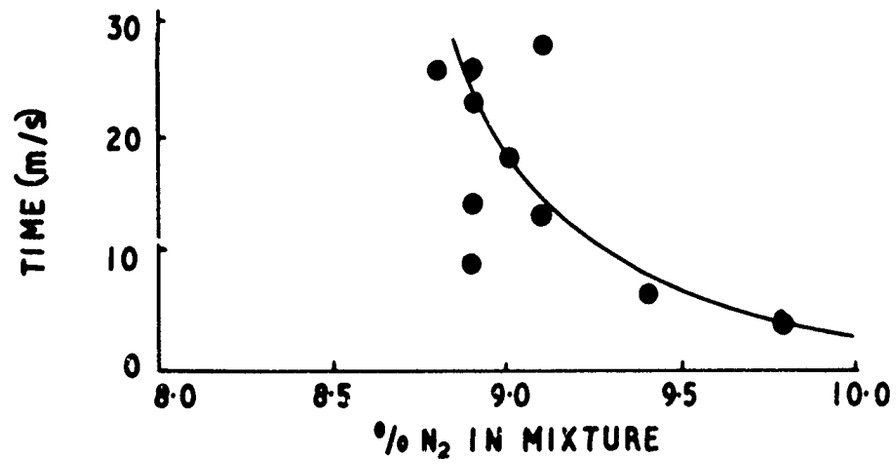


FIG. 19 % N_2 v TIME/PRESSURE

FIG. 20

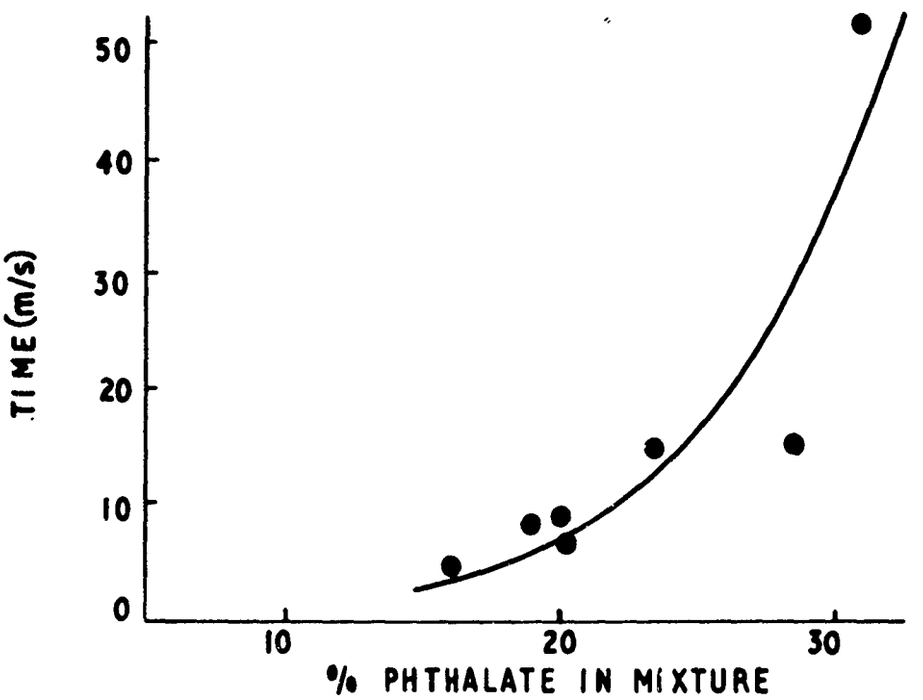


FIG. 20 % PHTHALATE v TIME/PRESSURE

Ministry of Defence
Royal Armament Research and Development Establishment
RARDE Memorandum 22/71

662.2:C:
543.876:
614.83

Explosibility hazard of unpigmented industrial nitrocellulose Part I Commercial samples

A J Taylor

September, 1971

The unpigmented nitrocellulose which is used in various non-explosive industrial applications is exempted from all the current explosive regulations. A review has been made of these regulations and their present application. Over the period 1965 to 1967, 23 samples of powder were received from industry by E2 (Home Office) Branch, RARDE and examined. All samples were considered to possess explosive properties to varying degrees, although some were known to be unrepresentative of normal commercial production.

Some of the factors thought to control hazard risk in these materials are discussed and recommendations are made for further work.

29 pp 20 figs 10 tabs 24 refs

Ministry of Defence
Royal Armament Research and Development Establishment
RARDE Memorandum 22/71

662.2:C:
543.876:
614.83

Explosibility hazard of unpigmented industrial nitrocellulose Part I Commercial samples

A J Taylor

September, 1971

The unpigmented nitrocellulose which is used in various non-explosive industrial applications is exempted from all the current explosive regulations. A review has been made of these regulations and their present application. Over the period 1965 to 1967, 23 samples of powder were received from industry by E2 (Home Office) Branch, RARDE and examined. All samples were considered to possess explosive properties to varying degrees, although some were known to be unrepresentative of normal commercial production.

Some of the factors thought to control hazard risk in these materials are discussed and recommendations are made for further work.

29 pp 20 figs 10 tabs 24 refs

Ministry of Defence
Royal Armament Research and Development Establishment
RARDE Memorandum 22/71

662.2:C:
543.876:
614.83

Explosibility hazard of unpigmented industrial nitrocellulose Part I Commercial samples

A J Taylor

September 1971

The unpigmented nitrocellulose which is used in various non-explosive industrial applications is exempted from all the current explosive regulations. A review has been made of these regulations and their present application. Over the period 1965 to 1967, 23 samples of powder were received from industry by E2 (Home Office) Branch, RARDE and examined. All samples were considered to possess explosive properties to varying degrees, although some were known to be unrepresentative of normal commercial production.

Some of the factors thought to control hazard risk in these materials are discussed and recommendations are made for further work.

29 pp 20 figs 10 tabs 24 refs

Ministry of Defence
Royal Armament Research and Development Establishment
RARDE Memorandum 22/71

662.2:C:
543.876:
614.83

Explosibility hazard of unpigmented industrial nitrocellulose Part I Commercial samples

A J Taylor

September 1971

The unpigmented nitrocellulose which is used in various non-explosive industrial applications is exempted from all the current explosive regulations. A review has been made of these regulations and their present application. Over the period 1965 to 1967, 23 samples of powder were received from industry by E2 (Home Office) Branch, RARDE and examined. All samples were considered to possess explosive properties to varying degrees, although some were known to be unrepresentative of normal commercial production.

Some of the factors thought to control hazard risk in these materials are discussed and recommendations are made for further work.

29 pp 20 figs 10 tabs 24 refs

For indexing