The British Plastics Federation

Reinforced Plastics Group
47 Piccadilly London W1V 0DN

REINFORCED PLASTICS CONGRESS 1976

Innovation – The Basis of Reinforced Plastics

The British Plastics Federation Reinforced Plastics Group

The BRITISH PLASTICS FEDERATION is the representative body of the plastics industry in the United Kingdom. It co-ordinates the efforts of its members to expand trade, both at home and overseas, by providing a forum in which technical standards for plastics are prepared and other matters of technical and commercial interest discussed. It also advises government departments on matters relating to plastics.

The activities of the British Plastics Federation are undertaken by twelve groups, each dealing with a specific aspect of the plastics industry. A group for reinforced plastics was established in 1958.

Reinforced plastics have achieved prominence as strong lightweight materials with unique moulding characteristics and properties which clearly distinguish them from other plastics. The British Plastics Federation, as early as 1952, set up a technical committee on glass fibre and asbestos reinforced plastics to cater for the problems of this new industry. As the industry expanded, the committee grew until it necessitated the formation of a group.

The aim of the REINFORCED PLASTICS GROUP is to promote in every way the interests of the industry:

1 By tackling technical and commercial problems associated with raw materials, fabrication and machinery.

2 By co-operating with outside agencies (e.g. government departments and other organisations) in the use of reinforced plastics.

3 By establishing and maintaining good relations with the press.

4 By the encouragement of research to widen the knowledge of the behaviour of reinforced plastics and to establish design criteria.

Any British manufacturer concerned with reinforced plastics is eligible for membership. The Group includes fabricators, suppliers of resins, reinforcements and ancillary materials, and machinery manufacturers.

The technical work of the Group is undertaken by the Technical Committee to which all members of the Group are entitled to send representatives. Thus it is a committee fully representative of the various elements that make up the reinforced plastics industry. The Technical Committee appoints sub-committees to deal with specific matters and currently topics such as specifications for polyester resin, reinforcing fillers and sheet and dough moulding compounds, methods of testing and design data are being studied. In all its technical work the Group is aided by co-opted representatives from appropriate government departments and other authorities. The Group gives assistance to the British Standards Institution and to other official bodies in the preparation of standards or codes of practice. The Group Management Committee organises biennially an International Conference on Reinforced Plastics which has become recognised throughout the world for its contribution to progress in the Industry. On other occasions informed discussion meetings are held for Group members only.

Membership of the Reinforced Plastics Group of the British Plastics Federation provides the opportunity:

1 To have access to the full resources and share in the activities of the British Plastics Federation, and its publicity and opportunities for business.

2 To share in the combined knowledge of the members of the group.

3 To contribute to the preparation of standards and design data for the industry through which public confidence in reinforced plastics can be upheld.

4 To join with the rest of the industry to expand trade in reinforced plastics.

5 To attend the various technical functions of the group.

6 To belong to the only UK trade association concerned with reinforced plastics.

7 For close collaboration with overseas reinforced plastics organisations.

Quality Mark

Reinforced Plastics is a unique high performance engineering material falling into that materials group known as composites, and it is a well proven engineering material. However, the products fabricated in reinforced plastics are only as good as the expertise of the companies making them. The Quality Mark was created by the Reinforced Plastics Group of the British Plastics Federation to assist the many companies, specifying authorities and end users to call upon existing standards and to ensure compliance with good practice in the production of reinforced plastics.

One of the reasons why the material is unique is that the reinforced plastics composite is produced at the same time as the product in the moulding fabrication process. Therefore, the product can only give the performance requirements if the material has been produced correctly under controlled conditions.

The possession of the Award indicates that the Company offers reinforced plastics products which are produced under tightly controlled conditions and the exacting standards of the Code of Practice embodied in the Quality Mark Scheme.

The basis of the Quality Mark Scheme is the Code of Practice which indicates factory conditions for production together with basic material specifications.

A company holding the Award will have proved that the exacting standards and practices contained in the Code of Practice are met. The Company's factory will have been thoroughly inspected by Lloyd's Register Industrial Services (LRIS) and will be subject to periodic inspection by that organisation.

The Quality Mark is a mark of quality, reliability, stability and confidence.

Groupement des Plastiques Renforces du Marche Commun

(Organisation of the Reinforced Plastics Associations of the Common Market) – GPRMC

The GPRMC organisation is constituted of national trade organisations of the countries of the EEC, regarded as representatives of the Reinforced Plastics Industry.

The Reinforced Plastics Group joined GPRMC in November, 1973 and has played an important role in its development. The aim of the GPRMC is to promote and protect, the common professional interests of the reinforced plastics associations and to ensure regular liaison between its members.

The GPRMC's main task is the examination of special problems arising in the technical, economic and social fields via the medium of working parties of experts.

The Committee de Direction is actively considering the adoption of the 'Quality Mark' and the feasibility of staging a European Reinforced Plastics Congress during 1979.

INNOVATION

– The Basis of Reinforced Plastics

REINFORCED PLASTICS CONGRESS 1976

Programme and Index

Monday 8 November

Delegates assemble

18.30–19.30	Civic Reception given for delegates by His Worship The Mayor and Corporation of Brighton in the Banqueting Room of the Royal Pavilion	

Tuesday 9 November

Congress Chairman: Chairman of the Reinforced Plastics Group, A. Craig

Chairman of Sessions: S. R. Badley, MBE

09.00	Opening of the Congress	Chairman: A. Craig, BTR Reinforced Plastics Limited
09.15	*Session 1: Innovation in basic materials and resins*	
	Paper 1 *page 11* The recent advances in phenol formaldehyde systems for GRP building applications	T. J. Stonley, Synthetic Resins Ltd., UK
	Paper 2 *page 25* A new high performance corrosion resistant resin	T. R. Loader and J. A. Sturrock, Atlas Chemical Industries NV, Belgium
	Paper 3 *page 31* The use of urethane rubber/epoxide resin blends as matrix materials for carbon and glass fibre composites	H. Wells and N. L. Hancox, Atomic Energy Authority, UK
	Support Papers	
	A *page 39* Kinetics and mechanism of polyesterification	I. J. Alexander, Scott Bader Company Limited, UK
	B *page 47* The moulding of phenolic resin impregnated carbon fibre to produce high quality laminates	M. J. Fry, C. R. Thomas and E. J. Walker, Ministry of Defence (PE), AWRE, Aldermaston, UK
	C *page 55* Contourkore ® in the growing GRP market	G. D. Dohn, Baltek Corporation, New Jersey, USA
10.00	Discussion	
10.45	Coffee	

11.15	*Session 2: Innovation in compounds and ancillaries*	
	Paper 4 *page 63* The rheology of glass fibre reinforced polyester moulding compounds	R. Burns and K. S. Gandhi, Pilkington Brothers Limited, UK
	Paper 5 *page 71* Polyester moulding compounds — comparison of in-house manufacture with packaged	Trevor Dawson, Freeman Chemicals Ltd., UK
	Paper 6 *page 77* Use of hollow silicate spheres of Q-cel in glass-fibre reinforced and syntactic foam cores	D. I. Netting, C. G. Smith and A. L. Tund, Philadelphia Quartz Company, USA
	Paper 7 *page 85* The influence of the initiation on the ultimate properties of unsaturated polyester resins	L. Roskott and A. A. M. Groenendaal, Akzo Chemie Netherland b.v., Netherlands A. J. Seager, Akzo Chemie UK Ltd, UK
12.10	Discussion	
13.00	Lunch	
14.15	*Session 3: Innovation in transport applications*	
	Paper 8 *page 93* A contribution to the safety design of FRP cars	Shoji Shimamura, Kimio Ishine and Collision Test Group of Mechanical Engineering Laboratory, Japan
	Paper 9 *page 101* Reinforced plastics in the development of transit containers	B. Baker and F. H. Bayley, EPS (Research & Development) Limited, UK
	Paper 10 *page 109* The influence of changing criteria on the choice of GRP	F. J. Parker, British Industrial Plastics Ltd., UK
	Paper 11 *page 117* Optimizing economical benefits by design and integration of SMC parts for vehicle bodies	K. Garholm and E. Johansson, Aktiebolaget Trelleborgplast, Sweden
15.00	Discussion	
15.45	Tea	
16.15	*Session 4: International Status Reports*	
	Page 123 Status, of reinforced plastics in Benelux, France, Germany, Italy, Spain and Switzerland.	Guy Gintrand, Saint Gobain Industries, France
	Page 125 Glass reinforced polyester in Israel	S. N. Abrahami, Ziklag Chemical Products Limited, Haifa
	Page 127 Glass fibre reinforced plastics in the UK	M. S. Monkhouse, TBA Industrial Products Ltd, Rochdale, England
	Page 129 Status of reinforced plastics in the USA — 1976	P. Robert Young, P. Robert Young Associates, Brooklyn, NY
	Page 133 Reinforced plastics in Zambia	K. J. Shaw, Prodorite (Zambia) Limited, Kitwe, Zambia

During the Congress other International Delegates will give presentations and reports on their countries.

	Wednesday 10 November	
09.00	*Session 5: Innovation in processing technology*	
	Paper 12 *page 135* Pultrusion of glass reinforced polyester — a new approach in the UK	R. A. Spencer, BTR Reinforced Plastics Limited, UK
	Paper 13 *page 143* Mechanized GRP production methods	Frank Ives and Monte Martinez, Venus Products Inc., USA
	Paper 14 *page 145* The production of reinforced thermoplastics and thermosettings on continuous mixers	Dr. R. Gentili and K. H. Stade, Buss AG, Basle, Switzerland
	Paper 15 *page 151* Bolting and riveting in fibre reinforced plastics	F. L. Matthews, A. Nixon and G. R. Want, Aeronautics Department, Imperial College, London, UK
10.00	Discussion	
10.45	Coffee	
11.15	*Session 6: Mechanical properties*	
	Paper 16 *page 161* Determination of the mechanical and elastic properties of pultrusion glass reinforced polyester profiles	Dr. U. Korin, Building Research Station, Technion, Haifa, Israel
	Paper 17 *page 167* Progress towards a safe-line design method for glass reinforced plastics under fatigue loading	M. J. Owen, Department of Mechanical Engineering, University of Nottingham, UK
	Paper 18 *page 175* Accelerated ageing of isophthalate and orthophthalate GRP laminates in relation to exposure conditions	A. Allavena, Amoco Chemicals SA, Switzerland L. Mascia, University of Aston, UK
	Paper 19 *page 183* Static and dynamic interlaminar strength of glass reinforced plastics thick laminates	Isao Kimpara and Mitsuo Takehana, University of Tokyo, Japan
	Support Paper	
	D *page 193* The fatigue behaviour of some glass reinforced plastics	A. O. Ankara, Middle East Technical University, Ankara, Turkey B. Harris, University of Bath, UK
12.15	Discussion	
13.00	Lunch	
14.10	*Session 7: Innovation in high performance composites*	
	Paper 20 *page 199* The special problems of high performance structures	J. Fray, Hawker Siddeley Aviation Ltd., UK
	Paper 21 *page 207* On the usefulness of glass fibre-carbon hybrids	L. N. Phillips, Royal Aircraft Establishment, UK

	Paper 22 *page 213*	
	The potential influence of research on mechanical design	F. J. Lockett, National Physical Laboratory, UK
	Paper 23 *page 221*	
	Carbon-fibres — performance and versatility in new applications	E. M. Trewin, Courtaulds Ltd., Carbon Fibres Unit, UK
	Support Paper	
	E *page 227*	
	The effects of mineral acids on the insulation properties of GR epoxy resin	R. Sheldon and G. Stapleton, Science Research Council, Rutherford Laboratory, UK
14.50	Discussion	
15.30	Tea	
15.40	*Session 8: Innovation in construction applications*	
	Paper 24 *page 229*	
	European long distance heat transportation plans create massive potential opportunities for FRP	N. Sprecher, Owens-Corning Fiberglas Europe SA, Belgium
	Paper 25 *page 241*	
	Modular GRP systems for station structures	B. J. Hawthorne and B. L. Merret, British Railways Board, UK
	Paper 26 *page 247*	
	Sanitary and building components from resin-concrete (the Marlit method)	S. D. Pikoulis, Building Materials Research Laboratories SA, Athens, Greece
	Paper 27 *page 255*	
	Analysis of the use of glass reinforced plastics in the construction industry	A. Jaafari, L. Hollaway and M. L. Burstall, University of Surrey, UK
16.20	Discussion	
17.00	Session ends	
19.30 for 20.00	Congress Dinner	
	Guests of Honour — Sir David Nicolson, FCGI BSc CEng FRSA (Chairman, BTR Ltd.), and Lady Nicolson	

Thursday 11 November

09.15-11.45 *Session 9: Debate on the motion*

That Reinforced Plastics has failed to take advantage of the opportunities presented by the Engineering Industry

For the motion:

Proposer — Michael Abrahams, PhD BSc MIMechE
Plastics Engineering Director
GKN Sankey Ltd

Seconder — George F. Sly, FPI MBIM
Managing Director
British Industrial Plastics Ltd
Chairman — Moulding Division and Engineering Division

Against the motion:

Proposer — Leslie Ainsworth, BSc PhD FInsP FPRI FSGT
Managing Director
Modern Composites Ltd

Seconder — Dennis H. Bowen, BSc PhD
Leader — Advanced Engineering Materials Group
Manager — Harwell Carbon Fibre Project
AERE, Harwell

11.45 Closing of Congress

A. Craig — Chairman, Reinforced Plastics Group

The recent advances in phenol formaldehyde systems for GRP building applications

T. J. STONLEY, Synthetic Resins Limited, UK

SUMMARY

During the past decade, there has been an increasing usage of GRP for building applications. Glass reinforced polyester resin has achieved a significant penetration into the functional and decorative building panel market for both internal and external components. Architects and engineers have been attracted to these systems in single skin or composite form by the design freedom and ease of fabrication. Whilst satisfying most of the structural design requirements, current GRP materials are unable to fully eliminate the increasing fears of authorities in relation to (i) flammability (ii) smoke emission and (iii) toxic fumes.

This paper examines recent advances in phenol formaldehyde resins for the manufacture of both glass reinforced laminates and composite foam systems. These P/F resin systems offer a major step forward in improved fire properties required by the building and other industries. The paper also discusses the part that it is felt that P/F resin systems will play in the development and expansion of the GRP industry into new and diversified applications and markets

BACKGROUND

The reaction between phenolics and aldehydes was first described by Adolf Baeyer in 1872 (Reference 1). In some cases, such as the reaction between pyrogallic acid and benzaldehyde, crystalline compounds were obtained, and since early organic chemists were primarily interested only in pure compounds, which could be crystallised and identified, the resinous reaction between phenol and formaldehyde received little attention until the period 1890-1910. The principal aim of the investigations during this period was the production of artificial shellac; none was particularly successful.

The now classical work of Dr. Baekland provided the foundation of the phenolic industry as we know it today.

He filed his first patents in 1907 and published his work 1909, disclosing the basic principles which were that the use of acids and alkalies was catalytic. He also showed that different resins were produced depending on whether an acid or an alkali was used as a catalyst. Furthermore, he made two proposals to overcome the difficulties experienced in moulding phenolic resins, these were

(i) the use of filler such as wood flour to overcome brittleness and achieve dimensional stability.

(ii) the use of heat and pressure during moulding—this obviated bubbling and porosity.

This heat and pressure patent can be said to have heralded the growth of phenolic resins.

During the first stages, phenolic resins were principally used in the manufacture of insulating parts for the electrical industry. The rapid growth of the electrical and radio industries helped to accelerate their wider use. Likewise with the introduction of 'horseless carriages', demand for an alternative to wooden brake shoes was satisfied by the introduction of phenolic bonded asbestos ones.

The second World War focused on the need for plastic parts with high mechanical properties, (Refs. 2, 3, 4, 5, 6) phenolic foams saw limited use in structural applications

Early research showed that fabrics and papers could be impregnated with phenolic resins and laminated to produce tough sheets. Hence a high pressure laminate industry grew up side by side with that of a press moulding one.

Other large volume uses for phenolic resins are:-

(i) bonding of plywood

(ii) abrasive wheels and cloths

The early foaming process for a phenolic system consisted of catalysing a liquid blend of resole type resin with an acid hardening agent in the presence of a low boiling point solvent, or to generate CO_2 or N_2 internally from carbonates or azo compounds. Whilst the excellent fire properties of phenolic foams were recognised and some acceptance was established in the early 1960's in a number of applications (e.g. roof decking and sandwich panels), the improved physical properties of urethane foams and their greater ease of processing resulted in their total dominance over the available phenolic foams. However, in recent years, this balance is now being redressed due to the availability of improved cure systems and processing equipment for phenolics. Furthermore, the ever increasing demand for improved fire properties of building materials has stimulated further development of the phenolic foam resin system to provide the industry with a complimentary low temperature cure phenolic laminating resin material.

INTRODUCTION TO RESIN SYSTEMS FOR LAMINATING AND FOAM REACTIONS

Both the resin and acid hardener systems developed are prepared from the condensation reaction of a phenol and formaldehyde in aqueous solution. The resin is a typical resole, Uravar 101, (R1), and the hardener a typical novolak, Uravar Z-102, (R1). Fig. 1 depicts the type of reaction paths used in general resole production.

It has been known for many years that the acidification of a

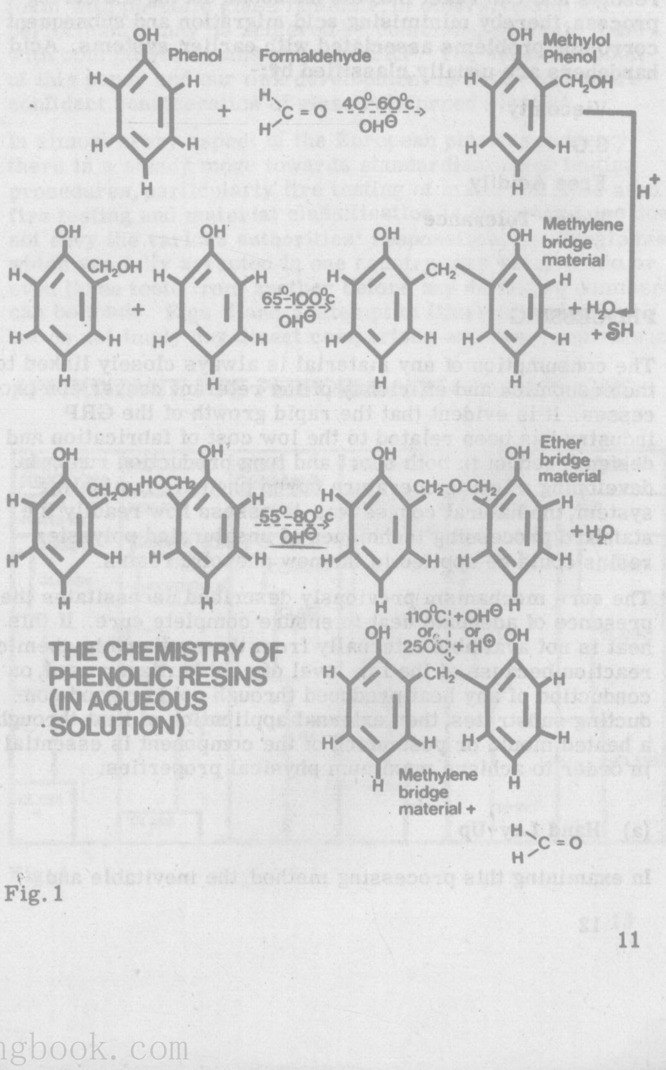


Fig. 1

phenol resole will cause it to cure with the generation of a quantity of heat, i.e. an exothermic reaction. Resole resins, by definition, are manufactured from phenols and a molar excess of formaldehyde, normally using alkaline catalysts, and have free methylol groups attached to the resin backbone. These methylol groups are unstable under acidic conditions, reacting immediately to form methylene bridges with the evolution of heat. (See Fig. 1, again).

It is this reaction we utilise for the manufacture of phenolic foams; the heat generated during the curing process being utilised to vapourise a low boiling point solvent.

The main characteristics of a resole which governs the reaction speed are methylol content, molecular size, free phenol content and pH. Viscosity is essentially a measure of molecular size and as such has a great bearing on the reactivity of the resole to the hardener. In general, a resin of high viscosity has a slower exothermic build-up than one of a lower viscosity, and as a result will not cure as fast or reach as high an exothermic temperature.

The free phenol content of a resin also influences reactivity; low free phenol content giving rise to a slow cure. The main parameters for classifying resoles are:-

Solids Content
Viscosity
S.G.
pH
Refractive Index
Peak Exotherm
Free Phenol Content
Free Formaldehyde Content
Water Content

Phenolic resole cure can be achieved by the addition of a variety of organic and inorganic acids. Preferred acids are those which have good compatibility with, and which can crosslink with the resin system.

Hardeners of the type Uravar Z-102 are in effect phenolic resin acids which have excellent compatibility with phenolic resoles and can react into the backbone during the curing process, thereby minimising acid migration and subsequent corrosion problems associated with earlier systems. Acid hardeners are usually classified by:-

Viscosity
S.G.
Free Acidity
Water Tolerance

PROCESSING

The consumption of any material is always closely linked to the economics and efficiency of the relevant conversion processes. It is evident that the rapid growth of the GRP industry has been related to the low cost of fabrication and design freedom in both short and long production runs. In developing a low temperature cured phenolic laminating system, the natural course was to assess how readily the standard processing techniques of unsaturated polyester resins could be applied to the new phenolic resins.

The cure mechanism previously described necessitates the presence of adequate heat to ensure complete cure. If this heat is not available internally from the exothermic chemical reaction because of the low level of acid hardener used, or conduction of any heat produced through cold or good conducting substrates, then external application of heat through a heated mould or postcuring of the component is essential in order to achieve maximum physical properties.

(a) Hand Lay-Up

In examining this processing method, the inevitable and immediate demand was to provide comparable cure and pot-life characteristics to the established unsaturated polyester resins. However it became evident that moulding became limited to small components since the minimum hardener level required to give ambient temperature cure gave only a 5-10 minute pot-life in a 1 kgm mass. The problem was obviated by using moulds with integral heating facilities; this allowed the use of lower hardener levels which gave an extended pot-life of 25-30 minutes.

(b) Spray-Up and Hand Lamination

This method overcame the short pot-life problem and involved the use of an air driven dispenser specially developed for use with these phenolic systems. The dispenser is based on a two pot, positive displacement pump system capable of handling resin: acid ratios of from 1 : 1 up to 20 : 1.

It has been shown that with this technique medium sized mouldings can be manufactured either with chopped roving or resin spray consolidation of glass mat.

(c) Resin Injection

This is an ideal method of processing low temperature cured phenolics and involves use of the dispenser as described above. Resin injection is a process well known in the industry and involves the injection of resin into a closed mould and then through the continuous filament glass fibre mat. This reinforcement is held in a pinch off which acts as a constriction to the resin which preferentially displaces air as the mould is filled under pressure from the dispenser.

Depending upon the type and material used for the mould construction, demould times of 5-10 minutes can be achieved after the tool has warmed up a little after the production of 4-5 components.

The technique can be extended from a single skin laminate to produce composites where a phenolic foam core is fully encapsulated with a phenolic laminate. The strength and integrity of such components can be greatly improved by the incorporation of resinated ribs during the resin injection process.

(d) Cold Press Moulding

This process is well established with unsaturated polyesters and lends itself, with few modifications, to cold cure phenolic resins.

In all the above techniques, standard mould construction and materials as used for polyester moulding are adequate. Needless to say, moulds utilising internal heaters capable of producing mould face temperatures of 40-50°C need gelcoats of high heat distortion characteristics.

Mould release systems for phenolic laminates are the conventional waxes but use of polyvinyl alcohol based membranes is not possible due to a chemical interaction between the membrane and the phenolic acidic hardener.

The above process are predominantly labour intensive. However, phenolic resins can be effectively processed on a continuous basis e.g. sheeting manufacture. The phenolic foam resins, upon which the laminating products are based, are already processed as continuous block foam, continuous paper faced foam, and by in situ injection and spray deposition of foam.

FIRE PROPERTIES OF PHENOLIC SYSTEMS

The behaviour of polymeric materials when subjected to the very high temperatures experienced in fires may be separated into three distinct problem areas:-

(i) Flame initiation and propagation
(ii) Smoke emission
(iii) Toxic fumes emission.

All known plastics will burn and whilst it is possible to prevent flame initiation and propagation by the use of suitable additives, it is not possible to prevent the ultimate thermal degradation of the base polymer.

This burning or thermal degradation proceeds by a splitting of the polymer backbone and the releasing of small incompletely oxidised polymer fragments which may or may not ignite. Neverthless this breakdown gives rise to large volumes of toxic smoke and fumes (e.g. HCN, HCl, Phosgene etc.). New surfaces are continually presented to the heat source which gives rise to unabated combustion. Flame retardant additives to reduce flame initiation are invariably toxic chemicals in their own right and increase the hazard.

When a fully cured phenolic (or resite) is subjected to fire conditions, it undergoes complete oxidation to a graphaceous char. This resultant carbon char acts as a barrier and effectively shields the substrate from the heat source. A classic example of this is the ablative heat shield on space re-entry vehicles.

Whilst it is difficult to show in simple terms the improved performance of phenolics in fire and high temperature conditions, some insight has been given by utilisation of thermogravimetric analysis (T.G.A.). It has been suggested (Reference 7) that the thermal degradation of cured phenolic systems takes place in three basic stages each of which may comprise of a large number of separate reactions:-

(i) Up to 300°C, post curing and loss of water occurs

(ii) From 250°C-600°C, thermal reforming occurs.

(iii) Over 700°C, ring stripping takes place with the loss of hydrogen and a more or less disordered graphitic structure is formed.

Our own work has tended to confirm these observations. Fig. 2 shows a typical TGA comparison of cured phenolic and cured polyester systems

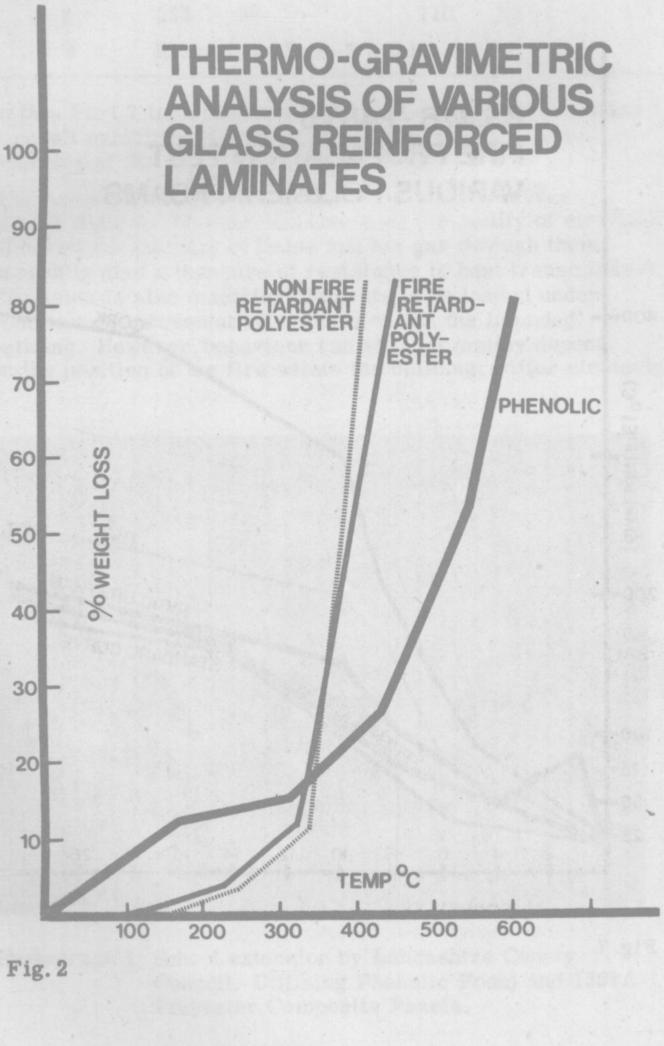


Fig. 2

It can be seen that up to 300°C, the phenolic system further condenses with a subsequent loss in weight of up to 15% by weight water. The polyesters, both fire retardant and non fire retardant appear to be more stable up to 300°C. However, the weight loss in these two systems has been accounted to primary gas formation (e.g. methane). In excess of 300°C the phenolic system performs far more stably than the polyester systems because the phenolics are only undergoing thermal reforming whereas the polyesters, even the fire retardant ones, are undergoing thermal degradation of the polymer backbone.

Another approach to thermal stability of polymeric materials is the Setchkin test for ignition temperatures. Fig. 3 shows figures obtained by RAPRA. Evaluations carried out in our own laboratories has also shown that in the absence of glass, phenolic castings do not ignite up to a temperature of 700°C.

IGNITION TEMPERATURES ON VARIOUS MATERIALS BY SETCHKIN TEST

MATERIAL	FLASH IGNITION TEMP. °C	SELF-IGNITION TEMP. °C
PHENOLIC GRP	520·540	571·580
POLYESTER GRP	346·399	483·488
PHENOLIC FOAM	565	615
RIGID P.U. FOAM	310	416

SOURCE: RAPRA REPORT AO207 NOV. '74.

Fig. 3

It is therefore evident that for GRP to expand at a rate greater than that of natural market growth and sustain wider acceptance for plastics in building applications, confidence in fire performance has to be improved. It is the belief that phenolic resins have the capability to make a significant contribution to this expansion. In some instances, stringent requirements will necessitate the use of phenolic foam with phenolic glass laminate; in others, optimised performance may be achieved by combining phenolic foam with both polyester and phenolic GRP. The essential point of this paper and our own development is wider and more confident consideration of glass reinforced plastics.

In almost every aspect of the European plastics industry, there is a steady move towards standardisation of testing procedures, particularly fire testing of materials. This area of fire testing and material classification is one where one does not envy the various authorities' responsibilities. Single tests which are fully accepted in one country may require two or even three tests from another before any definitive comment can be made. Figs 4 and 5 attempt to illustrate this point but do not imply any direct comparison and exact equivalence.

APPROXIMATE FIRE PERFORMANCE COMPARISONS

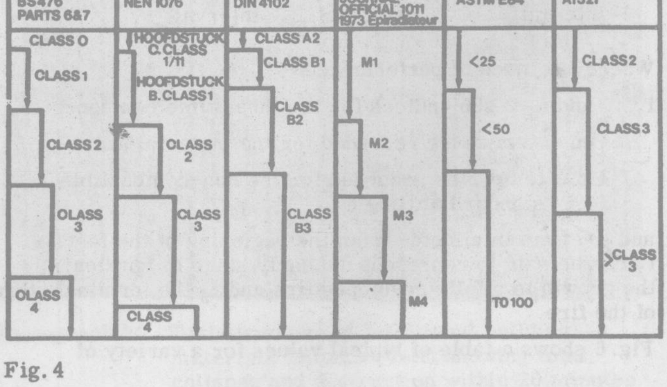


Fig. 4

FIRE TESTS ON MATERIALS: SIMILAR TESTS IN VARIOUS COUNTRIES 1976

TEST	UK	FRA	HOL	WG	US	CAN	DNK	NOR	SWE	ITLY	BEL	JAP	AUS	ISO
COMBUSTIBILITY	BS 476 PART 4	NF 92-201	NEN 1076 DRAFT 3881	DIN 4102	E136	B54:1	D 51056					JIS A1321	A3 AS 1520:1	R1182
IGNITION	BS 476 PART 5			DIN 53438										
CONTRIBUTION PROPAGATION	BS 476 PART 6	JNL OFFL 1101 1973 EPIR	NEN 1076 DRAFT 3883	DIN 4102			SPA 8							
FLAME SPREAD 1) SURFACES 2) ROOFS	BS 476 PART 7 BS 476 PART 3	DITTO	DITTO		E84 E162 E286 E108	E84	SFM 3						A30 AS 1530:3	
RESISTANCE	BS 476 PART 8	NF 92-201	NEN 1076	DIN 4102 PART 2	E119		DS 1051 DS 1052	NS 1501	SBN 67	ISO R834	NBN 713.020			R834
SMOKE	DD36 BS 5111 NBS-?		DRAFT 3883	DIN 53437	NBS CHAMB.							JIS A1321	A30	NBS ?
TOXICITY				DIN 53436								Basedon JIS A1321		
OXYGEN INDEX	IN DRAFT BS 3840				D 2863					UNI· CT240				

Fig. 5

As in common knowledge, the important fire tests in the UK for building applications are BS. 476, Parts 5, 6, 7, 8 and Draft 9.

BS. 476, Part 5 is the preliminary test for ignitability to determine whether or not a sample sustains flaming when exposed for a standard time to a standard flame. The test is carried out in conjunction with the Fire Propagation Test, BS. 476 Part 6, 1965. This introduced the classification 'Class 0'. This is regarded as the highest degree of resistance to spread of flame, followed in descending order by Class 1, 2, 3 and 4. as tested to BS. 476 Part 7. The rating was achieved more by definition than by test. The current definition for Class O to the Building Regulations now require:-

(a) the material of a wall or ceiling shall be non-combustible throughout.

(b) the surface material together with any substrate used, when tested to BS. 476 Part 6, 1968 shall have an index of performance $I < 12$ and a sub-index performance $i < 6$.

Class 0 is not defined in any British Standard. The Part 6 test measures the contribution that a material is likely to make to the growth of a fire.

The fire propagation test combines both direct flame and radiant heat to the specimen, and from the gases which leave the test chamber, a time/temperature curve is compared with one obtained from a standard specimen of asbestos board. The test is time weighted to the early part of the test; this is consistent with the fact that plastics during combustion cause a rapid increase in temperature and therby a desire to allow as much time as possible for safety of both people and premises.

The performance indices in this fire propagation test are calculated as follows:-

$$I = \underbrace{\frac{(\Theta m - \Theta c)}{10t}}_{\substack{i_1 \\ \text{at } \frac{1}{2} \text{ min} \\ \text{interval}}} + \underbrace{\frac{(\Theta m - \Theta c)}{10t}}_{\substack{i_2 \\ \text{at 1 min} \\ \text{interval}}} + \underbrace{\frac{(\Theta m - \Theta c)}{10t}}_{\substack{i_3 \\ \text{at 2 min.} \\ \text{interval}}}$$

Where I = index of performance

i_1, i_2 and i_3 = sub-indices for the three time components.

Θm = temp. rise recorded for the material at time t.

Θc = temp. rise recorded for the non-combustible standard at time t

and t = time in minutes from the beginning of the test. i_1 can be said to represent the early stage of ignition; i_2 the growth to a fully developed fire and i_3 the terminal stage of the fire.

Fig. 6 shows a table of typical values for a variety of

PERFORMANCE INDICES FOR A SELECTION OF MATERIALS

MATERIAL	THICKNESS MM	i.	I
FIBRE INSULATING BOARD	13	41	66·4P
SOFTWOOD	16	20·2	46·6P
PLYWOOD	6	19·5	41·1P
HARDBOARD	5	10·5	30·1P
FLAME RETARDANT P.U. FOAM	13	23·4	28·6P
G.R.P. POLYESTER	3	10·4	26·4P
DECORATIVE PLASTIC LAMINATE (PHENOL-FORMALDEMYDE BASE)	3	5·4	18·4P
PLASTERBOARD	9	5·4	9·7P
PVC COATED STEEL	>0·8	2·2	5·5P
PHENOLIC FOAM	25	3·9	10·6P
PHENOLIC LAMINATE	6	1·8	7·5P

P DENOTES PASSED PRELIMINARY IGNITABILITY TEST OF BS 476 PART 5 1968

Fig. 6

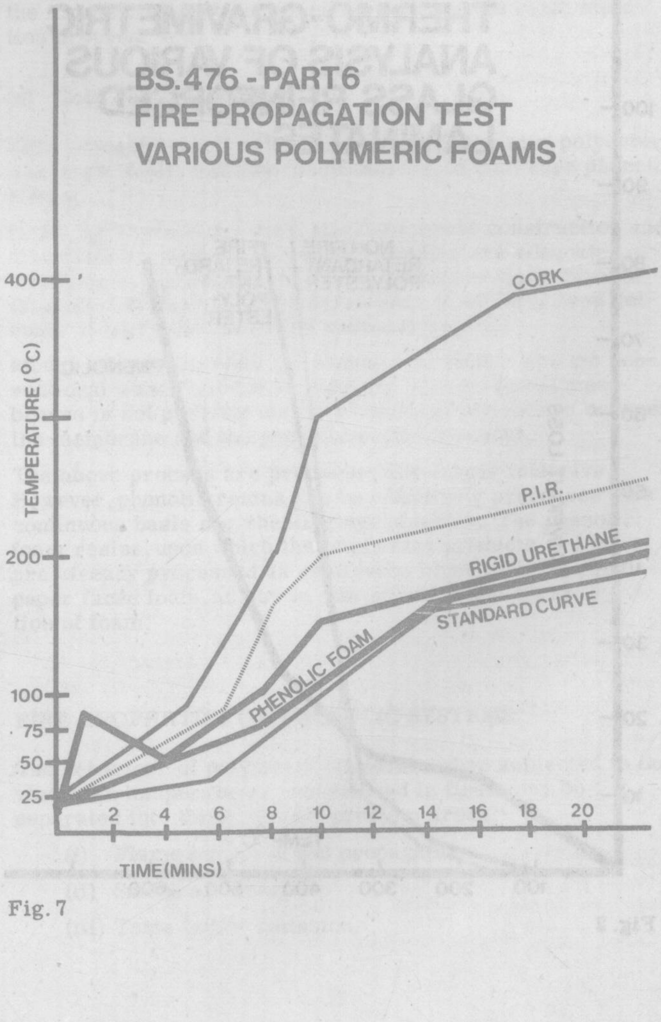


Fig. 7

materials in general use in building applications when tested to BS 476, Part 6. The figures for the polyester represent a non fire retardant system. However, polyesters such as Uralam 1361A, (R2), are available which have a Class 0 rating with indices of I — 9.9 and i 3.4. It is interesting to note that Uralam 1361A has already been used successfully with phenolic foam in a composite panel which is used in the construction of a school extension. This usage will be more fully described in the BS 476, Part 8 details and in the later conclusions section.

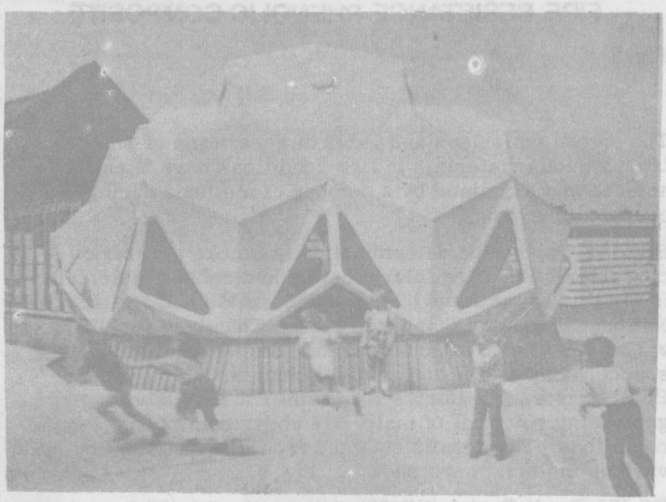
Fig. 7 shows graphically the performance of various polymeric foams used in composite GRP structures. To achieve a Class 0 Rating, the material had to obtain also a P classification (not easily ignitable) to BS 476, Part 5. The ease of obtaining this P classification generated criticism of the Class 0 rating to BS 476, Part 7, Surface Spread of Flame. In this test, a standardised specimen of the material is placed at right angles to a radiant gas furnace such that the temperature gradient along the surface varies from 500°C to 160°C. A pilot flame is applied to th- hot end of the specimen for 1 minute.

This test provides a means of assessing the spread of fire through a building by travelling across the surfaces of combustible materials which have been heated by radiation from the advancing fire. The classes with their limits are shown in the following table:-

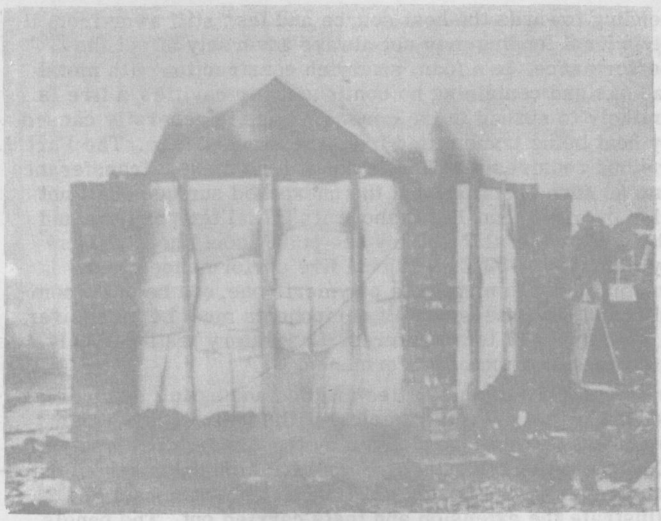
Classification	Flame Spread at 1½ min.		Final Flame Spread	
	Limit	Tolerance for one specimen in sample	Limit	Tolerance for one specimen in sample
	mm	mm	mm	mm
Class 1	165	25	165	25
2	215	25	455	45
3	265	25	710	75
4	Exceeding Class 3 Limits			

In this Part 7 test, phenolic laminates achieve a good Class 1 result exhibiting Nil flame spread and only a gradual charring of the surface.

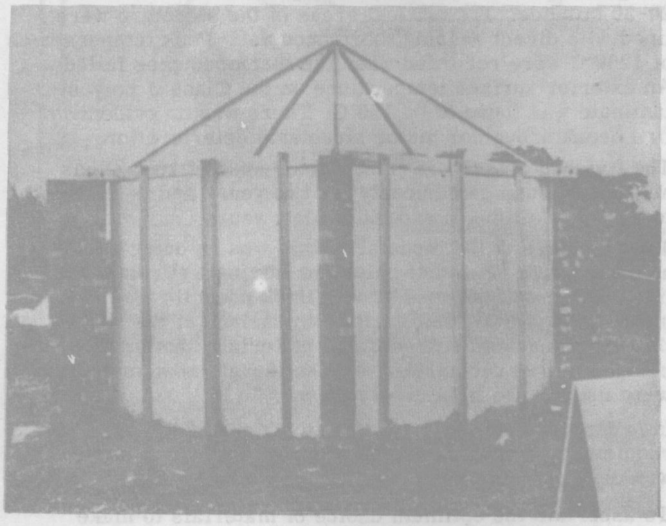
The fire resistance of elements of building is covered by BS 476, Part 8. This method assesses the ability of elements to resist the passage of flame and hot gas through them providing also a measure of resistance to heat transmission. Provision is also made for elements to be loaded under conditions representative to those within the intended building. However, behaviour can still ultimately depend on the position of the fire within the building; stiffer elements



Photograph 1 School extension by Lancashire County Council. Utilising Phenolic Foam and 1361A Polyester Composite Panels.



Photograph 2A Test structure of panels of phenolic foam/ 1361A polyester laminate after completion of fire test (35 minutes).



Photograph 2B Test structure of acrylic roof sheeting showing total destruction within 5 minutes of ignition.

Photograph 2C Test structure of traditional building materials (bitumen/felt) showing total collapse and destruction within 20 minutes of ignition.

bending towards the heat source and less stiff away from it. Structural loading may not always adversely affect the performance. In a foam sandwich construction with metal facings and containing no continuous air cavities, a fire is unlikely to spread in the core. Damage is generally caused by heat being transmitted from the exposed face. The Part 8 method requires that fire is not spread by heat transferance and as such specifies that the unexposed surface shall not rise by more than 140°C above its initial temperature and that the temperature of any one point should not increase by more than 180°C. The real fire performance of any material, not to mention a polymeric one, can be quite complex and the assessment of components must be taken over a wide range of temperatures. Laboratory tests can only give an indication of performance.

Increasingly, the authorities are demanding full evaluation of buildings or rooms complete with furnishings. Such a practical test was carried out by the Lancashire County Council in the design programme for a modular school extension room as previously mentioned. Photographs 1 and 2 illustrate the extension and tests carried out. The panels of the module were finally manufactured in a phenolic foam/ Class 0 fire retardant polyester GRP composite.

Each test unit was exposed to a controlled British Standard fire loading using dry timber platforms fired with Kerosene, representing a fire loading of 28.3 Kg/M^2 of floor area and designed to reach a minimum temperature of 800°C within 20-30 minutes. The critical areas of the structure were lined with direct reading thermocouples. Peak temperatures of 1200°C were recorded when the thermocouples failed. An exterior surface temperature on the Class 0 polyester laminate was found to be 120°C. There was no evidence of fire breakthrough or major structural deterioration.

The finished classroom (with a floor area of 18 m^2) has now been in use continuously for two years and is expected to have a life time in excess of forty years.

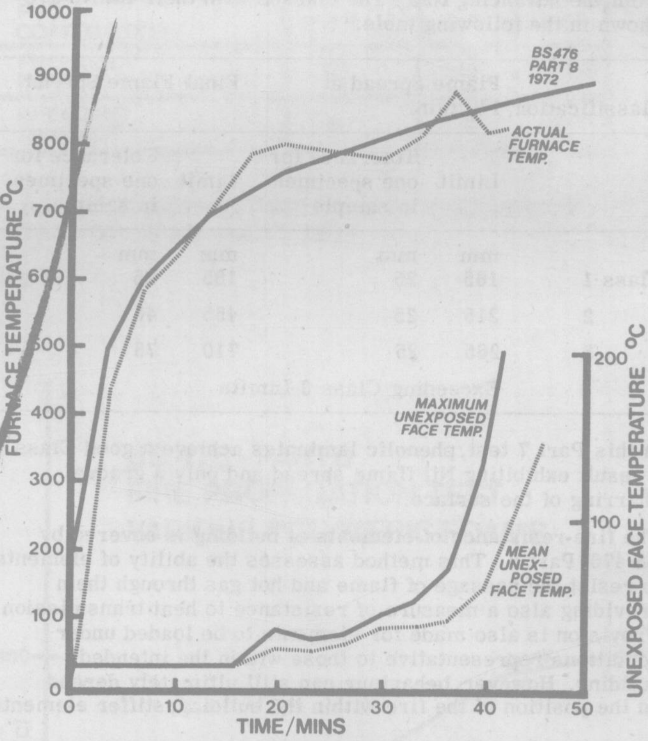
The structure of the modular panels was an outer skin of a Class 0 fire retardant polyester laminate (Uralam 1361A) lined with a self-skinned 48 mm thick phenolic foam insulant of foam density 6-8 lbs/cu. ft. Comparison of the cost of the structure against traditional materials showed that the composite was uncompetitive, even though these materials were used in the final construction.

In order to reduce without sacrificing any of the prerequisite fire properties, the phenolic laminating system was developed from the existing foam system.

To ascertain the optimum choice of materials to make structure cost competitive, a series of small scale Part 8 fire tests were conducted. The earliest structure used a phenolic laminate/phenolic foam/phenolic laminate composite with the foam at a nominal density of 2-3 lbs/cu. ft. The composite was cold laminated together with no interfacial bonding between the inner and outer laminates. This panel achieved a Part 8 fire rating of 43 minutes as shown in Fig. 8. Failure at this time was due to structural collapse of the poorly designed composite and not due to the failure of the materials used. A most recent modification in the design of another similar panel has achieved a Part 8 fire rating of 64 minutes.

A comparison is shown in the following table of this fire resistance rating to that of other more traditional materials and structures (Ref. 9).

Construction	Fire Resistance Rating on non load bearing framed walls and composite walls
1. Double skin steel panels with a 3" cavity filled with mineral wool insulation.	28 mins. No Grading
2. Steel skins with $2\frac{1}{2}$" urethane foam	6 mins. No Grading
3. Double skin steel panels with $1\frac{1}{2}$" mineral wool and $\frac{1}{2}$" asbestos board insulation.	37 mins. $\frac{1}{2}$ Hour Grading
4. Double skinned partition; on one $\frac{1}{2}$ linings were plasterboard. On the other, metal faced insulation board, (total thickness 8")	58 mins. $\frac{1}{2}$ Hour Grading
5. Steel framed panel lined internally with $\frac{3}{8}$" plasterboard and faced externally with aluminium sheet. Filled with P.U. foam. Total thickness $3\frac{7}{12}$".	38 mins. $\frac{1}{2}$ Hour Grading
6. Phenolic laminate faced panel with 3" phenolic foam and reinforcing strips.	64 mins. 1 Hour Grading
7. $\frac{1}{8}$" compressed asbestos cement sheet facings with autoclaved aerated concrete blocks infil. Total thickness $2\frac{1}{2}$".	120 mins. 2 Hour Grading



FIRE RESISTANCE PHENOLIC COMPOSITE

Fig. 8

The smoke emissions and rates of generation of smoke from various materials in fire conditions have been considered and examined by a number of methods during the course of our work.

BS 5111, Part 1, the determination of smoke generation characteristics of cellular plastics and rubber materials, is similar to the American XP2 Smoke Method and also the National Bureau of Standards Smoke Chamber Test. The variations in the test methods include the location of light source, sample size and sample: chamber volume ratio. BS 5111 is a laboratory scale method to evaluate the smoke generating potential of materials under continuous flaming conditions. The results obtained from the examination of various materials are shown in Fig. 9.

BS 476, Draft Part 9 (DD 36) utilises the BS 476 Part 6 apparatus and measures the smoke density across a room of known density under specific air flow conditions. Fig. 10A

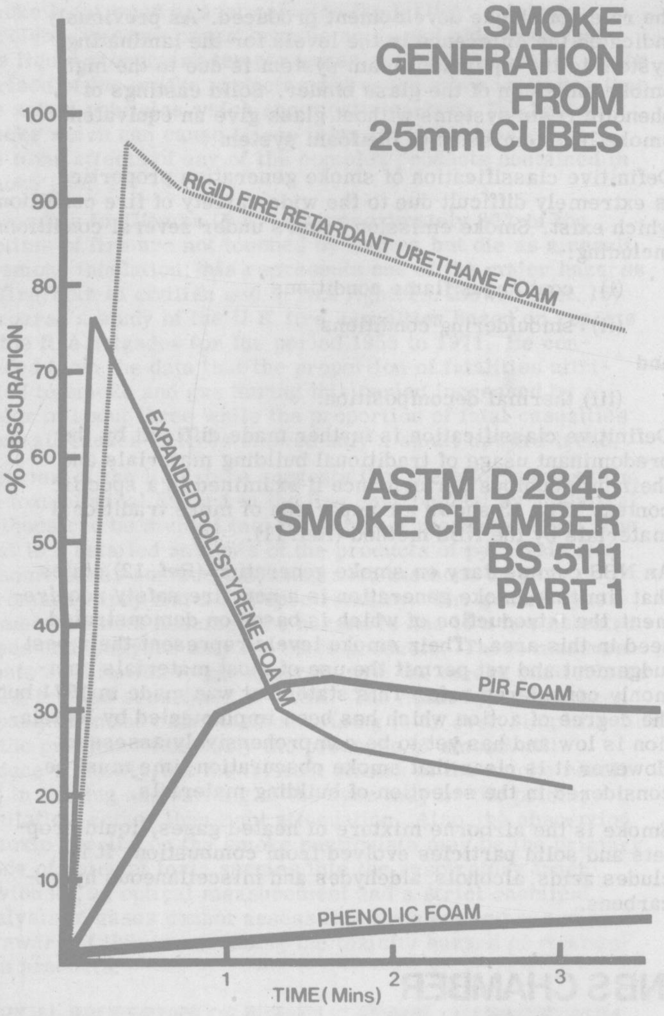


Fig. 9

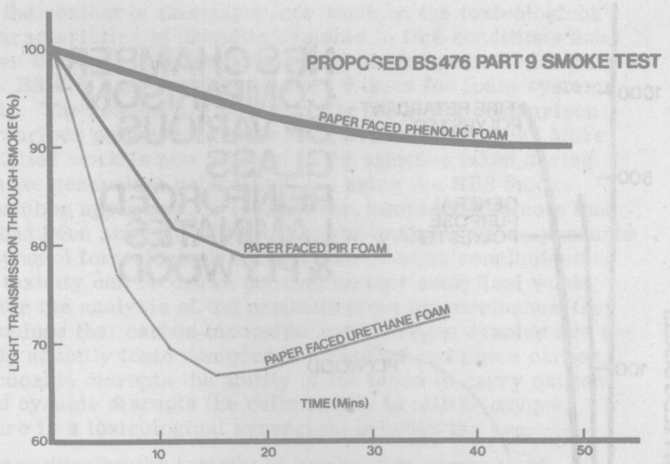


Fig. 10A

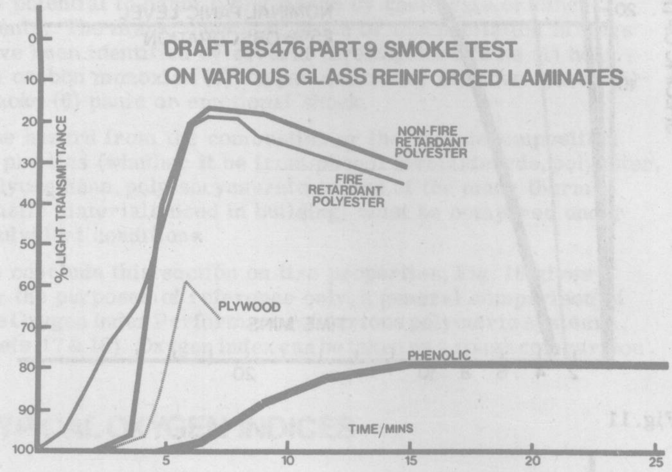


Fig. 10B

shows the typical values for cellular materials used in composite structures. It can be seen in Fig. 10B that the phenolic laminating system Uravar 101/Z102 in a 2:1 resin: glass laminate gives a light transmission of 80%. The higher value of light transmittance of foam based on 101/Z102 is accounted to the fact that there is no glass present and hence no binder on the glass to produce a higher smoke emission.

DD 36 and the NBS Smoke Chamber procedures are the two methods currently favoured by the authorities for the evaluation of smoke generation of building materials in fire conditions. The following chart gives a brief comparison of the two methods:-

	N.B.S.	D.D. 36
Volume of Chamber V	18 cu. ft. = 0.5 m^3	15 m^3 – 35 m^3
Area of Specimen A	3 sq.ins. = 76 mm^2	228 mm^2
Length of Light Path L	3 ft. = 914 mm (vertical)	1000 mm (horizontal)
Fan circulation	No	Yes
Gas flame	propane/air	natural gas/air
Electric heating	radiant panel from start, constant 2.5 watts/cms	Flaming: after 2m45s input 1.8 kw reducing at 5m to 1.5 kw non flaming: 1-5 kw. from zerotime.

The results obtained for the N.B.S. chamber are expressed as specific optical density which takes into account the volume of the chamber V, the area of the specimen A, and the path length L of the light beam:

$$D_S = \frac{V}{A.L.} \log 10 \frac{100}{T}$$

whereas the results for DD 36 express the optical density, which does not take into account the parameters V, A and L:

$$D = -\log 10 \frac{T}{100} \left(= \log 10 \frac{100}{T} \right)$$

Ds may, of course, be calculated if the parameters are known and the graphs for DD 36 in this paper are shown on this basis for a more direct comparison with the NBS method.

In many respects the NBS chamber is the more severe test particularly in the flaming made as both the flame and radiant heat are applied at zero time. The specimen area to chamber volume ratio is higher for the NBS chamber and consequently higher optical densities are obtained in the same time.

The NBS Chamber is probably at the moment the best laboratory method available to evaluate the smoke and combustion products evolved when a substance is burnt under a set of specific conditions. The method calls for a measurement of smoke density under both flaming and non-flaming conditions. Our initial work has been limited to examining smoke generation under the former condition. In recording the values as shown in Figs. 11 and 12, calculations have been made on a weight of sample basis. It can be seen again that the systems of the type Uravar 101/Z102 give a significant reduction in both the smoke levels and