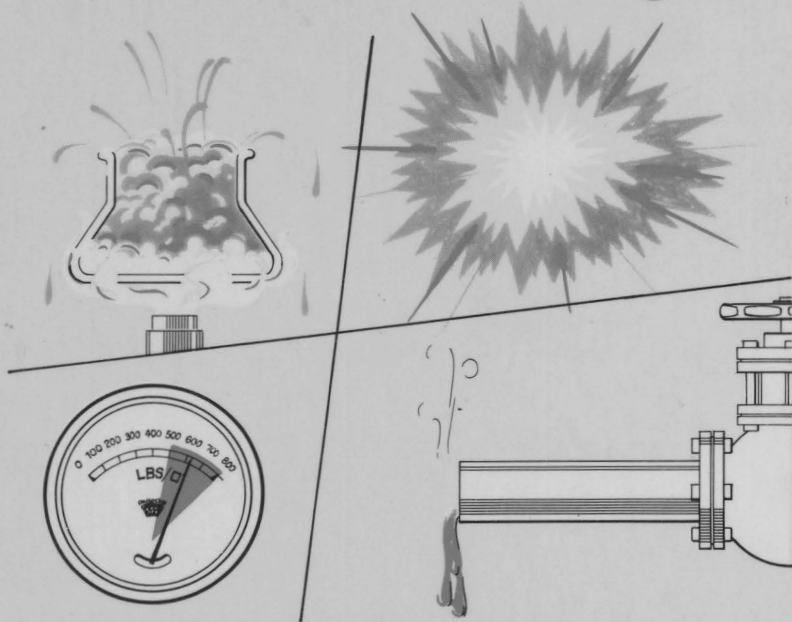


European Federation of Chemical Engineering  
Europäische Föderation für Chemie-Ingenieur-Wesen  
Fédération Européenne du Génie Chimique

EFCE Publication Series No. 59

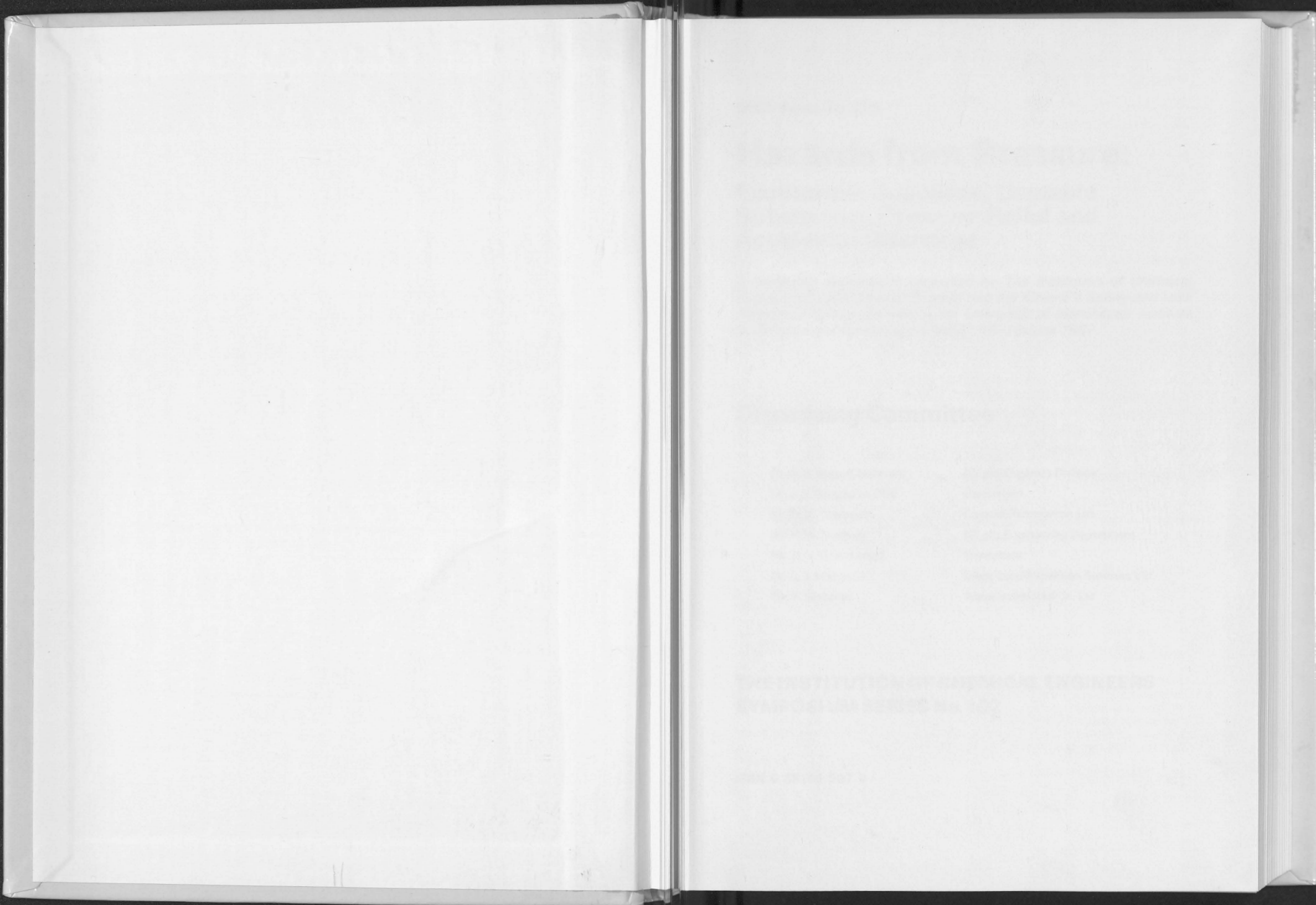
# Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge.



The Institution of  
Chemical Engineers

Pergamon  
Press





EFCE Event No. 359

# Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge

*A three-day symposium organised by The Institution of Chemical Engineers (North Western Branch) and the IChemE's Safety and Loss Prevention Group and held at the University of Manchester Institute for Science and Technology (UMIST), 16-18 June 1987.*

## Organising Committee

Dr. N. Gibson (Chairman)	ICI plc, Organics Division
Dr. J. H. Burgoyne, CBE	Consultant
Mr. B. A. Czarnecki	Costain Petrocarbon Ltd.
Mr. H. A. Duxbury	ICI plc, Engineering Department
Mr. D. V. Greenwood	Consultant
Dr. A. J. Margetts	Lihou Loss Prevention Services Ltd.
Mr. P. Webster	Associated Octel Co. Ltd.

**THE INSTITUTION OF CHEMICAL ENGINEERS  
SYMPOSIUM SERIES No. 102**

ISBN 0 85295 207 4



## PUBLISHED BY THE INSTITUTION OF CHEMICAL ENGINEERS

Copyright © 1987 The Institution of Chemical Engineers

*All rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the copyright owner.*

First edition 1987 - ISBN 0 85295 207 4

### MEMBERS OF THE INSTITUTION OF CHEMICAL ENGINEERS (Worldwide) SHOULD ORDER DIRECT FROM THE INSTITUTION

Geo. E Davis Building, 165-171 Railway Terrace, Rugby, Warks CV21 3HQ.

#### *Australian orders to:*

R M Wood, School of Chemical Engineering and Industrial Chemistry,  
University of New South Wales, PO Box 1, Kensington, NSW, Australia 2033.

**Distributed throughout the world (excluding Australia) by Pergamon Press Ltd,  
except to IChemE members.**

U.K.	Pergamon Press Ltd., Headington Hill Hall Oxford OX3 0BW, England.
U.S.A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon Press Canada Ltd., Suite 104, 150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada
FEDERAL REPUBLIC OF GERMANY	Pergamon Press GmbH, 6242 Kronberg-Taunus, Hammerweg 6, Federal Republic of Germany
JAPAN	Pergamon Press, 8th Floor, Matsuoka Central Building, 1-7-1 Nishishinjuku, Shinjuku-ku, Tokyo 160, Japan
BRAZIL	Pergamon Editora Ltda, Rua Eça de Queiroz, 346, CEP 04011, São Paulo, Brazil
PEOPLES REPUBLIC OF CHINA	Pergamon Press, Qianmca Hotel, Beijing, People's Republic of China

#### **British Library Cataloguing in Publication Data**

Hazards from pressure: exothermic reactions, unstable substances, pressure relief and accidental discharge: a three-day symposium - (EFCE event; no. 359). - (The Institution of Chemical Engineers symposium series; no. 102), 1. Hazardous substances 2. Chemical industries - Safety measures

I. Gibson, N, II. Institution of Chemical Engineers, *North Western Branch III. Safety and Loss Prevention Group IV. Series V. Series 660.2'804 TP149*

ISBN 0-08-034820-3 Pergamon

## PREFACE

Exothermic reactions, unstable substances, pressurised systems and accidental discharges can lead to hazardous situations in the process industries if they are not under control. Safe manufacturing practice requires constant vigilance and the adoption of systematic procedures to assess sources of potential risk, to define safety operating procedures and to implement and maintain such measures.

Symposia were organised by the North Western Branch of the Institution of Chemical Engineers in 1981 and 1984 on Runaway Reactions, Unstable Products and Combustible Powders and on the Protection of Exothermic Reactors and Pressurised Storage Vessels.

Since these symposia, considerable advances have been made in our knowledge of these topics. This symposium will assemble the most up to date information, with expert reviews of current art being supplemented by reports of recent advances.

The papers contribute to all the essential stages of understanding hazard technology, identifying hazards in particular processes, analysing and assessing risk, and defining and maintaining safe operating procedures.

The discussion sessions and informal contacts will provide an invaluable opportunity for participants from universities, industry and the regulatory authorities to exchange information on process safety.

NORBERT GIBSON

## ERRATA

Page 75, last paragraph, 5th line from bottom – 1.5 should read 1.05.

Page 117, Table 2, last column – 144.1 should read 1441.

Page 202, first paragraph, line 5 should read "offensive substances and of rendering them harmless or"

Page 218, Equation (2) should read:

$$\dot{m} = \frac{C_D A_r P_s}{\sqrt{Z R T_s}} \sqrt{\delta \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}}}$$

where the units of R are J/kg/°K

Pages 230 and 231, Tables 1 and 3 should be replaced by the following:

	1/4 tonne		1 tonne		5 tonne			
	40%	80%	40%	20%	80%	60%	40%	20%
Percentage fill (nominal)	40%	80%	40%	20%	80%	60%	40%	20%
Tank total surface area (m <sup>2</sup> )	3.8	10.4	10.4	10.4	27.7	27.7	27.7	27.7
Wetted surface area (m <sup>2</sup> )	1.68	6.28	4.32	3.02	18.1	15.2	11.3	8.7
Initial vol. of propane (l)	185	1635	789	308	7640	5900	3676	2250
Initial depth of liquid (m)	0.22	0.68	0.35	0.18	1.17	.934	.66	.474
Ambient temperature (°C)	5	14.0	-3	-3	9.5	12	1.5	11
Initial tank pressure (bar)	5.5	6.1	4.1	4.1	4.8	4.6	4.2	5.5
Initial propane mass (kg)	100	870	420	160	3860	3109	1930	1170
Average wind speed (m/s)	-	-	-	-	4.7	4.8	4.6	1.3

	1/4 tonne		1 tonne		5 tonne			
	40%	80%	40%	20%	80%	60%	40%	20%
Percentage fill	40%	80%	40%	20%	80%	60%	40%	20%
Av. heat flux into propane before PRV opens (kW/m <sup>2</sup> )	73	84	59	33	61	76	68	56
Av. Heat flux into tank wall before venting (kW/m <sup>2</sup> )	14	5	4	12	9	6	7	9
Av. heat flux into propane during venting (kW/m <sup>2</sup> )	85	50	54	76	-	53	66	43
Av. heat flux from the fire to water calorimeter (kW/m <sup>2</sup> )	-	-	-	-	77	-	80	79
Av. boil-off rates (kg/s)	-	-	-	-	1.4	1.9	2.2	1.0

Page 262, Figure 3 should appear as follows:-

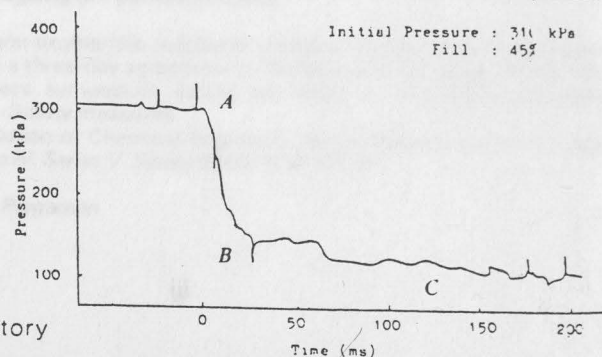


FIGURE 3 -  
Internal Pressure History

## CONTENTS

### Unstable Substances

1. Pressure rise during homogeneous decomposition and deflagration. *T. Grever and O. Klais (Hoechst AG)* 1
2. Calcium hypochlorite. A fire and explosion hazard. *V.J. Clancey (Burgoyne Consultants Ltd)* 11
3. Methane formation during hydrogenation reactions in the presence of Raney nickel catalyst. *O. Klais (Hoechst AG)* 25
4. Case studies on unstable substances. *J. Bond (BP Chemicals Ltd)* 37
5. Spontaneous ignitions in dust layers: comparison of experimental and calculated values. *B.J. Tyler and D.K. Henderson (UMIST)* 45

### Reaction Stability

6. Review Paper: Chemical reaction hazards: an integrated approach. *N. Gibson, R.L. Rogers and T.K. Wright (ICI plc)* 61
7. Isothermal heat flow calorimeter. *T.K. Wright and C.W. Butterworth (ICI plc)* 85
8. A simple method of estimating exothermicity by average bond energy summation. *A.D. Craven (Burgoyne Consultants Ltd)* 97
- †\*9. Heat transfer from exothermically reacting fluid in vertical unstirred vessels. *J.R. Bourne (ETH, Zurich), F. Brogli, F. Hoch and W. Regenass (Ciba-Geigy AG)* 315
10. A strategy for thermal hazards assessment in batch chemical manufacturing. *J.L. Cronin, P.F. Nolan (Polytechnic of the South Bank) and J. A. Barton (Health and Safety Executive)* 113
- \*11. Procedures for the safety assessment of programmable logic controllers used for reactor trip systems. *A.J. Margetts (Lihou Loss Prevention Services Ltd.,)* 301

\* These papers are printed out of page sequence.

† This paper was received in summary form only. The full paper is to be published in Chemical Engineering Science.



## Vessel Pressure Relief

12. Pressure relief and venting: some practical considerations related to hazard control. 133  
*H.K. Fauske (Fauske & Associates Inc)*
13. A computer model for sizing two-phase emergency relief systems, validated against DIERS large scale test data. 143  
*H.H. Klein (Jaycor, USA)*
14. Case studies in the application of DIERS venting methods to fine chemical batch and semi-batch reactors. 157  
*N. Gibson, N. Maddison and R.L. Rogers (ICI plc)*
15. Calculation methods for reactor relief: a perspective based on ICI experience. 175  
*H.A. Duxbury and A.J. Wilday (ICI plc)*
16. The use of DIERS methods for two phase relief of vaporisers. 187  
*A.J. Wilday (ICI plc)*

## Discharges

17. Review Paper: Safe disposal of relief discharges. 201  
*J.H. Burgoyne (Dr.J.H. Burgoyne & Partners)*
18. Flow through pressure relief devices and the dispersion of the discharge. 215  
*K. Moodie and S.F. Jagger (Health and Safety Executive)*
19. Two phase flashing releases following rapid depressurisation due to vessel failure. 247  
*R.J. Bettis, P.F. Nolan (Polytechnic of the South Bank) and K. Moodie (Health and Safety Executive)*
20. Leakage through cracks: the applicability of available prediction methods. 265  
*L. Friedel (Hoechst AG) and F. Westphal (Universität Dortmund)*
21. Flaring of natural gas from inclined vent stacks. 289  
*D.K. Cook, M. Fairweather, G. Hankinson and K. O'Brien (British Gas Corporation)*

## Discussion of Papers.

325

## Index

## Pressure rise during homogeneous decomposition and deflagration

Th. Grewer and O. Klais, Hoechst AG, Frankfurt/M.

Only a small part of the non-explosive substances are deflagrable. But a number of incidents have been caused by their deflagration. We have measured the temperature-time curves of the deflagration of some of these substances in a closed vessel. The rate of pressure increase was to a first approximation proportional to the pressure, except for one substance where it was proportional to a higher power of pressure. The pressure-time-curves of homogeneous decomposition were also measured but were more complicated than the results of the deflagration measurements.

Keywords:- pressure rise, homogeneous decomposition, deflagration,

The progressive exothermic decomposition of substances, commonly known as "deflagration", has frequently led to unpleasant incidents in the chemical industry. While it is true that only a small proportion of the substances produced are capable of deflagration, for the few that are the probability of its occurrence is especially large.

Deflagration is a familiar process in rocket fuels and explosives. In these cases the process is usually rapid and can easily become a detonation. Here we wish to consider slow deflagration which can appear in certain chemical compounds as an undesirable occurrence. These substances are usually not capable of detonation.

The following table lists some of these substances that are capable of deflagration and shows their deflagration rates [cf. 1].

Table 1: Deflagrable substances

Substances	Deflagration rate (cm/min)
4-Nitrosophenol	8
1-Nitrosophthal-(2)	0.74
Hydroxylammonium sulfate	5.6
Ammonium dichromate	2.2
Sodium-3-nitrobenzene sulfonate	4.5
Diphenyltriazene	2.0
Pigment orange CI 12075	1.8