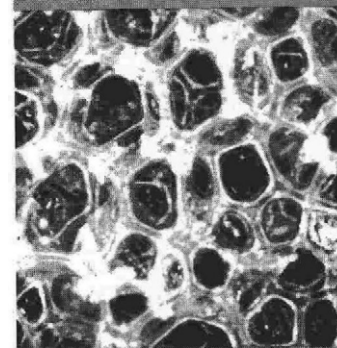


ABSTRACT

The commercial development and growth rate of rigid urethane foams has not met the forecasts presented by the chemical industry. Difficulty in meeting building code requirements and specifications established by regulatory groups coupled with relatively poor comparative economics of applied insulation has retarded the growth and acceptance of many foam products. A review of extended foams systems based on the incorporation of low cost commodity chemicals into foam systems will be presented. These modified systems, while significantly lower in cost, have gained only limited acceptance due to the loss of dimensional stability, lower heat distortion properties, and increased permeability.



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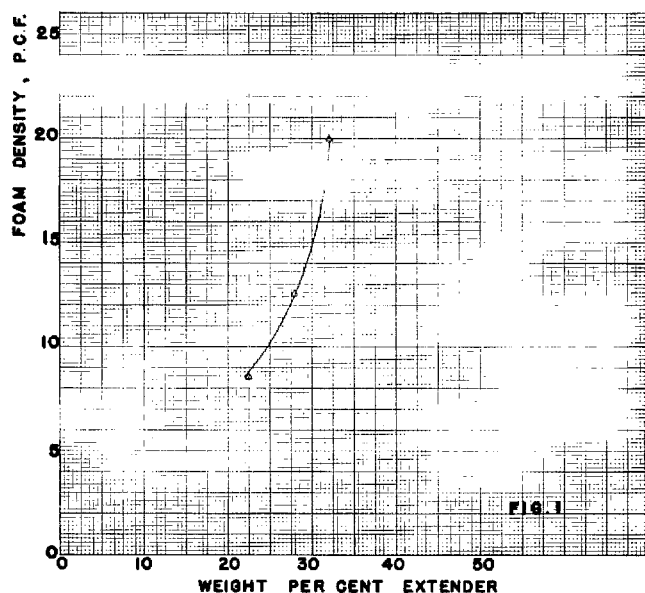


Figure 1. Relationship between foam density and weight percent of lignin.

Rigid urethane foams obtained by the reaction of diisocyanate with hydroxyl containing polyols in the presence of a blowing agent and suitable catalyst system have exhibited high strength to weight properties, low permeability to vapors and liquids, and low thermal conductivity. However, major penetration of these materials into areas governed by such factors as building codes and specifications set by regulatory agencies will not become a reality until the flammability characteristics, permeance properties, and physical strengths are improved.

Extended Foams

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It is the author's opinion that composites based on the extension of present foam systems will be developed which will lead to marked improvement of the physical properties of existing rigid urethane foams. A brief review of the literature together with a report on several novel foam composites which have been developed within the past few years will be presented.

Chemical Extension of Foam Systems

The incorporation of lignin, a phenolic polyether containing several alcoholic hydroxyl groups, in rigid and semirigid urethane foams has been reported in the literature (1). Foams based on this polyol while substantially lower in costs displayed poor dimensional stability when subjected to humid aging. Figure 1 presents the relationship between foam density and concentration of lignin extender. Figure 2 presents the relationship between foam strength-weight ratio and weight per cent of lignin extender.

The literature (2) further describes the extension of urethane foams with Vinsol (3). A typical rigid urethane foam formulation based on Vinsol

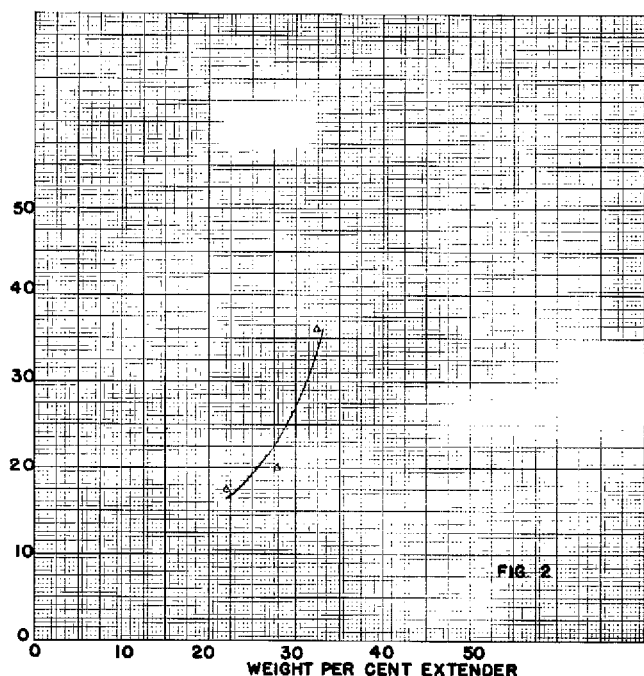


Figure 2. Relationship between strength-weight ratio and weight percent lignin extender.

is shown in Table 1. The physical properties of Vinsol extended rigid urethane foam are illustrated in Table 2.

Crude tall oil has been used as an extender for low density rigid urethane foams. Tall oil is a natural product obtained as a residue from the alkaline or sulfate process of wood pulp manufacture. The primary source of this material is the soft resinous type woods, such as pine and fir, which are used for kraft paper manufacture.

Rigid foams were prepared from crude tall oil, crude p,p' diphenylmethane diisocyanate, nitrogen-based polyether polyols, trichloromonofluoromethane, and a foam stabilizer (4, 5). Typical formulations are presented in Table 3.

Rigid foams having 85-95% closed cells with low thermal conductivity and fair to moderately good dimensional stability under accelerated humid aging are prepared from the formulations presented in Table 3. Table 4 presents a summary of the physical properties for foams containing different

Table 1. Vinsol Extended Urethane Foam

	PBW	% WT.
Component A		
Polymethylene polyphenylisocyanate	106	44.4
Component B		
Propylene oxide/pentaerythritol adduct M.W. 450	50	20.9
Vinsol	50	20.9
Fluorocarbon 11	30	12.6
Silicone oil	1.0	0.6
Tetramethylbutane diamine	1.0	0.6
	238.0	100.0%

amounts of crude tall oil (38%, 34%, and 30% by weight of total polymer).

Tall oil pitch (5), tall oil heads (5), and coal tar pitch (6) are examples of other low cost extenders used to modify rigid urethane foam. Foams based on these extenders while lower in cost per unit volume than conventional systems do not pos-

Table 2. Properties of Vinsol Extended Rigid Urethane Foam

Density	2.15 p.c.f.
"K" initial at (75°F mean)	0.152
"K" weather room 2 weeks	0.160
Water absorption, 24 hours immersion, 1 foot head	+62.1% by weight +2.10% by volume
Compressive Strength @ % Deflection	p.s.i.
1	10.3
2	20.6
3	28.8
4	34.4
Elastic limit	2.0 20.9
Maximum load	5.0 37.3
WVTR	2.64 perm-inches

Table 3. Typical Formulations for Rigid Foam Derived From Crude Tall Oil

Formulation	1	2	3
Crude Tall Oil	75	70	65
N,N,N',N'-tetrakis (2-hydroxy propyl) ethylenediamine	25	30	35
Crude p,p'-diphenylmethane diisocyanate	70	80	90
Fluorocarbon 11	25	25	25
Silicone stabilizer	1	1	1
Index number	100	100	100

Table 4. Physical Properties of Rigid Foams Derived From Crude Tall Oil

Formulation	1	2	3
Crude tall oil, % by wt. of total polymer	38	34	30
Density, p.c.f.	2.2	2.2	2.0
Tensile strength, p.s.i.	25-35	25-25	25-30
Compressive strength at yield, p.s.i.	15-20	15-20	20-25
Closed cell, %	85-95	85-95	85-95
"K" factor (23°C)			
Initial	0.13-0.14	0.13-0.14	0.14-0.15
50 days R.T., 50% R.H.	0.14-0.15	0.14-0.15	0.15-0.16
Dimensional stability, vol. change, % 4 wks.-100°C, ambient humidity	-5-10	-7-10	5-10
Water absorption, g/in ³	0.5-0.8	0.5-1.0	0.5-1.0
Cell size (cells/inch)	55-70	55-70	55-70

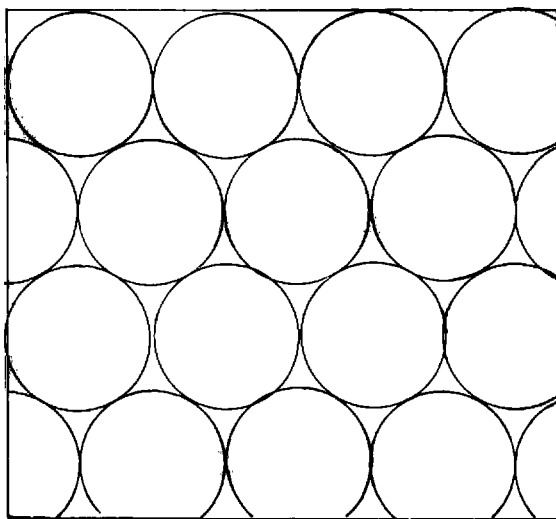


Figure 3. Closest packing of spheres.

sess sufficient dimensional stability to warrant their specification in construction applications.

Thus it is obvious that while a number of low cost chemical by-products may be incorporated in urethane foam systems, the physical properties of such extended foams are degraded, especially with regards to humid aging characteristics.

Foam Composites

Laboratory evaluation of composites based on low cost organic, as well as non-burning inorganic fillers was initiated.

Composites were prepared incorporating the following fillers: asbestos fibers, cellular glass pellets, excelsior, fibrous glass, glass flake, glass microballoons, glass wool, mica, perlite, phenolic microballoons, polystyrene beads, sand, synthetic fibers, vermiculite, wood fiber.

The preparation of foam composites is dependent upon control of mechanical and chemical variables. The size, configuration, density, surface, thermal properties, and flammability characteristics of the extender must be considered during design of composites. Important interactions occur during processing of composites, thus the foam formulation may require modification to obtain a desirable structure.

Factors Affecting Composite Density

Extender size—Urethane foam has the tendency to form a skin when in contact with a substrate during expansion. Thus for a given loading volume, small fillers, which possess large surface area will cause greater densification of the foam matrix than will larger fillers with low surface area.

Extender configuration and packing volume—The configuration of the extender will govern the packing volume within the cavity to be filled. The theoretical packing volume for perfect spheres of uniform diameter is approximately 74% (Figure 3). The packing volume may be increased by varying the diameter of the spheres so that the spheres of

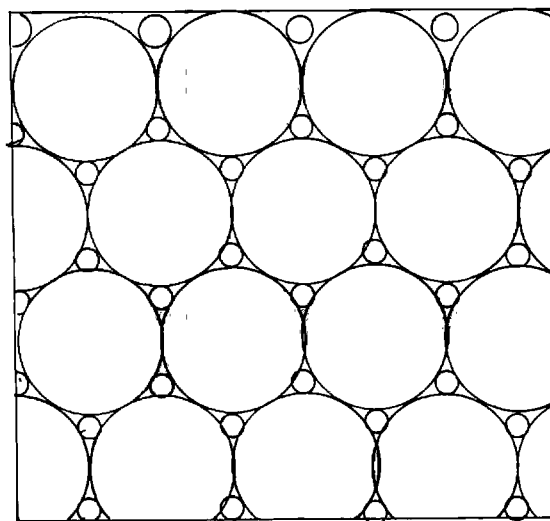


Figure 4. Scientific packing of spheres.

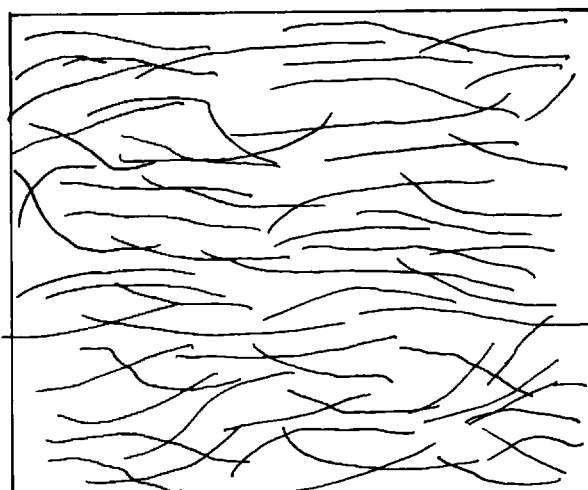


Figure 5. Typical composite cross sections of fiber-like extenders.

smaller diameter fill the interstices created by the packing of the larger spheres (Figure 4).

If the extender is non-spherical in configuration it is probable that only a relatively low volume of filler could be incorporated into the composite structure without encountering major densification of the foam matrix. Figure 5 indicates the typical cross-section encountered when the composite is based on a fiber-like extender.

Extender density—The density of the extender will have an effect upon the density of the foam matrix within the composite. This, however, appears to be of secondary importance and is possibly the result of a series of interactions which include extender size, extender configuration, extender density, extender heat transfer characteristics, etc.

If the extender has an efficient thermal conductivity (low K-factor) it may act as a heat sink as has been demonstrated in the preparation of composites using urethane foam as the matrix. It therefore may become necessary to adjust the foam catalyst level to compensate for loss of exotherm during preparation which would result in a higher matrix density.

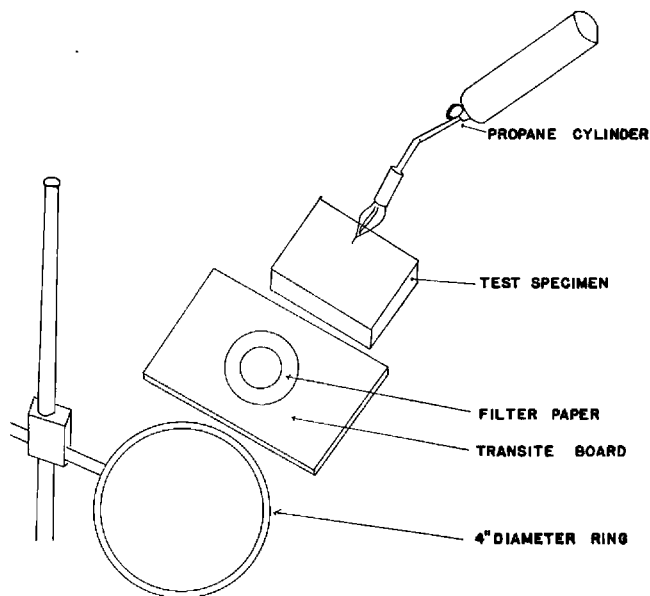


Figure 6. Schematic of Bureau of Mines Apparatus for horizontal test method.

Method of preparation—Several methods have been developed as a means of incorporating an extender into the foaming mass during the processing of composites. These include pre-mixing the extender into one or more of the foam raw materials, injecting the extender into the foaming stream in the mixing chamber, injecting the extender into the foaming mass downstream of the mixing chamber prior to initiation of rise, or injecting the extender into the mold cavity before or after the foaming mass has been introduced.

It may be necessary to modify the foam formulation used as the matrix. In fact a variety of modifications may be made to reduce the density of the matrix and thus obtain a more favorable economic balance. These modifications might include the following:

1. Addition of fluorocarbon blowing agent
2. Adjustment of initiation of rise time to allow for greater "flow-through" of the foaming mass
3. Increase the surface temperature of the extender to reduce density at interface
4. Coat the extender with materials such as catalyst, isocyanate, blowing agent, or other components of the system to reduce the ten-

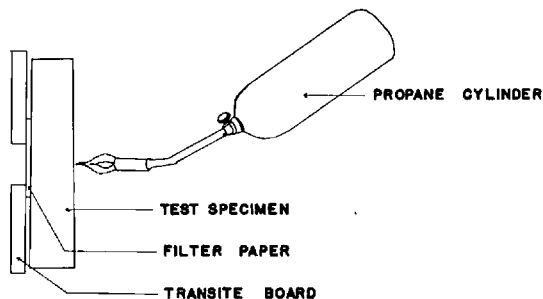


Figure 7. Schematic of Bureau of Mines Apparatus for vertical test.

Table 5. Bureau of Mines Fire Endurance Test (Horizontal Method)

SAMPLE DESCRIPTION	ENDURANCE TIME
Cellular Plastics	
Polystyrene bead board (non S.E.)	7 sec.
Expanded polystyrene (non S.E.)	7 sec.
Expanded polystyrene (S.E.)	9 sec.
Urethane foam (non S.E.)*	20 sec.
Epoxy foam (S.E.)	1 min. 20 sec.
Urethane foam (S.E.)	19 min. 20 sec.
Cellular Composites	
Styrene bead foam/glass pellet composite	9 sec.
Styrene bead foam/pelletized glass microballoons composite	11 sec.
Urethane foam (non S.E.)/mica composite	20 sec.
Urethane foam (non S.E.)/glass flake composite	20 sec.
Urethane foam (non S.E.)/vermiculite composite	5 min. 22 sec.
Urethane foam (non S.E.)/glass flake composite	39 sec.
Urethane foam (non S.E.)/glass pellet composite	10 min. 40 sec.
Urethane foam (non S.E.)/pelletized glass microballoons composite	10 min. 48 sec.
Urethane foam (S.E.)/glass flake composite	3 hr. +
Urethane foam (S.E.)/glass pellet composite	3 hr. +
Urethane foam (S.E.)/pelletized glass microballoons composite	3 hr. +
Miscellaneous Control Samples	
Fiber glass board (12.0 p.c.f.)	7 min. 45 sec.
White pine (25.2 p.c.f.)	53 min. 15 sec.

*Urethane foam (TDI, sorbitol adduct, F-11 system)

**Urethane foam (polymeric isocyanate, chlorinated polyester polyol, F-11 system)

density to form a high density skin at the interface.

Properties of Cellular Composites

Flammability characteristics—Numerous methods exist for the evaluation of the flammability properties of cellular plastics and foam composites. The test developed by the personnel of the Bureau of Mines was employed as a small scale bench method to determine the fire endurance properties of limited size samples.

Horizontal Test—A schematic drawing of the Bureau of Mines apparatus is illustrated in Figure 6. A 6" × 6" × 1" specimen is placed upon a transite board as shown in Figure 6. A piece of laboratory filter paper is placed under the test specimen over the cut-out section of transite. The flame source utilized is a propane burner with a pensil flame

Table 6. Modified Bureau of Mines Fire Endurance Test (Vertical Method)

SAMPLE DESCRIPTION	ENDURANCE TIME
Cellular Plastics	
Polystyrene bead board	9 sec.
Expanded polystyrene (non S.E.)	10 sec.
Expanded polystyrene (S.E.)	12 sec.
Urethane foam (non S.E.)*	38 sec.
Epoxy foam (S.E.)	5 min. 44 sec.
Urethane foam (S.E.)**	14 min. 2 sec.
Cellular Composites	
Styrene bead foam/glass pellets composite	11 sec.
Styrene bead foam/pelletized glass microballoons composite	12 sec.
Urethane foam (non S.E.)/mica composite	1 min. 40 sec.
Urethane foam (non S.E.)/glass flake composite	1 min. 44 sec.
Urethane foam (non S.E.)/vermiculite composite	1 min. 53 sec.
Urethane foam (non S.E.)/glass flake composite	1 hr. 10 min.
Urethane foam (non S.E.)/pelletized glass microballoons composite	1 hr. 15 min.
Urethane foam (S.E.)**/glass flake composite	2 hr. 5 min. 3 hr. + (test discontinued)
Urethane foam (S.E.)**/glass pellet composite	3 hr. + (test discontinued)
Urethane foam (S.E.)**/pelletized glass microballoons composite	3 hr. + (test discontinued)
Miscellaneous Control Samples	
Fiber glass board (12.0 p.c.f.)	10 min. 10 sec.
White pine (25.2 p.c.f.)	1 hr. 30 min.

*Urethane foam (TDI, sorbitol adduct, F-11 system)
 **Urethane foam (polymeric isocyanate, chlorinated polyester polyol, F-11 system)

burner tip (designed to concentrate the flame source). The flame is adjusted to a cone of approximately 1.5" in length (temperature 2000°F-2100°F) and the tip of the flame is positioned in contact with the sample surface at the beginning of the test. Failure, end of test, is indicated when the filter paper catches fire or chars and cracks.

A description of samples utilized in this study and test results are presented in Table 5.

Vertical Test—A schematic drawing of the Modified Bureau of Mines apparatus is illustrated in Figure 7.

The vertical test method is identical to the horizontal test method described previously except for positioning of the sample and the burner.

A description of the samples utilized in this study and test results (vertical method) are presented in Table 6.

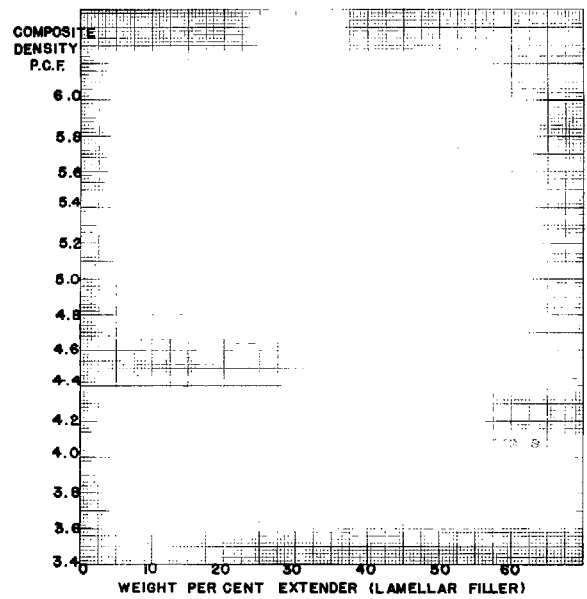


Figure 8. Relationship between extender loading volume and composite density.

Summary of the Small Scale Fire Endurance Tests

1. The horizontal test method was more severe than the vertical test method, thus only the results of the horizontal test will be reviewed.

2. All foams or foam composites based on expanded polystyrene (a thermoplastic material) failed in a very short period of time.

3. Composites based on inorganic lamellar extenders exhibited a slight improvement in fire endurance when compared to unfilled foams (20 seconds to 39 seconds). Marked improvement was observed when similar composites based on self-extinguishing formulations were compared to unfilled foams (3 hours plus to 19 minutes 20 seconds).

4. Composites based on inorganic fillers possessing moderate volume and good thermal conductivity characteristics exhibited substantially improved fire endurance characteristics when compared to unfilled foam (10 minutes 40 seconds compared to 20 seconds for combustible systems, and 3 hours plus

Table 7. Tunnel Test (ASTM-E-84) Exploratory Results

PROPERTY	URETHANE FOAM	URETHANE* FOAM/GLASS FLAKE COMPOSITE	URETHANE* FOAM/GLASS PELLET COMPOSITE
Propagation of Flame Spread	40	30	25-30
Fuel Contribution	N.M.	10	35
Smoke Density	+400	+400	65

*Polymeric isocyanate, chlorinated polyester polyol, F-11 blowing agent.

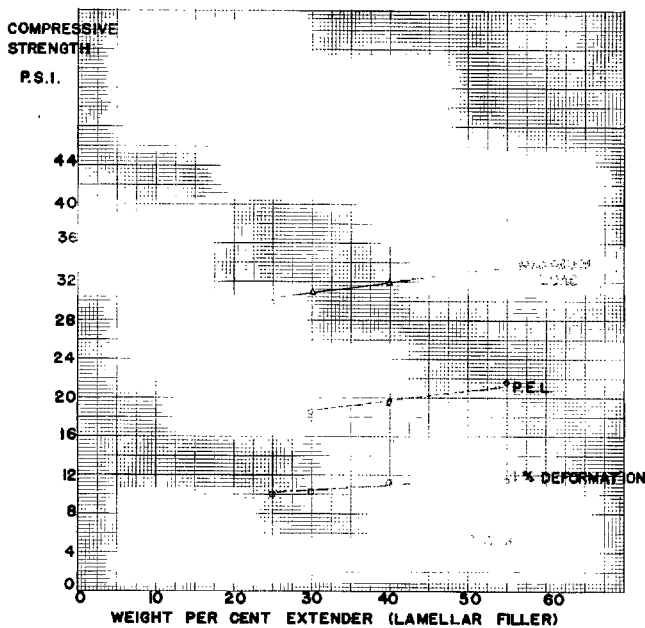


Figure 9. Relationship between extender loading volume and composite compressive strength.

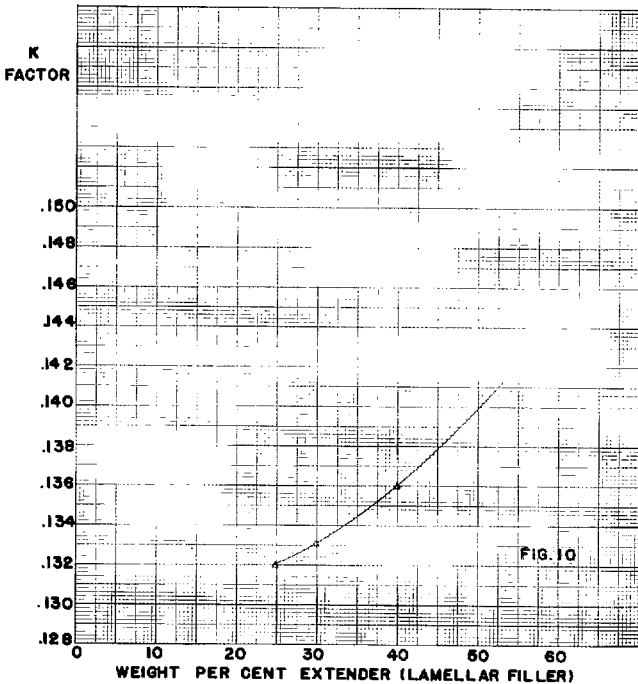


Figure 10. Relationship between extender loading volume and composite thermal conductivity.

compared to 19 minutes 20 seconds for self-extinguishing systems).

The evaluation of the fire endurance characteristics of cellular composites by a small scale bench test indicated the desirability of attaining additional information by recognized large scale test methods. A series of foams and composites were prepared by pilot plant techniques and the flammability properties determined by ASTM-E-84 (Tunnel Test).

Table 7 presents the results of exploratory tests conducted in the U.L. Tunnel.

A review of the data presented in Table 7 indi-

Table 8. Typical Properties of Pellet/Foam Composite

Urethane system	Polymeric isocyanate, sucrose adduct, Fluorocarbon-11 blowing agent	
Pellet size	$\bar{x} = 0.4530$	
Pellet density	$\sigma = 0.0045$	
Weight %, pellets	7.7 p.c.f.	
Weight %, foam	69.0	
Volume loading, pellets	31.0	
Volume loading, foam	57.1	
Composite density	42.9	
Foam density	6.4 p.c.f.	
WVTR (perm-inches)	4.6 p.c.f.	
Compressive Strength, p.s.i.	Initial	4 Weeks W.R.
5% deflection	42.1	28.4
10% deflection	56.7	42.6
P.E.L., p.s.i. at % Defl.	20.3 at 0.75	21.0 at 3.51
Thermal conductivity @ 75°F Mean	0.145	0.150
Dimensional stability, % volume change after 4 weeks in W.R.	+3.92	N.C.*

*Tests not complete.

cates the major reduction in propagation of flame spread and smoke density characteristics obtained by the incorporation of inorganic extenders possessing moderate volume.

Properties of Composites Based on Lamellar Extenders

The density of the composites as well as the foam matrix is dependent on the type of extender and extender concentration. An indication of the relationship between composite density and concentration of extender (lamellar filler) is presented in Figure 8.

Only a slight increase in composite strength is observed as the concentration of extender (lamellar filler) is increased (Figure 9). An approximate 7% increase in thermal conductivity (K-factor) was observed in foam composites based on lamellar fillers when the concentration of filler was increased from 25% to 55% by weight (Figure 10). Cellular composites based on lamellar fillers have measured water vapor transmission rates of less than 1 perm-inch. The rate of K-factor deterioration in hot humid environments is less than that measured for unfilled organic foams.

Properties of Composites Based on Inorganic Bulk Fillers

Properties of a cellular composite extender with an inorganic bulk filler are presented in Table 8. The physical strength properties of composites based on bulk fillers depends greatly on the "packing volume" of the filler. The transfer of loads through such composites is indicated in Figure 11. Thus it can be shown that maximum strength can be obtained only if the extenders maintain point to point contact.

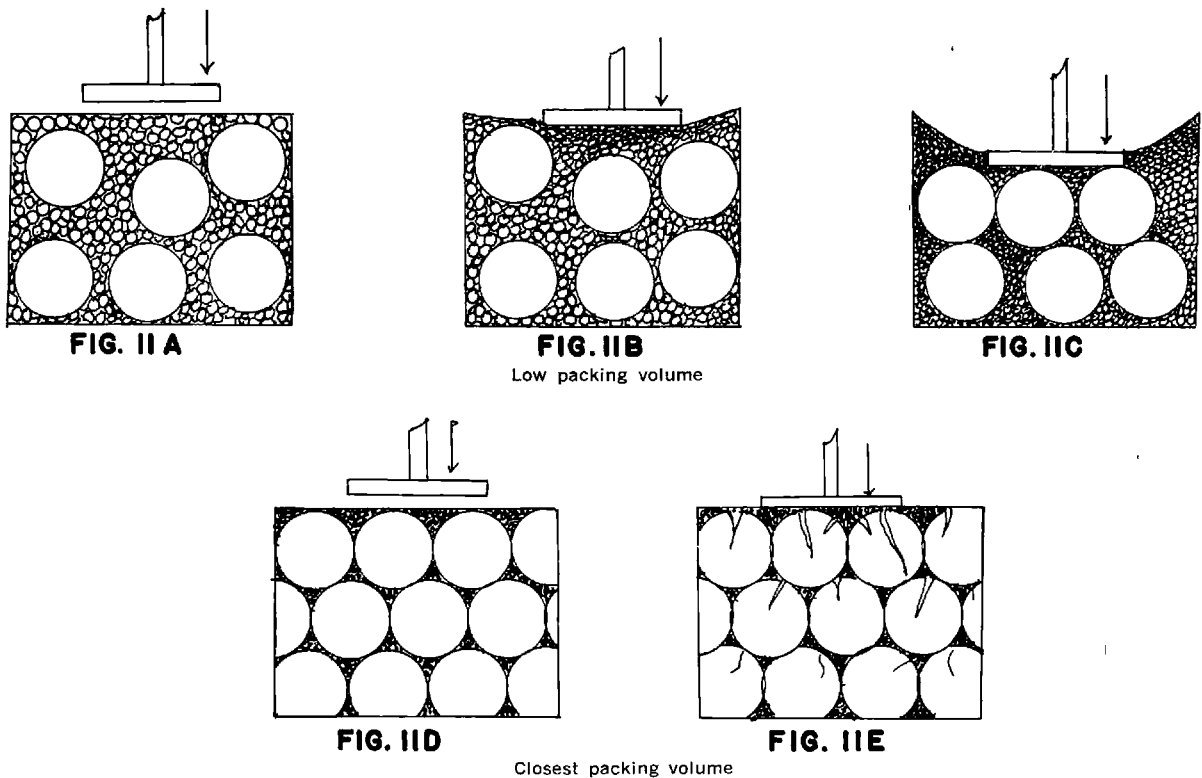


Figure 11. Effect of Extender Packing Volume on Composite Physical Properties.

Conclusions

The development of cellular composites based on low cost, bulk, inorganic fillers bonded together by char forming, fire retardant urethane foam has led to significant improvement of flammability characteristics. Low flame propagation rates, significant reduction in smoke density, and major improvements in fire endurance characteristics of this new class of materials should help to accelerate the rate of development and growth of cellular plastics in the building and construction industry. It would also appear feasible that the use of increased concentrations of low cost chemical extenders, such as wood derivatives, could be used to formulate foam systems which, while not possessing sufficient physical properties to merit consideration as foams, could be used as low cost matrix systems for cellular components.

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