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Cellular Plastics

PROCEEDINGS OF A CONFERENCE

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Foreword

Spectacular progress has been made in the field of cellular materials in the last ten years. A constant stream of technical information has been disclosed in a mounting number of publications, and a wide variety of new products has become commercially available. By far the largest segment of materials is represented by foamed plastics. Also known as cellular or expanded plastics, they can be made in flexible, semirigid, or rigid foams, in densities which in some cases have been as low as 0.1 lb/cu ft to as high as 80 lb/cu ft. For most applications, properties such as low density and high strength-to-weight ratios are of importance, while in many other instances their good thermal and electrical insulating properties make them very desirable. Some foams excel in impact absorbing capacity, vibration damping, and acoustical insulation, while others are characterized by outstanding abrasion and chemical resistance.

Cellular materials affect profoundly the lives of civilians and military personnel, be it in the areas of transportation, low- and high-temperature insulation, clothing, construction, or other facets of our daily life. From comfort seating and bedding to refrigerators and trucks, to applications in the missile and rocket industry, cellular materials have found a place in almost every conceivable industry. They are used either as a replacement for older and more conventional materials such as metals, wood, paper, rubber, asbestos, and leather, or in entirely new applications where their combination of properties has made their use an obvious choice.

Testimony of the importance of cellular materials in today's world is not only their acceptance by industry and the military services, but also the fact that scientific and technical organizations are concerned exclusively with cellular materials. The Cellular Plastics Division of the Society of Plastics Industry, the Gordon Research Conference on Cellular Materials, and the *Journal of Cellular Plastics* are living symbols of the growing interest in the field of cellular plastics.

The Committee on Foamed Plastics, Advisory Board on Military Personnel Supplies, National Academy of Sciences – National Research Council, has organized this Conference on Cellular Materials jointly with the Clothing and Organic Materials Division, U.S. Army Natick Laboratories, with the purpose of aiding communication between industry and the military services and other branches of government concerned with cellular materials. It should serve as a review of the state of the art in industry and of the needs and requirements of the services and branches of government. This is the second conference of this kind, the first being held three years ago in Boston, Massachusetts, and I am confident that the interchange of ideas and talent by the participants in this conference will help the services and industry solve important problems and accomplish important tasks that lie ahead.

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Chairman, JAMES H. SAUNDERS
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Army Support of Cellular Materials and Related Plastics Technology

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INTRODUCTION

Many military uses for cellular materials, particularly foamed plastics, have been reported in the literature. Some of the U.S. Army's activities in the use of cellular materials are well known. Among these activities are those of the U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia, in their "buildings in barrels" concept and its application in Camp Century, Greenland, to molded prefabricated shelters. More recently, improved experimental models have been fabricated for test in Vietnam.

The Limited War Laboratory at Aberdeen Proving Ground, Aberdeen, Maryland, has been experimenting with dust suppression mats for helicopter landings and take-offs in forward areas, free-air-drop water containers for supply of troops in forward areas, and lightweight hulls for delta craft. The use of plastics is playing an important role in these endeavors.

Self-propagating foamed-in-place materials for forming shelters have been under development at the Army Natick Laboratories, Natick, Massachusetts. In addition, foam plastics for packaging insulation of refrigerators and for insulated food containers have been developed. Plastic containers for supply of water and of petroleum, oil, and lubricants to troops by ground and/or airdrop have also been designed and tested.

The Plastics and Packaging Laboratory at Picatinny Arsenal, Dover, New Jersey, is concerned with development of plastics for packaging ammunition and materials such as weapons and fragile equipment parts.

Expedient ground-surfacing systems using plastics for military roads and airfields have been explored at the Army Engineer Waterways Experiment Station, Vicksburg, Mississippi. The Corps of Engineers has been generally interested in the logistics, cost, and time advantages of structural plastics in permanent and semipermanent construction of all types of facilities.

Since the above areas receive extensive discussion elsewhere, the main purpose of this paper will be to discuss three potential new areas where foam plastics, cellular materials, and possibly organic materials in general may find future applications. The Army is currently reviewing requirements for cellular materials in the following areas: (1) a research program in new permanent materials for construction, (2) a study for the development of a mobile plastics fabrication unit, and (3) a review of applications of cellular materials in limited warfare. Progress and future plans in each of the above areas are discussed below.

PERMANENT CONSTRUCTION MATERIALS AND TECHNIQUES

One of the major potential long-range uses of cellular materials is their use as a general material of construction. The U.S. Army, through the Corps of Engineers, has a total annual construction work load in excess of $2 billion. This funding is divided into civil works and military construction activities. The source of funding for these areas comes from a variety of government agencies. The continuing military construction portion of this effort should average approximately $500 million per year. This includes only the routine types of construction and does not include the Corps' massive construction efforts such as that proposed under the Civil Works Interoceanic Canal study or the Military Construction Nike-X program. Much of this work is highly specialized in nature with no civilian counterpart.

Although the Corps of Engineers has maintained a significant research activity to support its construction mission, the program has been quite small compared with the magnitude of the military construction and civil works effort. For the most part, this research has been prompted by specific and immediate needs to solve design and construction problems. For some time it has been realized that a longer-range view of the requirements for construction materials was needed. Supporting research should be performed to provide more functional and economic methods in building structures, research and test facilities, all types of storage, roads and airfields, and utilities of all types. In answer to this need a new Army project, "Permanent Construction Materials and Techniques," was initiated in fiscal year 1966. The objective of this project is to provide new knowledge essential for permanent and semipermanent construction under normal and hostile environments to support demands for fixed weapon systems, improved and extended communication centers and logistic support systems, and hardened installations. Administratively, this new project was included with the twelve other programs on materials that support the Army exploratory development requirements for armor, fuels, lubricants, ceramics, metals, composites, and electronics. Thus, construction materials will now be considered as one component in the over-all spectra of the requirements for Army materials.

An extensive background study has been made during the initial stages of the creation of this new project. This initial study has the objective of systematically developing a long-range construction research program in five phases as follows:

Phase I	Future Construction Requirements
Phase II	Adequacy of Existing and Projected Technology
Phase III	Current and Planned Investigational Activity (Government and Industry)
Phase IV	Necessary Research and Development to Meet Future Requirements
Phase V	Final Integrated 10-Year Program

A committee of experts provided by the Building Research Advisory Board (BRAB) of the National Academy of Sciences – National Research Council is assisting in this program development. All phases of this initial study are scheduled for completion in fiscal year 1966. In performing these studies the whole Army military construction long-range program is being analyzed. The study analyzes all the various routine construction tasks and consolidates them in the areas listed in Table 1. This table presents the long-range (beyond 1971) requirements for military construction in

TABLE 1

Long-Range Military Construction Categories in General Order of Dollar Magnitude

1. Structures and support items
2. Research and development test facilitie
3. General storage
4. Roads
5. Utilities
6. Airfield pavements
7. Ammunition storage
8. Water supply
9. Heat source and transmission lines
10. Power and distribution lines
11. Railroads
12. Coastal construction
13. Sewage and industrial treatment
14. Grounds and drainage
15. Demolitions
16. Electrical and electronic
17. Petroleum-oil-lubricant (POL) dispensing
18. POL storage

general order of dollar magnitude. To support these routine tasks and other specialized tasks, research needs were identified in five major construction disciplines. These disciplines are described in the following paragraphs.

Materials for Permanent Construction

The objective of this task is to develop a basic understanding of the properties of materials for permanent and semipermanent construction purposes. New applications, formulations, and fabrication techniques will be considered. Studies are now under way on potential applications of a Mobile Plastics Fabrication Unit (MOPFU), state of the art of structural plastics, and fabrication equipment for field use. Progress on this task will be discussed more extensively in the following section.

Environment Isolation and Control

The objective of this task is to provide knowledge essential for economic and functional means of protecting permanent structures, and men and machinery within permanent structures, from the effects of hostile environments. Based upon requirements identified under earlier studies, further investigations will be initiated in the propagation of ground motion from forces of vibratory (steady-state) or impulse ground excitations to foundations of structures. This will involve the study of elastic properties of a foundation as related to elastic ground motion, to propagation of ground motion away from an exciting source such as missile test stands, and to the effects upon structures of ground motion originating from external sources. This will provide fundamental information for the selection and application of materials such as cellular plastics for ground motion attenuation.

Design and Construction Techniques

The objective of this task is the improvement of design and construction concepts for permanent construction. It is concerned with (1) design techniques and analytical procedures, (2) construction methods and equipment, (3) quality control, (4) maintenance of facilities, and (5) planning, scheduling, and management systems. In-house and contractual efforts will be used to develop information for design manuals and planning, scheduling, and management systems. New work will be oriented to Army construction missions to formulate a scientific method for data collection and utilization for construction. The goal will be a man–machine system for design and control of construction operations.

Power Plants

The objective of the task on power plant construction is to develop new essential knowledge peculiar to military requirements in the design, operation, and maintenance of fixed and floating nonnuclear power plants. Essential knowledge is required in hardened above and below surface plants, in precise uninterrupted power, and in system reliability and maintainability. Experience on the development of the Nike-X power plant program and other specialized defense power plants will be used to develop broad concepts for the construction, operation, and maintenance of hardened precise uninterrupted power plant facilities. Background information will be developed for a data collection center to support design and construction of specialized military power facilities demanding precise power delivery, special protection, a high degree of reliability, and reduced maintenance.

Testing Techniques

The objective of this task is to develop new tests of construction materials and of structures to assure functionality, maintainability, and reliability. Efforts will be directed at minimizing the time, cost, and complexity of testing operations without compromising effectiveness.

The creation of the first two tasks (that is, Materials for Permanent Construction and Environment Isolation and Control) demands a new look at available materials that have been neglected in military construction. Specifically, new applications of plastics and cellular materials in construction should result from these studies. The other three tasks will identify new requirements and techniques for introduction of these and other materials to the construction process.

MOBILE PLASTICS FABRICATION UNIT

In January 1966, the Office of Director of Defense Research and Engineering authorized the Army to initiate a feasibility study of the concept of a Mobile Plastics Fabrication Unit for exploration of plastics technology in counterinsurgency and remote area conflict situations. Responsibility for this task was assigned to the Corps of Engineers under the newly established project, Permanent Construction Materials and Techniques. Plastics are already familiar through military and civilian applications in diverse uses such as packaging, buoyancy devices, shock attenuation, prosthetic devices, and in construction. The use of plastics in structures was given added impetus after the successful application of plastics in the

Seattle Fair of 1962 and the New York World's Fair of 1964–1965. Over-all Army interest in plastics, which predates these events, was previously indicated in descriptions of some of the programs underway in several Army laboratories. These programs highlight the diversity of plastic materials, techniques of fabrication, and potential and proven applications. Certainly, they clearly indicate that the present state of the art has not yet produced the "universal plastic," and it is doubtful that such a possibility exists. The current crisis in Vietnam and its attendant logistics problems have illustrated a potentially fertile area for the application of field processed plastics. Lacking a universal plastic, the question of how most efficiently to satisfy many needs is raised. One approach is the development of a mobile unit or units with capabilities of processing a number of plastics and with the capability of being placed in operation in a matter of several hours or less. Consideration of this approach has resulted in the concept of a Mobile Plastics Fabrication Unit. The concept is initially aimed at supplying logistic needs in Vietnam while keeping in mind that such a facility could be readily adapted to other theaters with other climatic problems.

The plan of attack to develop concepts and a program leading to a Mobile Plastics Fabrication Unit(s) consists of four phases, studied concurrently and completed during the second quarter of 1966. The four phases are as follows:

1. To identify and evaluate the potential applications of a Mobile Plastics Fabrication Unit.
2. To identify and evaluate suitable plastics, formulations, and associated environmental considerations in fabrication and use.
3. To establish the type of fabrication equipment required.
4. To outline a program and define future plans and directions for the development of MOPFU and its operational techniques.

In spite of the multitude of potential applications for the output of the MOPFU, the initial development item will probably only be directed toward a limited number of applications. It would be rather difficult to plan ahead to resolve all of the potential applications that might appear. It will be necessary to review for use in the MOPFU most of the available plastics. The products of the MOPFU are expected to be not only foamed plastics, but also rigid hard plastics. The final selection of materials, however, will probably be limited, to reduce the complexity of the operating procedures that would be required. Fabrication techniques such as the folded plate, sprayed polyurethane, filament wound, and foamed-in-place will be considered. Molding extrusion, injection, compression, blow, rotational, and thermal forming techniques must also be considered to be able to include operations with other than foamed plastics. It is expected that the MOPFU will be a Class II engineer item operated by engineer troops and issued to an engineering unit as a major item of equipment. The concept of mobility will also have to be further examined. It is possible that the MOPFU will have to be suitable for either ground-vehicle, ship-mounting, or air-drop capability. Full consideration will also have to be given to the potential environmental location of a MOPFU. This will be necessary because previous experience has often showed that little correlation exists between foam properties as produced in a laboratory or production plant and the properties of the same foam as produced under field conditions. This problem is probably more critical for foams than for other types of plastic products to be produced. The assessment of all of these problem areas may result in a future plan or program for engineering development of a Mobile Plastics Fabrication Unit. It is quite possible that the output of the study may also be used for the preparation of what is known as a qualitative material requirement or a small development requirement.

The need for a MOPFU has grown out of an extensive consideration of the number of items of plastics in use by the field Army. For a number of years, the Army has had a very active research and development program on polymer chemistry and plastic materials. This work has had as two of its objectives the development of lighter weight hardware and throwaway items. Early in the investigations to evaluate the MOPFU it was learned that the Army has over 300 individual plastic items in its logistics pipeline. These items and new items for plastic fabrication must be examined to determine the logistics and operational advantages for their field fabrication from plastics. A preliminary review of the literature, visits to Army installations, and conferences with some personnel in the plastics industry have revealed some candidate materials and applications that may be explored by either foam or standard plastics technology. Foam technology has produced buildings up to 20 feet in incremental lengths by spray foaming over removable, reuseable, inflated fabric forms or by joining prefabricated arch-sections of sandwich construction of polyurethane foam core and fiberglass polyester resin exterior sheet laminates. Construction of dome-shaped structures for shops and warehouses by spiral generation of polystyrene foam-board has been demonstrated. Foams have also shown some potential in protective construction such as foxhole or underground shelters and in attenuation of ground shock and motion in structural foundations. For heliports in forward areas, foam technology has some potential in providing a dust-suppression mat. Low-density polystyrene and polyurethane foams can be used to provide additional buoyancy in small assault boats, life preservers, rafts, and steel pontoons. Foams may also have some application in the manufacture of decoys and in producing camouflage effects. In the plastic technology area, production of such items as containers and pipe may lend itself to a MOPFU unit.

Other potential activities of MOPFU are the provision of maintenance and repair facilities for vehicle bodies, small boats, and pontoons by means of fiberglass-reinforced polyester resin applied by spray-on or hand lay-up techniques. Protective coatings for metal parts and equipment may be accomplished by the use of fluidized beds and spray-on coatings. In another area, surveys of commercially available equipment for both foam and plastic technologies are under way with a view of determining their size, weight, power requirements, and cost. Evaluation of this information will provide the basis for incorporation in the MOPFU. Consideration is not being given to the possible reuse by the MOPFU of some of the plastic throw-away items in the Army's logistics pipeline.

ARMY EXPLOITATION OF CELLULAR MATERIALS TECHNOLOGY

There are myriad possibilities for applications of plastics by the Army. Reference to possibly 300 of these applications was mentioned in the previous section. This section briefly summarizes applications that are more in the future and are related to counterinsurgency and remote-area conflict situations. These applications are also interpreted in terms of production through a mobile field preparation concept. Table 2 summarizes a number of potential foam plastic applications in a counterinsurgency and remote-area conflict location. This list is oriented more toward foam plastic applications than toward rigid hard plastics. However, as the rigidity and the hardness of foams increase, they approach the characteristics exhibited by hard rigid plastics. As a result, it is very difficult to say where foam applications leave off and plastics technology begins.

The characteristics that make foamed plastics of benefit to the applications described are buoyancy, resiliency, insulation qualities, void-filling characteristics, and structural rigidity. These properties are interpreted in Table 2 in terms of structural characteristics, mobility of flotation advantages, special benefits to the individual soldier, and benefits in civic action or psychological warfare. Because of the extensive number of applications that would be possible in a counterinsurgency and remote-area conflict situation, attention would eventually have to be given to utilizing the indigenous raw material resources of the areas where the applications are used. Otherwise an extensive logistics requirement would be needed to continue to operate the MOPFU. Most of the applications indicated in Table 2 are also for passive purposes. It is also quite possible that foamed plastics could be used for active devices such as foamed explosives, a foam thrower, or a sticky foam for use as an intrusion barrier.

Army interest in cellular materials does not end with plastics and organics alone; other cellular materials may be of just as significant an

TABLE 2

Some Potential for Foam Plastic Technology in a Counterinsurgency and Remote-Area Conflict Situation

Mobility	Protection of the Soldier and Construction	Civic Action, Psychological Warfare, and Miscellaneous Military
Unsinkable utility boats[a]	Prosthetic devices[a]	Packaging materials for returning expensive items to CONUS[a]
Foam assault boats[a]	Quick personnel shelters[a]	Refugee shelters[a]
Pontoons[a]	Maintenance sheds[a]	Pacification and housing
Minesweeper floats[a]	Magazines/Igloos[a]	Schools, hospitals, pagodas[a]
Bridges[b]	Caches[a]	Fishing boats[a]
Docks[a]	Hospitals[b]	Sheds[a]
Life preservers[a]	Water reservoirs[b]	Bridges[b]
Barges[a]	Camouflage/Deception[a]	Rafts[a]
Weapons rafts[a]	Air-drop packages[a]	Docks[a]
Swimmer supports[a]	Filters[a]	Life preservers[a]
Artificial islands for heliports[b]	Cots[a]	Cold storage units[a]
Construction fill[b]	Splints[a]	Insulation
Hasty route preparation[b]	X-ray tables[a]	Antenna
Gully fill[b]	Mattresses[a]	Potting for energy absorption
	Padding[a]	Earphone pads
	Decoys[a]	
	Slabs and forms[a]	
	Insulated food boxes[a]	
	Marking devices[a]	

[a] Immediate possibility.

[b] Possibility after 1 or 2 years of research, development, testing, and evaluation.

interest to the Army. Other cellular materials might be made from metal, for example. It is not unlikely to consider that a cellular metal structure would be of value, for instance as a porous electrode in a battery or fuel cell. The desirability of having a porous metal structure versus a porous or cellular plastic structure would be mainly in terms of the advantages that the metal would hold. The advantages that a cellular metal material would provide would be in terms of environmental stability, greater rigidity, a requirement for porosity, or the need for an increased surface area. The porosity would be the factor that would be of value in the abovementioned applications. The surface-area factor might possibly be utilized for the purpose of catalytic activity in electrodes or in structures requiring some form of gas decomposition, such as in a gas generator. Foamed structures have even been considered in solid rocket propellant grain structures. Another advantage of a foamed metal structure would be a lowered weight with essentially the same rigidity or structural strength. Because of end-use advantages offered by cellular materials, the Army also maintains an active interest in support of programs on syntheses of new cellular materials, the mechanism of foam formation, and novel applications of foam substrates. It is significant to note that whether the material is of a foam or cellular character is often secondary to why an investigation is being conducted. For this reason it is difficult to analyze, to determine, and to evaluate the total Army effort that might be related to cellular and foamed materials.

SUMMARY

Discussion is presented on U.S. Army interest in research on construction materials, development of a mobile plastics fabrication unit, and applications of cellular materials. Studies are under way in the above areas which may lead to increased uses of foamed plastics and cellular materials.

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Navy Applications for Cellular Plastics

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INTRODUCTION

Navy applications for cellular plastics* include void filling, thermal insulation, shock absorption, packaging, bedding, deep submergence flotation, and salvage. The bulk of the Navy's current work in cellular plastics, however, is specifically oriented toward developing an improved external structural void filler system for submarines, a substitute buoyancy system for gasoline flotation for deep submergence vehicles, a more efficient and more fire resistant thermal hull insulation for submarines, and a foam-in-salvage system for the recovery of sunken vessels.

VOID FILLING

Submarine voids (diving planes, rudders, and transition rings) external to the pressure hull of submarines are filled with syntactic foam composed of hollow phenolic microspheres dispersed in a polyester matrix. These voids are filled with a buoyant material of sufficient compressive strength to prevent excessive plate deflection of submarine appendages when subjected to ambient hydrostatic pressures.

Although submarine appendages might be designed to be free flooding, this would introduce problems of internal corrosion, increased noise level, and reduced buoyancy. A typical 42–44 lb/cu ft density syntactic foam

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*The views expressed herein are those of the author and are not necessarily those of the U.S. Navy.

for filling voids exterior to the pressure hull of submarines is composed of 20 parts of phenolic microballoons to 100 parts of polyester resin. Depending on submarine design, approximately 1,500 to 1,800 cu ft of syntactic foam is required to fill voids external to the pressure hull. This amounts to approximately 60,000 to 80,000 lb of filler material per submarine for a 42–44 lb/cu ft foam. To facilitate weight reduction on submarines, the Navy is developing an improved syntactic void filler composed of 0.25-in.-diameter epoxy hollow spheres and glass microspheres in a polyester resin matrix. Adoption of this new 33 lb/cu ft density void filler system would result in a weight saving of approximately 25 percent over the present filler system. Cross sections of both filler systems are shown in Figure 1. It is anticipated that further density reduction to 25 lb/cu ft may be possible with further development work. It should be noted that although there are commercially available foam-in-place polyurethane foams that meet the low density and high compressive strength requirements for a submarine void filler, high water absorption following extended hydrostatic exposure obviates their use for this application—at least at present.

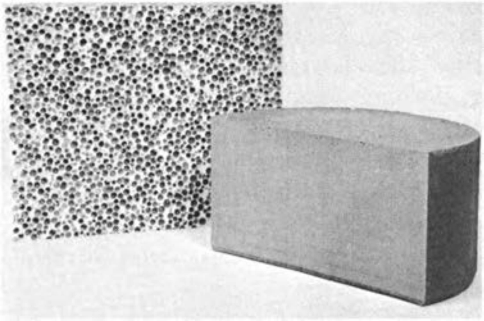

FIGURE 1
Submarine void fillers.

BUOYANCY FOR DEEP SUBMERGENCE VEHICLES

Syntactic foams to provide positive buoyancy for deep submergence vehicles can be formulated by dispersing high-strength low-density glass microspheres into an epoxy matrix. Poured-in-place syntactic modules are subsequently subjected to an elevated heat schedule to develop optimum physical properties. The Navy has prepared a specification for procurement of syntactic buoyancy material for the AUTEC 6,500 ft operating depth vehicles. This specification provides for a 38-pcf density material proof tested to 4,500 psi for intermediate depth vehicles and a 44-pcf material proof tested to 10,000 psi for deeper depth vehicles. A Qualified Products List will be established as qualification tests are completed under this specification. The Navy is also investigating the fabrication and testing of large castings of syntactic foam. Test specimens taken from 8 in. × 10 in. × 59 in. modules have been exposed to hydrostatic and cyclic fatigue tests to 10,000 psi. After exposure to one thousand 20-min cycles between 0 and 10,000 psi, less than 1 percent water absorption was obtained on uncoated 1-in.-diameter × 2-in.-length cylindrical 44-pcf density Navy test specimens. This low water absorption is typical of a suitably compounded and processed syntactic foam formulation. An in-service performance evaluation of syntactic foam test specimens on the bathyscaphe *Trieste II* has been initiated. Performance data will be obtained at intervals up to 1 year.

A study of compounding and processing problems associated with syntactic foam formulations has indicated the critical need for rigid quality control for the glass microsphere fillers incorporated. Unless this control is exercised, uniform-high-strength castings cannot be consistently fabricated.

The Navy's Special Projects Office is considering the design of a 20,000-ft operating depth search vehicle which will require a more efficient buoyancy system than any developed to date by either the Navy or private industry. Candidate buoyancy systems will require weight-to-displacement ratios as low as 0.3 to 0.4 and will require proof testing to 30,000 ft. After completion of an extensive survey of candidate buoyancy systems, the Navy is currently evaluating glass and ceramic macrosphere composite structures for the above application.

Because of successful experience in relating ultrasonic attenuation to voids and compressive strength in filament wound plastics, the Navy is extending its investigation of this nondestructive technique to locating internal flaws in syntactic foam modules.

THERMAL INSULATION

The Navy now specifies rigid polyurethane foam for thermal insulation for refrigerated spaces on all combatant ships. Polyurethane foam is a more efficient insulation material than the fibrous glass it replaces, and it will not become matted.

For thermal hull insulation on submarines, the Navy procures flexible elastomeric foams in sheet and tube form. To improve thermal-insulation properties and to reduce flame-spread and smoke-development properties of presently procured material, the Navy is investigating both rigid polyurethane and modified polyvinyl chloride foams. Since these foams have stabilized k factors of 0.16 and a density of 2 lb/cu ft as against 0.28 and 8 to 10 lb/cu ft, respectively, for presently procured material, both weight and space savings could be effected. In addition, improved fire resistance will be realized if these newer insulation materials pass Navy tests and are subsequently authorized for installation. It is estimated that weight savings of 18,000 lb could be effected on a fleet ballistic missile submarine installation by adopting either of these newer insulation systems. A value engineering study is under consideration to select the system showing the most favorable cost-to-effectiveness ratio. One very important unknown factor yet to be determined for these newer rigid thermal insulation systems is whether the somewhat friable nature of these new systems will result in excessive breakage during submarine installation.

FOAM-IN-SALVAGE

The Navy is investigating the feasibility of employing the novel foam-in-place polyurethane foam process for salvaging sunken vessels. After evaluating carbon dioxide and halocarbon blown foams, a laboratory study concluded that the use of foam-in-place polyurethane foam was feasible down to the depth investigated—375 ft in water.

Large-scale feasibility was commercially demonstrated in the ocean when the polyurethane froth process was used to float a 350-ton barge from approximately 40 ft in 50°F water off Eureka, California. The portability and simplicity of the foam equipment was of considerable interest to Navy Salvors, since movement of foam ingredients involved only positive gas pressure from nitrogen bottles rather than mechanical pumping systems.

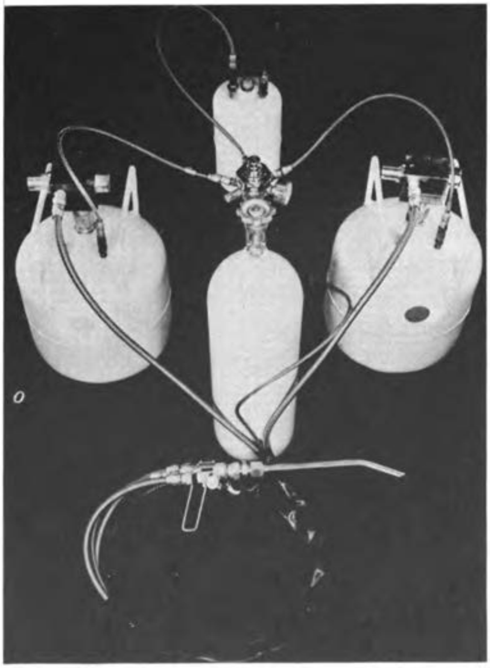

FIGURE 2
Commercial urethane froth foam equipment.

FIGURE 3
Foam removal operation.

The Navy subsequently demonstrated large-scale feasibility of the polyurethane frothing process to a depth of 200 ft in the ocean. Successful demonstrations were made at 50-ft intervals to 200 ft. Because of less efficient process control, the demonstration at 200 ft at SEALAB II at La Jolla, California, was not as satisfactory as the foam produced earlier during the San Francisco Bay demonstrations. Current development objective calls for an operational Foam-in-Salvage system in water temperatures ranging from 29 to 80°F. Density objectives call for 2 lb/cu ft for a 50-foot-depth pour and a maximum of 6 lb/cu ft to 200 ft. Studies have been initiated to explore the feasibility of Foam-in-Salvage and allied systems to extend salvage capability to 600 ft. Finally, a large-scale unique application for the Foam-in-Salvage frothing process involved a stranding type salvage operation on the destroyer *Frank Knox* in the South China seas. The magnitude of the logistics problem of air transporting massive quantities of foam material and equipment halfway around the world indicates the portability and ease with which this system can be employed wherever needed in the world. The equipment used is shown in Figure 2. The problem of foam removal after salvage can be enormous. At the present time, only crude mechanical methods have been employed. Figure 3 shows the residual foam remaining adhered to cables, equipment, and raceways after the salvage and foam removal operations on the *Frank Knox*. Easy, inexpensive, rapid, and more efficient foam removal methods would be of interest to the Navy.

Some Factors Affecting the Utilization of Foam Plastics in Operations of the Agency for International Development

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To develop an intelligent appreciation for the motivations which result in the activities of the Agency for International Development (AID), it might be best to look at the thinking of the Congress when it passed the Foreign Assistance Act of 1961. Section 102 of this law restated the view that peace depends upon the wider recognition of the dignity and interdependence of men, and that the best assurance for the survival of the free institutions in the United States would be the worldwide proliferation of an atmosphere of freedom.

But, this statement continued:

> To this end, the United States has in the past provided assistance to help strengthen the forces of freedom by aiding peoples of less developed friendly countries of the world to develop their resources and improve their living standards, to realize their aspirations for justice, education, dignity, and respect as individual human beings, and to establish responsible governments.
>
> The Congress declares it to be a primary necessity, opportunity, and responsibility of the United States, and consistent with its traditions and ideals, to renew the spirit which lay behind these past efforts, and to help make a historic demonstration that economic growth and political democracy can go hand in hand to the end that an enlarged community of free, stable, and self-reliant countries can reduce world tensions and insecurity.

Within the framework of this declaration some $3 billion to $5 billion have been expended annually since 1961 in attempts to secure these desirable objectives. The directives, which give substance to the policy, have reflected the ebb and flow of events and the dominant thinking on problems of economic and social development. Industrial revolution is the outstanding element in Western developmental experiences, and the rapid recovery of Europe under the Marshall Plan seemed to say to many people that a dash of technology added to any underdeveloped society would automatically promote economic and social development through the growth of industry. Because of this background, industrialization was the guiding principle in our planning for aid to developing countries for many years. But the record of performance does not wholly support the assumption. Of late, efforts to promote economic and social development through absorption of technology and industry have had to be fortified by insights from the behavioral sciences. These insights attempt to discover patterns of synergistic factors which would promote the desired absorption.

Industry continues to be a need of developing countries. Without it, desired manufactured goods will be hard to get (given the international market condition in which exported agricultural products continue to fall in price while the cost of imported manufactured goods continues to rise). A new emphasis upon agriculture, education, and health as priority areas for AID activity has been declared to satisfy the pressing welfare needs of the peoples of aid-receiving countries. Nevertheless, the multiplier effect of modern technology upon the activities in each of these sectors will be indispensable if the desired developmental performance is to be realized.

A multibillion dollar package of technical assistance projects and other development devices, such as grants and loans, is assembled annually from plans prepared by individual countries and submitted through the USAID missions maintained in them. This constitutes the major part of the aid program of the United States and is administered by the Agency for International Development. A large portion of these expenditures is channeled through U.S. business organizations, but a different kind of participation now seems to be required of them. In an effort to discover how to deepen the involvement of the private sector in U.S. aid efforts, a committee, broadly representative of leaders from the mainstreams of American life, recently examined the problem.

The findings confirmed the growing belief that foreign aid is likely to go on indefinitely unless it is amplified by initiatives undertaken in the private sector. The annual multibillion dollar AID programs can supply directly only a small fraction of the human and financial resources required for the growth of developing countries. The annual deficit in capital goods alone is in the neighborhood of $5 billion to $20 billion! It is unrealistic to expect a government-financed foreign aid program to make this up. The full U.S. moral commitment to foreign aid can be fulfilled only by stimulating all segments of the private sector—business organizations, labor unions, education associations, professional societies, and foundations—to commit themselves more fully to economic development. (U.S. business organizations operating in developing countries have in the past been mainly engaged in extractive industries, e.g., oil and minerals, and the rate at which new capital has been going into developing countries has been quite modest.) The committee proposed that an intensified relationship between AID and all other sectors of the U.S. economy should be developed, with the former playing a more effective role as energizer and catalyst for the involvement of the latter in foreign aid operations.

AID had already taken major steps in this direction. Its Specific Risk Guaranties program now insures American owners against losses from inconvertibility of currencies, nationalization and confiscation of property, and losses from war and revolution. The Extended Risk Guaranties can effectively insure investors against virtually every other risk.

Given all the capital in the world, the less-developed countries would in all probability remain exactly that—less-developed—because they do not have the human and institutional resources to make effective use of the capital. One of the basic problems in the development effort is that of transferring the skills, the technology, and even the attitudes to individuals and institutions so that the capital can be made to produce on a rising curve as the indigenous people become more skilled.

Given the need for foreign aid, our government's concern that the private sectors be more involved, and our government's willingness to offer incentives for that purpose, how is a sophisticated material and technology such as foam plastics to be fitted into the world of foreign aid which typically is agricultural, a consumer of imported manufactured goods, poor in human resources, and often also poor in natural resources?

It may be worthwhile to look at foam plastics as a substitute for materials presently in use. This approach is obviously self-limiting.

It is likely to be more fruitful to seek in foam plastics a new material for specific applications made possible by its special properties. This free approach will give rise to novel design problems, but these can now be addressed by exploiting new degrees of freedom conferred by the properties themselves, with proper recognition of the restraints which they introduce.

Policy directives, which recommend both substantive and sector priorities, will indicate areas where help, perhaps from foam plastics applications, is most needed. Experience in foreign aid has led to upward revision of the sector priorities for agriculture, education, and health; it is therefore reasonable to look at activities in these sectors for significant opportunities for foam plastics utilization. Each one will have problems which can be examined with this point in mind.

For most developing countries, agriculture means mainly food, for both subsistence and export. It also supplies fibers for clothing and other utilitarian functions. Finally, it also often contributes to provision of shelter. Food problems of many developing countries are quite acute, and the production of increased food is a high-priority responsibility of agriculture. In the short run, however, elimination of losses due to handling damage, spoilage, and vermin activity may be the most effective way of quickly increasing the available supplies of food. This would seem to be a point of attack that would attract support for the proponents of foam plastics. Eliminating these losses may be equivalent to as much as a 30 percent increase in available food in a typical developing country.

A structural use of foam plastics that is transferable to developing countries with slight adaptation is the production of shelter for farm animals.

Meat, fish, and dairy products need particular protection from unfavorable environments. Modern storage facilities and techniques developed for use in temperate zones may run into unexpected problems in hot humid environments. But on the plus side, systematic attempts to exploit low night temperatures where they occur could offer a novel design opportunity for foam plastics.

The problem of supplying roofs for minimal structures is a pervasive one affecting hundreds of millions of people with family incomes under $200 a year. Provision of elementary shelter in the beginning may be all that will be possible; but, as we shall be hearing in another session, other possibilities may be coming into view.

In education and health, the role of foam plastics, although it may be secondary, could facilitate the attainment of the major objectives of these sectors by its adaptability in providing immediately available shelter for people, communal buildings such as recreational halls, health centers, and schools. If it can supply fixed shelter, it will become a stabilizing influence on a shifting wandering population. This would bring into the lives of millions of people their first enduring experience of a home—a minimal one, it is true—but still one which will give new meaning to the concepts of family and community.

One aspect of work in underdeveloped countries must be mentioned here because of its unique importance. For these countries, field activities should aim to provide a service, of which the technology is only a part. It is likely to be futile to sell less than this. The people, who in our country would provide the complementary functions, do not exist in most underdeveloped countries. Further, even when such people can be found, they may be unwilling to "soil their hands," if it takes that to do what is required.

The developing world is made up of societies in transition. What they are satisfied with today may not be acceptable tomorrow. On the other hand, technological innovations, such as foam plastics, which today may be incompatible with slowly changing regulations in developing countries, may be logically introduced in these countries later. Plastics in the more economical foamed form may be just the material from which to satisfy particular "short-run" social and technological needs. Using this medium, mistakes need not be frozen into the social structure by high costs of correction. Its aggressive use could provide the developing countries with opportunity to experiment with ideas before making final choices of materials or methods. It will be possible to abandon *our* solutions to their problems without major losses when the time comes for them to substitute *their own* solutions. If in the long run the material is found to do a job in a new and better way, then the investment will have attracted an added premium.

The magnitude of the housing needs of developing countries suggests that it is quite useless to attempt to satisfy it by means of conventional methods. One estimate indicates that of the tens of millions of housing units that are needed now, three quarters or more are needed at unit costs of $10 to $25. Only token amounts could be absorbed at cost ranges in the hundreds of dollars. The effective demand for quantities in Western cost ranges of thousands of dollars per unit was purely symbolic.

The social and economic implications of a major breakthrough in housing methods are staggering, in view of the facts. All sectors of the economy would feel the impact. The AID has been exploring the feasibility of using low-density foams by themselves or in association with indigenous materials as structural elements for housing or housing parts.

SUMMARY

The paper notes briefly the philosophy of the legislative authorization for the AID and the flexibility in the executive directives which have guided the planning and programming of United States foreign aid activities. This aid has been generous, but institutions from the private sector will need to exercise more initiative if the development of the underdeveloped countries is to be decisively influenced. The AID offers incentive programs to encourage this. Recent adjustment in sector priorities emphasizes work in agriculture, health, and education. This imposes greater support responsibility upon all other sectors including technology and industry. Some applications of foam plastics in this context are mentioned.

SESSION 2

Chemistry and Physics of Cellular Materials

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Recent Advances in Cellular Materials

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INTRODUCTION

Cellular plastics have gained increased acceptance in commercial applications as insulation, structural and semistructural components, flotation and buoyancy materials, packaging media, and cores for ablative heat shields. Considerable research and development efforts are presently being directed toward the improvement of the chemical, physical, and mechanical properties of expanded plastics. Within the scope of this presentation I shall attempt to review several of the major recent advances in foam technology. I shall cover only those developments related to polyolefin, polysulfide, polystyrene, and urethane foams.

ADVANCES IN THE CHEMISTRY AND DECOMPOSITION MECHANISM OF CHEMICAL BLOWING AGENTS

The technology of expanding rubber and plastics has been significantly advanced in recent years by the development of a variety of organic blowing agents. Reed[1] and Lasman[2] have presented two comprehensive reviews of blowing-agent technology.

The requirements of the "ideal" blowing agent are as follows:[1]

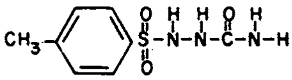
1. Gas must be released over a definite and short range.
2. Gas must be released at a controllable but reasonably rapid rate.
3. The gases involved should be noncorrosive.

4. The compound should disperse readily in the stock and preferably dissolve.
5. The compound should be cheap in application.
6. The compound must be stable in storage.
7. The residue should not have an unpleasant odor.
8. The residue should be colorless and nonstaining.
9. The compound and residue should be nontoxic.
10. The compound should not give rise to a large exotherm on decomposition.
11. The compound should not affect the rate of cure.
12. The compound should function well in an open or closed mold.

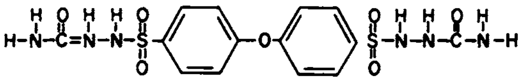
In the selection of a blowing agent for a specific application, the decomposition temperature and efficiency of gas evolution are most important. Decomposition temperature refers to the point at which the dry material begins to produce gas at a reasonably rapid rate. The efficiency is usually expressed as gas evolution in cubic centimeters per gram measured at standard temperature and pressure (STP).

Decomposition of Organic Blowing Agents

One of the most recent additions to available blowing agents is *p*-toluenesulfonyl semicarbazide[3] (I). This material, which decomposes at 235°C, is useful for expanding plastics such as high-density polyethylene, polypropylene, rigid polyvinyl chloride, ABS polymers, polycarbonates, and nylon. Another compound *p,p'*-oxybis(benzenesulfonyl semicarbazide)[3,4] (II) decomposes at 215°C.



I



II

Hunter[3,4] reported that the quantity of gas produced by the two blowing agents is similar (143–145 cc of gas per gram at STP). In the case of *p*-toluenesulfonyl semicarbazide this corresponds to approximately 1.5 moles of gas per mole of compound. The *p,p'*-oxybis(benzenesulfonyl semicarbazide) being bifunctional produces approximately 3.0 moles of gas

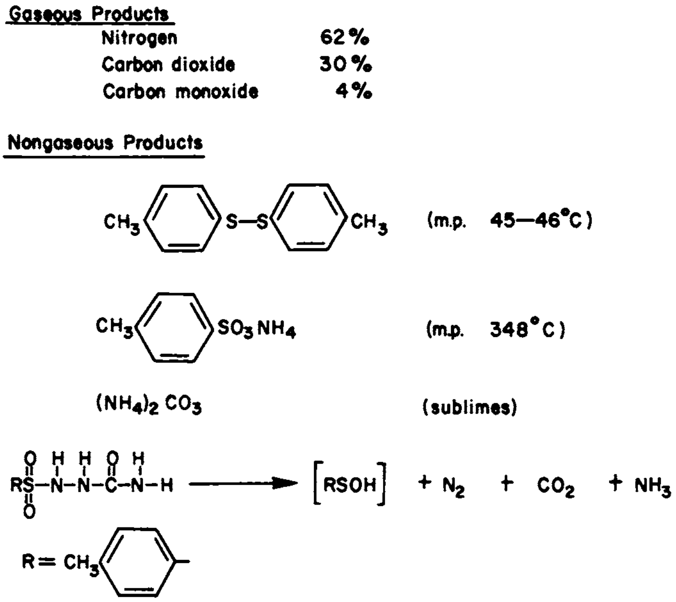


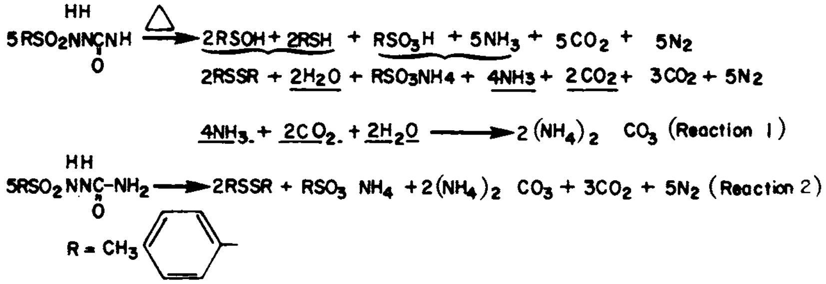
FIGURE 1
Decomposition products of *p*-toluenesulfonyl semicarbazide.

per mole of compound. Substantial quantities of carbon dioxide as well as nitrogen were observed in the decomposition gases.

The gaseous and nongaseous products formed by the dry decomposition of *p*-toluenesulfonyl semicarbazide are shown in Figure 1.

The equation shown in Figure 1 is a possible representation of the initial decomposition reaction. The products identified (except carbon monoxide) may be obtained by subsequent disproportionation and recombination of the initial decomposition fragments.

Reactions 1 and 2 illustrate the stoichiometric representation of possible reactions occurring in the decomposition of *p*-toluenesulfonyl semicarbazide.


$$5RSO_2NNCNH \xrightarrow{\Delta} \underbrace{2RSOH + 2RSH} + \underbrace{RSO_3H + 5NH_3} + 5CO_2 + 5N_2$$
$$2RSSR + \underline{2H_2O} + RSO_3NH_4 + \underline{4NH_3} + \underline{2CO_2} + 3CO_2 + 5N_2$$
$$\underline{4NH_3} + \underline{2CO_2} + \underline{2H_2O} \longrightarrow 2(NH_4)_2\ CO_3 \quad \text{(Reaction 1)}$$
$$5RSO_2NNC\text{-}NH_2 \longrightarrow 2RSSR + RSO_3\ NH_4 + 2(NH_4)_2\ CO_3 + 3CO_2 + 5N_2 \quad \text{(Reaction 2)}$$

The ammonia is not recovered as such but partially combines with sulfonic acid (as RSO_3NH_4) and partially combines with carbon dioxide and water as ammonium carbonate. According to Reactions 1 and 2 a total of 8 moles of gas is formed from 5 moles of blowing agent. This represents 1.6 moles of gas per mole of *p*-toluenesulfonyl semicarbazide which is in reasonable agreement with the 1.5 moles of gas reported by Hunter.

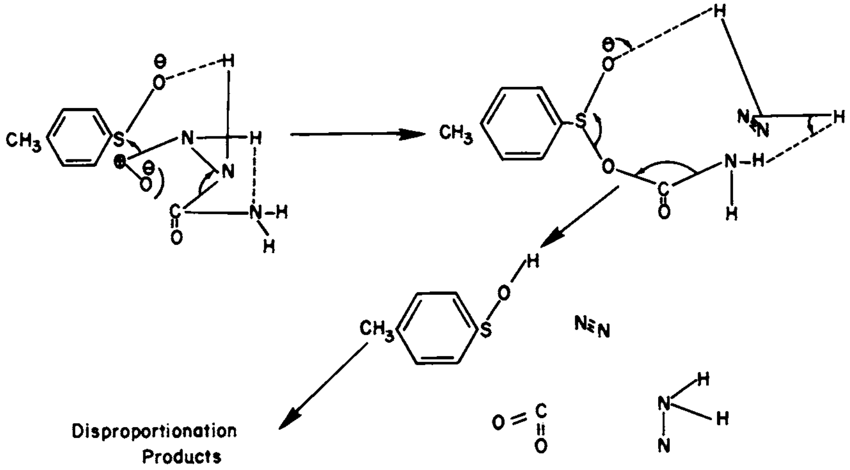


FIGURE 2
Possible mechanism for decomposition of *p*-toluenesulfonyl semicarbazide.

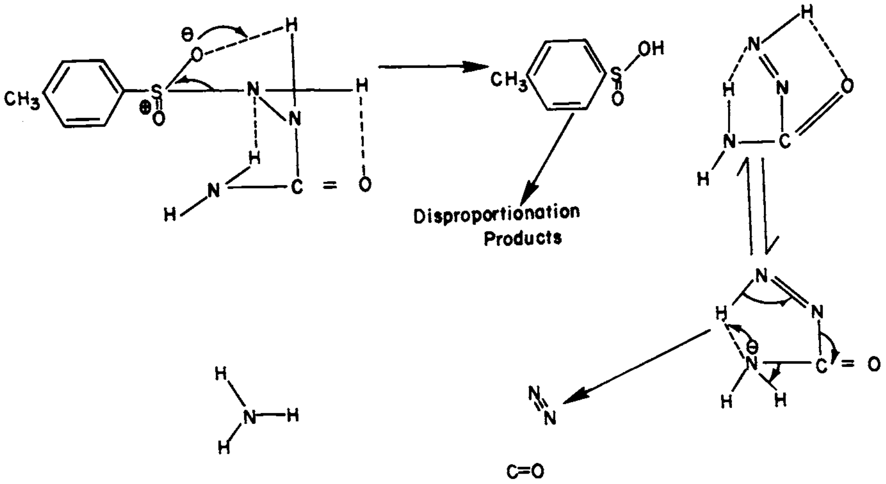


FIGURE 3
Possible mechanism for decomposition of *p*-toluenesulfonyl semicarbazide.

The rapid decomposition of *p*-toluenesulfonyl semicarbazide suggests that a concerted mechanism is involved. It appears that strong hydrogen bonding may account for the high heat stability. At the 235°C decomposition temperature, excitation within the molecule is sufficient to produce electron shifts and cause simultaneous breaking and reforming of bonds.

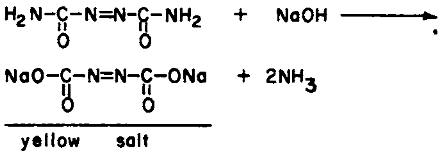
Hunter has proposed two possible mechanisms for the decomposition of *p*-toluenesulfonyl semicarbazide (Figures 2 and 3).

In Figure 2 the dotted lines illustrate the hydrogen bonding. Electron shifts are indicated leading to the formation of carbon dioxide, nitrogen, and ammonia. The *p*-toluene sulfuric acid will decompose to other products as described earlier.

In Figure 3 an alternate shift of bonds is shown which results in the formation of carbon monoxide, nitrogen, ammonia, and *p*-toluene sulfinic acid. The latter disproportionates to stable products.

Blowing Agents Activated by Water

Hunter and Kleinfeld[4] reported on the use of blowing agents, activated by the presence of water, to expand liquid polysulfide polymers. Sodium azodicarboxylate was prepared by treating azodicarbonamide with sodium hydroxide to obtain the following reaction:



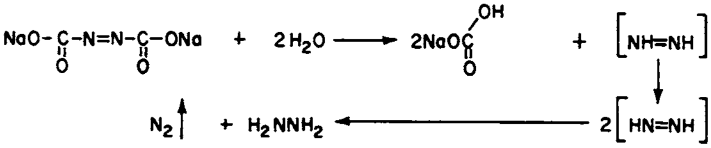
$$H_2N-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-NH_2 + NaOH \longrightarrow$$

$$\underset{\text{yellow salt}}{\underline{NaO-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-ONa}} + 2NH_3$$

(Reaction 3)

The salt is stable as long as it is kept free of water.

The decomposition of sodium azodicarboxylate is (Reaction 4):



$$NaO-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-ONa + 2H_2O \longrightarrow 2NaO\underset{\underset{O}{\|}}{C}{}^{\diagup OH} + \left[NH=NH\right]$$

$$\left[NH=NH\right] \downarrow \quad 2\left[HN=NH\right] \longrightarrow N_2\uparrow + H_2NNH_2$$

(Reaction 4)

Liquid polysulfide polymers having the structure represented in Figure 4 cure by converting terminal thiol (SH) to disulfide (SS) bonds resulting in a long-chain polysulfide elastomer.

Curing of polysulfide polymers is accomplished by oxidizing peroxide as represented in Figure 4.

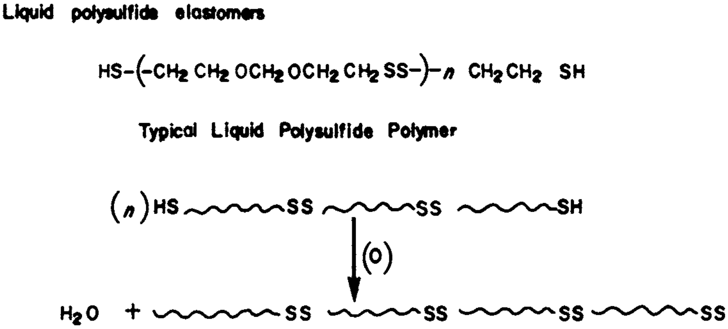


FIGURE 4
Liquid polysulfide elastomers.

Thus, if a water-sensitive blowing agent such as sodium azodicarboxylate is added to a liquid polysulfide polymer, the blowing agent is decomposed by water released during peroxide curing.

If lead peroxide is employed as the curing agent, additional nitrogen is released by its reaction with hydrazine (Reaction 5).

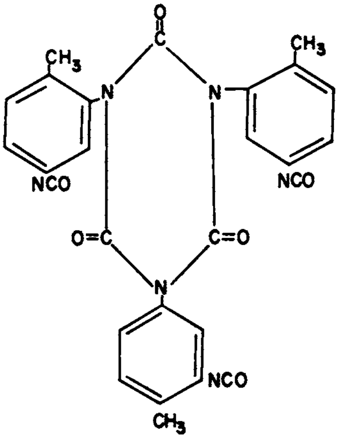
$$H_2NNH_2 + 2PbO_2 \longrightarrow N_2\uparrow + H_2O + 2PbO \quad \text{(Reaction 5)}$$

Polysulfides prepared as described above are transformed into elastomeric foams.

RECENT ADVANCES IN URETHANE FOAMS

Development of High-Temperature Foaming Systems

Many urethane foam systems have been developed which are satisfactory for continuous service in excess of 200°F. Considerable effort has been directed toward the development of systems that possess the necessary chemical and physical properties that will permit specification for continuous service above 300°F. Nicholas and Gmitter[5] have reported on heat-resistant foams prepared by the trimerization of isocyanate terminated prepolymers. A commercially available prepolymer is the reaction product of the 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate with a hydroxyl-terminated triol adipate. *N,N′,N″*-tris(dimethylaminopropyl)-*syn*-hexahydrotriazine (HHT) and 2,4,6-tris(dimethylaminomethyl)phenol, alone or in combination with a diepoxide cocatalyst, led to high yields of trimerization. The typical structure of an isocyanurate ring is shown in III.



III

Nicholas and Gmitter reported that they added the catalyst component to the prepolymer blend and agitated the mixture mechanically for 15 sec. Foaming commenced within 30 sec and was complete within 2 min.

Properties of typical rigid isocyanurate foams are presented in Table 1.

TABLE 1
Physical Properties of a Typical Rigid Isocyanurate Foam

Density, lb/ft^3	4.5
Thermal conductivity k factor, Btu/hr/sq ft/in./°F	0.14
Compression strength, psi	
(a) Before aging at	
75°F	81
300°F	84
350°F	68
400°F	56
450°F	48
(b) After heat aging for 24 hr at	
300°F	88
400°F	82
450°F	54
(c) After humid aging	
7 days at 158°F (95–100 percent relative humidity)	81
Dimensional stability, percent volume change	
(a) After heat aging for 24 hr at	
300°F	0
350°F	0
400°F	−2
450°F	−5
(b) After humid aging	
7 days at 158°F	0

Figure 5 compares the compressive strength of isocyanurate foams at moderate to elevated temperatures.

Figure 6 compares the compressive strengths of isocyanurate and urethane foams at elevated temperatures.

Figure 7 shows the weight retention of typical isocyanurate foams at elevated temperatures.

The thermal degradation of selected foams was studied by differential thermal analysis techniques. Evaluation of results indicated that replacement of the urethane linkages by more stable groups would lead to a further improvement in the thermal stability of the isocyanurate-containing foams.

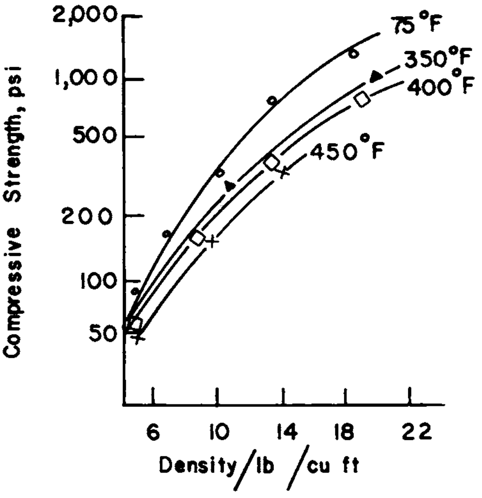


FIGURE 5
Compressive strength of polyisocyanurate foam at various temperatures.

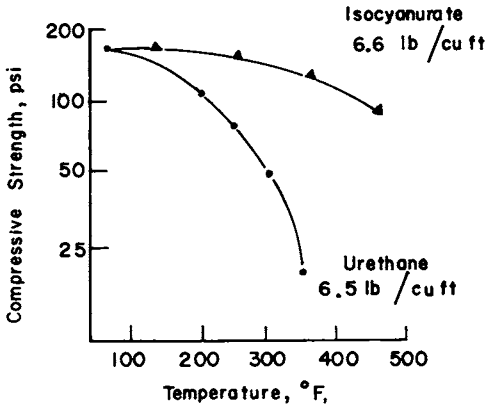
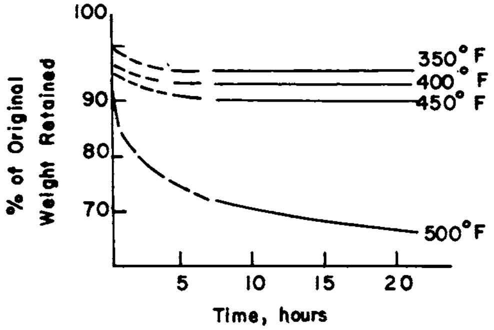


FIGURE 6
Compressive strength versus temperature of polyisocyanurate and polyurethane foams.

FIGURE 7

Weight retention of typical isocyanurate foam at elevated temperatures.



Extended Urethane Foams

The incorporation of light-weight, bulky, inorganic fillers in rigid urethane foam systems has been reported in the literature.[6] Composites were prepared incorporating asbestos fibers, cellular glass pellets, glass microballoons, vermiculite, and other fillers. 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 the design of composites. Important interactions occur during processing of composites, thus the foam formation may require modification to obtain a desirable structure.

Several methods have been developed as a means of incorporating an extender into the foaming mass during the processing of composites. These include premixing 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.

Foam composites extended with cellular glass beads had greatly improved flammability characteristics. Table 2 shows the properties of a typical pellet–foam composite.

The major advantages gained by the incorporation of inert fillers in urethane foam are the improved flammability characteristics. Fire endurance characteristics were determined using the Bureau of Mines Burn-Through Test. A schematic drawing of the apparatus used is shown in Figure 8.

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 pencil flame burner tip (designed to concentrate the flame source). The flame is adjusted to a cone of approximately 1.5 in. in length (temperature 2,000–2,100°F) and the tip of the flame is positioned in contact with

TABLE 2

Typical Properties of Pellet–Foam Composite

Urethane system	Polymeric isocyanate, sucrose adduct, Fluorocarbon-11 blowing agent
Pellet size	$\bar{x}$ = 0.4530 = 0.0045
Pellet density	7.7 lb/cu ft
Weight %, pellets	69.0
Weight %, foam	31.0
Volume loading, pellets	57.1
Volume loading, foam	42.9
Composite density	6.4 lb/cu ft
Foam density	4.6 lb/cu ft
Water vapor transmission rate	0.75 perm-in.

Compressive Strength, psi	Initial	4 Weeks in Controlled Environment
5% deflection	42.1	28.4
10% deflection	56.7	42.6
Proportional limit, psi at % deflection	20.3 at 0.75	21.0 at 3.51
Thermal conductivity at 75°F mean	0.145	0.150
Dimensional stability, % volume change after 4 weeks in controlled environment	+3.92	Tests not complete

the sample surface at the beginning of the test. Failure, end of test, is indicated when the filter paper catches fire, chars, or cracks. A description of samples evaluated in conjunction with foam composite research and a summary of test results are listed in Table 3.

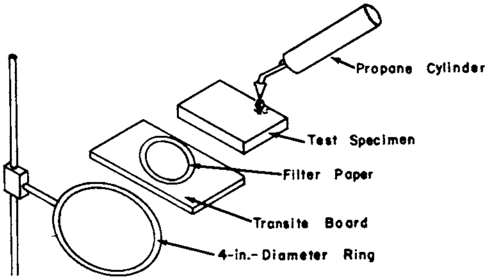


FIGURE 8

Schematic of Bureau of Mines apparatus for horizontal test method.

TABLE 3
Bureau of Mines Fire Endurance Test (Horizontal Method)

Sample Description	Endurance Time
Cellular Plastics	
Polystyrene bead board[a]	7 sec
Expanded polystyrene[a]	7 sec
Expanded polystyrene[b]	9 sec
Urethane foam[a, c]	20 sec
Epoxy foam[b]	1 min 20 sec
Urethane foam[b]	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[a, c]–mica composite	20 sec
Urethane foam[a]–glass flake composite	20 sec
Urethane foam[a, c]–vermiculite composite	5 min 22 sec
Urethane foam[a, c]–glass flake composite	39 sec
Urethane foam[a, c]–glass pellet composite	10 min 40 sec
Urethane foam[a, c]–pelletized glass microballoons composite	10 min 48 sec
Urethane foam[b, d]–glass flake composite	3 hr +
Urethane foam[b, d]–glass pellet composite	3 hr +
Urethane foam[b, d]–pelletized glass microballoons composite	3 hr +
Miscellaneous Control Samples	
Fiberglass board (12.0 lb/cu ft)	7 min 45 sec
White pine (25.2 lb/cu ft)	53 min 15 sec

[a] Non-self-extinguishing.
[b] Self-extinguishing.
[c] Urethane foam (tolylene diisocyanate, sorbitol adduct, F-11 system).
[d] Urethane foam (polymeric isocyanate, chlorinated polyester polyol, F-11 system).

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 was prepared and the flammability properties determined by the ASTM-E-84 (Steiner Tunnel) test.

Table 4 presents the results of exploratory tests conducted in the Underwriters Tunnel.

Exploratory efforts have demonstrated the feasibility of preparing composites utilizing bulky, inert, low-density fillers to improve the flammability characteristics of urethane foam.

TABLE 4
Tunnel Test (ASTM-E-84) Exploratory Results

Property	Urethane Foam	Urethane[a] Foam–Glass Flake Composite	Urethane[a] Foam–Glass Pellet Composite
Propagation of flame spread	40	30	25–30
Fuel contribution	—	10	35
Smoke density	+400	+400	65

[a] Polymeric isocyanate, chlorinated polyester polyol, F-11 blowing agent.

RECENT ADVANCES IN POLYETHYLENE FOAMS

Attempts have been made to convert polyethylene (a thermoplastic polymer) to a thermoset material in order to improve thermal stability and stress crack resistance. Several investigations have reported on research in this area.[7-11] It has been difficult to relate the progress obtained in solid polymers to that carried out in filled cross-linked polyethylene foams.

Incorporation of fillers in foaming systems has offered more immediate results. Nutter and Benning[12] have reported on research to determine the effect of fillers in cross-linked high-density polyethylene foams. The types and properties of fillers used are listed in Table 5.

TABLE 5
Fillers for Polyethylene Foams

Filler	Composition	Average Particle Size (μ)	Oil Absorption, % Weight of Filler	pH	Specific Gravity
Hydrite-R	Aluminum silicate	0.77	36	4.2–5.2	2.58
Hydrite-121	Aluminum silicate	1.5	32	4.2–5.2	2.58
Hi-Sil-233	Silica	0.022	150	7.3	1.95
Spheron-9	Carbon black	0.029	120	4.5	1.8
Wollastonites	Calcium silicate				
P-1		4.1	22	9.9	2.9
P-4		2.8	23	9.9	2.9
C-1		5.4	21	9.9	2.9
C-6		6.8	20	9.9	2.9
F-1		7.4	28	9.9	2.9
7004	Chrysotile asbestos (Shorts)	—	—	9.5–11	2.6

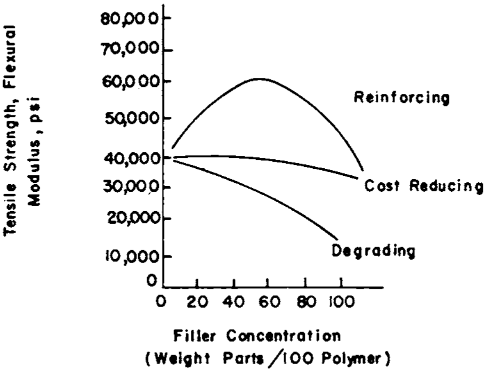


FIGURE 9
Filler type based on relationship of filler concentration to foam physical properties.

Fillers may be classified according to functional utility as illustrated in Figure 9.

Reinforcement of polyethylene polymers only occurs when the particles are smaller than 0.12 μ. Carbon black and silica are the only fillers used by Nutter and Benning that may be classified as reinforcing.

Foam density is the most important factor affecting the physical strengths and performance characteristics of cellular materials. Figure 10 indicates that calcium silicate (a nonreinforcing filler) has less effect on foam density than carbon black (a reinforcing filler). Since the small particle has an increased surface area it can be reasoned that the foam that forms a high-density skin at the interface in the reinforcement will exhibit an increase in density that is proportional to the decrease in reinforcement size.

Figure 11 indicates the difference in compressive strength properties exhibited by reinforced and extended foam structures.

Figure 12 shows the effect of varying concentration of reinforcing fillers and extenders on foam tensile properties.

The cell structure observed in filled foam does not appear substantially different from that observed in unfilled materials. Cell size distribution of

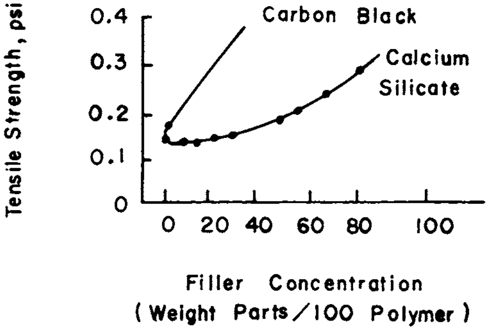


FIGURE 10
Foam density versus filler concentration for reinforced and extended foam structures.

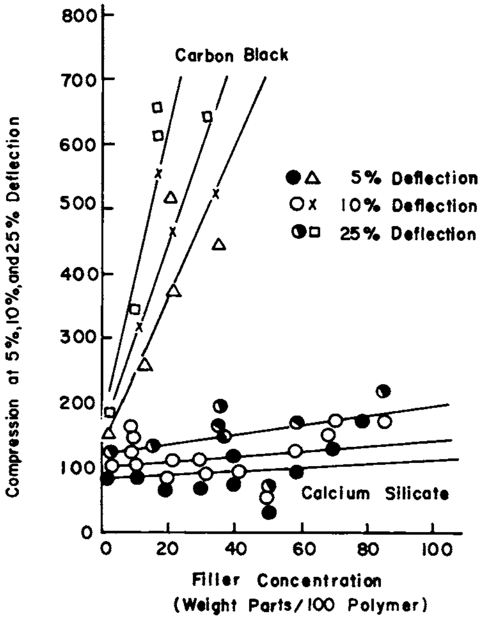


FIGURE 11

Compressive strength at 5, 10, and 25 percent deflection versus filler concentration for reinforced and extended foam structures.

filled foams appears to be narrower than that observed in unfilled foams; this improved cell size distribution may result from more efficient nucleation of the blowing agent during foam formation.

Nutter and Benning have shown that it is possible to effect major changes in the properties and performance of cellular polyethylene foams without causing major change in the foam structure.

RECENT ADVANCES IN POLYSTYRENE-BASED FOAMS

Self-extinguishing Polystyrene Foams

A substantial advance in the flameproofing of polystyrene foam was made when Eichhorn[13] and Jahn and Vanderhoff[14] discovered that the incorporation of certain peroxides or other free radical sources produces a powerful synergistic effect permitting a reduction to about one half the level of bromine required without peroxide.

Ingram[15] has suggested that the synergistic effect of free radical sources in the presence of halogen-containing self-extinguishing agents is due to abstraction by a free radical (formed by thermal decomposition of the synergist) of the α or α and β hydrogens from the polystyrene side chain. The newly formed polystyrene free radical may then either accept a free halogen atom or abstract a halogen from the self-extinguishing agent to yield α-halo and α,β-dihalo polystyrenes, which are probably better self-

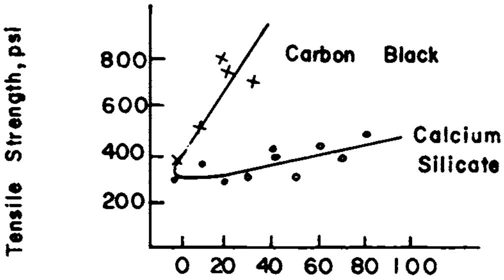


FIGURE 12
Tensile strength versus filler concentration for reinforced and extended foam structures.

extinguishing agents than the additives. Ingram[15] has prepared and screened a number of *N*-nitroso and *N*-halo compounds to demonstrate that the synergistic effect is not limited to peroxides.

Foams Based on Styrene–Acrylonitrile Copolymers

Ingram[16] has reported on polystyrene foams, produced via the bead process, which possess good resistance to fuel oil and gasoline. These foams are based on copolymers of styrene and acrylonitrile.

Figure 13 shows the effect of the concentration of acrylonitrile on foam samples exposed to nonleaded gasoline.

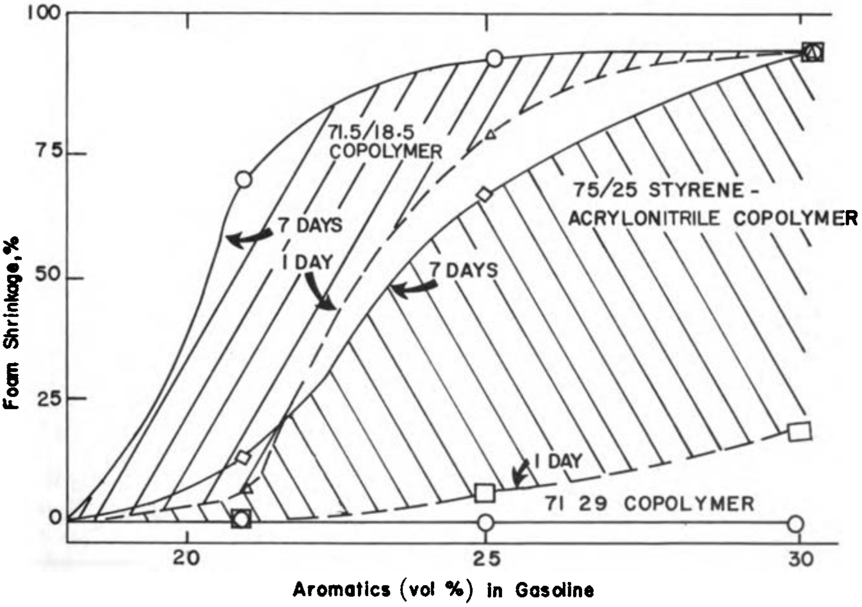


FIGURE 13
Shrinkage versus aromatics in gasoline.

It can be seen that foams containing more than 28 percent of acrylonitrile show no shrinkage during a 6-day exposure test, while foams containing 25 percent or less acrylonitrile shrink to less than half their initial volume.

An added advantage of the acrylonitrile–styrene copolymer based foams is the ability to retain the *n*-pentane blowing agent for longer periods of time (Figure 14).

MISCELLANEOUS ADVANCES IN FOAM TECHNOLOGY

Two recent developments in foam-processing technology are worthy of mention. The first, not as yet reported in the literature, is a modification in the polystyrene polymer used for processing expandable beads. The modified formulations permit considerably reduced mold cycle times due to the ability to effect a rapid cooling of the product after molding. The second development, reported only recently, is the utilization of microwave-curing techniques to shorten the cycle times for flexible and rigid urethane foams. All the reports in the literature mention the use of a 2,450-cps frequency and a varying power factor to cure the foam. Some foam formu-

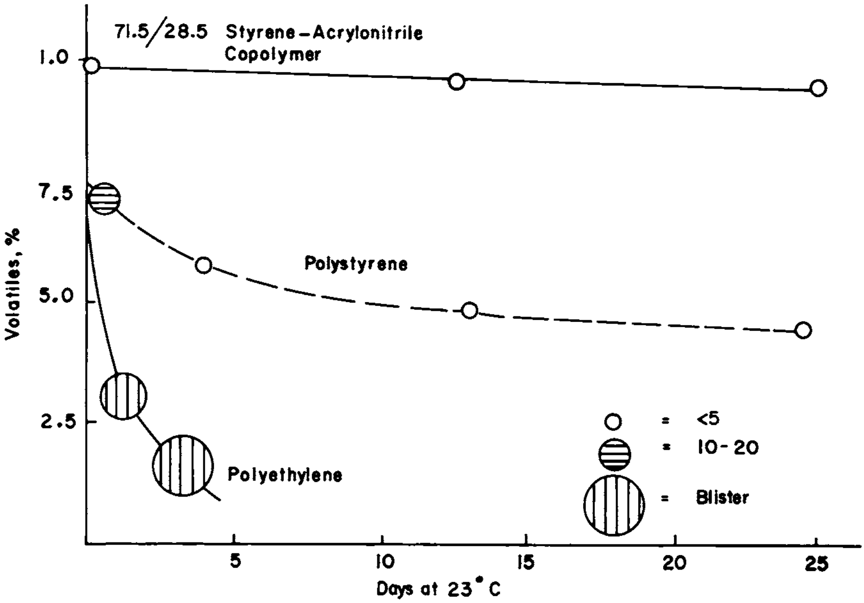


FIGURE 14
Retention of *n*-pentane blowing agent.

lations become opaque during early stages of cure to this frequency. Early experiment in our laboratories indicate that the technique of varying the microwave frequency during curing may offer possibilities of obtaining a greater degree of polymerization, especially in sterically hindered systems.

CONCLUSIONS

In summary, I should like to mention that research is presently being carried out to determine the mechanism of catalysis of urethane foams, to synthesize more stable and higher-temperature-resistant polymers, and to develop systems possessing improved resistance to fire. Due to the increased interest in this fascinating class of materials, I am sure that in the years ahead many new developments will be reported which will open areas for commercial development not possible at this time.

REFERENCES

1. R. A. Reed, *Brit. Plastics*, *33*, 469 (1960).
2. H. R. Lasman, *Modern Plastics Encyclopedia*, McGraw-Hill, New York (1966), pp. 394–402.
3. B. A. Hunter, "Chemical Blowing Agents—Chemistry and Decomposition Mechanisms," Lecture presented at the Polymer Conference Series, Wayne State University (1966).
4. B. A. Hunter and M. J. Kleinfled, *Rubber World*, *153* (3), 84 (Dec. 1965).
5. L. Nicholas and G. T. Gmitter, *J. Cellular Plastics*, *1* (1), 85 (1965).
6. I. N. Einhorn, *J. Cellular Plastics*, *1* (1), 25 (1965).
7. W. F. Abbey, B. C. Carlson, and R. T. Zimmerman, *Rubber Age*, *86*, 837 (Feb. 1960).
8. B. C. Carlson, *SPE J.*, *17*, 265 (1961).
9. H. R. Lasman, *SPE J.*, *18*, 1184 (1962).
10. A. C. Bluestein, *Rubber Age*, *96*, 57 (Oct. 1964).
11. C. J. Benning, *SPE J.*, *21*, 1083 (1965).
12. J. J. Nutter and C. J. Benning, *Proc. SPE Anter*, Montreal, Canada (March 1966).
13. J. Eichhorn, *Am. Chem. Soc. Div. Org. Coatings and Plastics, Chem. Papers*, *23*, (1), 37 (1963).
14. A. J. Jahn and J. W. Vanderhoff, *Am. Chem. Soc. Div. Org. Coatings and Plastics, Chem. Papers*, *23* (1), 61 (1963).
15. A. R. Ingram, *Am. Chem. Soc. Div. Org. Coatings and Plastics, Chem. Papers*, *23* (1), 95 (1963).
16. A. R. Ingram, *J. Cellular Plastics*, *1* (1), 69 (1965).

Viscoelastic Behavior of Open-Cell Foams

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INTRODUCTION

Flexible open-cell foams are commonly used for vibration damping or shock absorption because of their ability to dissipate a relatively large fraction of the input energy during a compressive deformation, i.e., they are characterized by a relatively low "rebound." The energy is dissipated not only by the inherent hysteresis of the matrix material, but also by the physical process of forcing air to flow in and out of the foam. This may be termed "pneumatic damping," and has been qualitatively described by some workers.[1,2] It can be relatively large at low rates of compression. A theoretical treatment of pneumatic damping has been given by Kosten and Zwikker,[3] using a simple mechanical model consisting of a piston, spring, and capillary tube (Figure 1) to represent the foam structure. Their model is somewhat oversimplified and does not permit calculation of the damping characteristics from independent measurements, although the form of their result is qualitatively correct. In the present work, theoretical equations are given which related the pneumatic damping to the physical properties of the foam and the air. Experimental results are then described and compared with the theoretical predictions.

The resistance to air flow of the foam structure is the controlling factor in pneumatic damping. Consequently, a study of the permeability of open-cell foamed materials was also undertaken. This has been described in detail elsewhere.[4,5] A brief summary is given below.

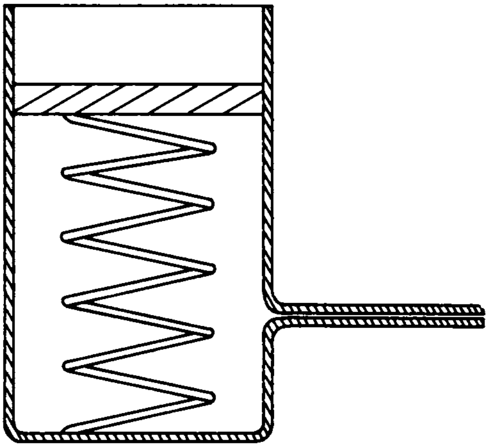


FIGURE 1
Simple model for pneumatic damping in open-cell foams (Kosten and Zwikker[3]).

PERMEABILITY OF OPEN-CELL FOAMS[4,5]

The pressure gradient, $\partial P/\partial \chi$, necessary to maintain flow through an open-cell foam is given by a two-term equation,

$$\frac{\partial P}{\partial \chi} = \frac{\eta}{K} v + \frac{\rho}{B} v^2, \tag{1}$$

where v is the flow velocity, η and ρ are the viscosity and density, respectively, of the fluid, and K and B are coefficients characteristic of the structure of the foam. The above equation is valid for either gas or liquid flow, the coefficients K and B being independent of the nature of the permeating fluid.

The first term on the right-hand side of Equation (1) reflects viscous flow losses and is dominant at relatively low flow rates. The second term, dominant at high flow rates, represents inertial flow losses resulting from the irregular flow. A model structure may be employed to relate the coefficients K and B to the structure of the foam. If the foam is represented by an array of straight tubes of diameter d, K is given by

$$K = d^2/32. \tag{2}$$

If a modification of the above model is considered, consisting of an array of tubes of diameter d containing a series of rounded orifices, the number per unit length being $1/d$, B is given by the relation

$$1/B = (D^2 - 1)^2/2d, \tag{3}$$

where D is the ratio of the diameter of the pipe to the diameter of the constrictions.

Experimental data were obtained for three basic types of open-cell foams. Normal polyurethane foam, type I, has a structure consisting of ribs outlining the individual cells, with thin broken membranes, or cell walls, between them. Reticulated polyurethane foam, type II, has had all of these membranes removed. Rubber foam, type III, prepared from latex, has somewhat thicker ribs outlining essentially spherical cells, with no membranes between them. All the foams examined had a negligible proportion of closed noncommunicating cells.

Values of K and B were determined for four different samples of each of the three types of foam. For types II and III the values of K were found to be in accord with the relation

$$K = 0.012d^2$$

for a wide range of cell diameters d, from about 0.01 to 0.20 cm. This relation is of the same form as Equation (2), the numerical factor being about one third of the theoretical value. In view of the simplified nature of the model, this agreement is very satisfactory.

For the type I foams, the values of K were found to be considerably smaller at equivalent cell sizes, and they were not proportional to d^2. This difference in behavior is attributed to the thin membranes observed between the cells. The permeability will be determined by the size of the apertures in the membranes in this case, rather than by the cell size, and there is not necessarily any relation between them. The effective diameters of the apertures were calculated from the measured values of K to be about one half to one eighth of the average cell diameters, which is in reasonable agreement with observation.

Values of the parameter D were calculated from the measured values of the coefficient B, by means of Equation (3). They were found to be about 5.5, 1.3, and 1.8 for types I, II, and III, respectively. The large value for the type I foam is in accord with its observed structure and reflects the constrictive effects of the cell membranes. The values for the types II and III foams are also in reasonable agreement with their structural features. The value of D seems a useful qualitative measure of the apertures between cells, relative to the cell size.

THEORETICAL TREATMENT OF PNEUMATIC DAMPING[6]

Under a small sinusoidally varying compression, $e = e_0 \sin \omega t$, where e is the fractional compression, t is the time, and ω is the angular frequency, the response of a foamed material may be expressed as

$$\sigma/e_0 = E \sin (\omega t + \delta),$$

where σ is the instantaneous stress, E is the dynamic modulus, and δ is the phase angle between stress and deformation. A convenient measure of mechanical damping is tan δ, as it is proportional to the fractional energy dissipated per deformation cycle. It is given by

$$\tan \delta = E''/E',$$

where E',E'' are the components of the modulus in phase and 90° out of phase with the deformation.

Pneumatic damping may be analyzed qualitatively in terms of the mechanical model of Kosten and Zwikker (Figure 1). The spring represents the stiffness of the foam matrix and the capillary tube represents the viscous loss mechanism. At low compression frequencies the air-flow losses increase with frequency, causing an increase in the loss component E'' and hence in tan δ. At higher frequencies, however, the flow resistance forces become large relative to the compressibility of the air, and the air is more readily compressed than forced to flow. Consequently, the energy dissipated by air flow increases to a maximum and then decreases as the compression frequency is increased further. The compression of the air is essentially an elastic process and contributes to E'. Thus E will increase with frequency to attain a constant value at high frequencies when the flow of air is negligible. These qualitative predictions of the dependence of E and tan δ upon the deformation frequency are illustrated in Figure 2.

Although the treatment of Kosten and Zwikker is qualitatively correct, the length and diameter of the capillary tube have no real physical meaning. Recently, a theoretical treatment has been proposed that successfully relates the pneumatic damping observed in flexible open-cell foams to the properties of both the foam and the air.[6] Basically, the pressure distribution developed within the foam structure as a result of the resistance to fluid flow is calculated and then integrated over the cross section of the test piece to yield the average compressive stress. This stress contribution is then added to the stress resulting from compression of the foam matrix.

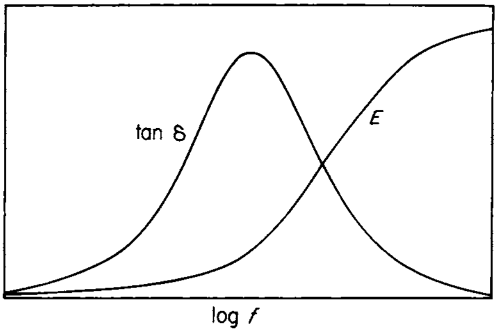


FIGURE 2
General form of the relations between the dynamic modulus E, loss angle δ, and frequency f of compressive deformation.

The flow of compressible (air) and incompressible (liquid) fluids has been treated in this way. In the latter case, the lateral deformation of the foam matrix at right angles to the compression, resulting from the force of the flowing fluid, is of importance and must be taken into account. For both cases, the frequency dependence of E and $\tan \delta$ is qualitatively as shown in Figure 2.

The expressions derived for E and $\tan \delta$ for small compressions of an infinitely long block of width L, containing air, are

$$E = S_m' \left[\left(1 + \frac{1}{\alpha} - \frac{8}{\alpha}\psi_1\right)^2 + \left(d_0 + \frac{8}{\alpha}\psi_2\right)^2 \right]^{1/2} \tag{4}$$

and

$$\tan \delta = \frac{\alpha d_0 + 8\psi_2}{\alpha + 1 - 8\psi_1}, \tag{5}$$

where

$$\psi_1 = \sum_{n=1,3,5}^{\infty} \frac{n^2\pi^2}{(n^2\pi^2)^2 + (\alpha\gamma)^2},$$

$$\psi_2 = (\alpha\gamma) \sum_{n=1,3,5}^{\infty} \frac{1}{(n^2\pi^2)^2 + (\alpha\gamma)^2},$$

$$\alpha \cong \phi S_m'/S_g,$$

$$\gamma = \omega\eta L^2/\phi S_m'K, \tag{6}$$

and

$$d_0 = S_m''/S_m'.$$

S_m' and S_m'' are the elastic and loss components, respectively, of the compressive modulus of the foam matrix (S_m' and S_m'' are assumed independent of frequency, a valid approximation for most rubberlike materials at frequencies less than about 100 cps), S_g is the effective bulk compressive modulus of the air (approximately the external pressure), ϕ is the volume fraction of open cells in the foam, and ω, η, and K have been defined previously. Similar expressions are obtained for the case of a cylindrical block of foam, of radius r. L^2 is replaced by $3r^2/2$ in the definition of γ and the functions ψ_1 and ψ_2 are slightly different.[5,6]

The inertial flow resistance, characterized by the coefficient B in Equation (1), and the lateral deformation of the foam matrix, have been assumed negligible in the derivation of Equations (4) and (5). The agreement with experiment described later suggests that these approximations are valid.

The theoretical treatment thus yields relations for the pneumatic damping in terms of three dimensionless quantities, α, γ, and d_0. The first involves the ratio of the stiffness of the foam matrix to that of the contained air. The second, defined by Equation (6), contains the frequency of deformation f ($= \omega/2\pi$) and the test-piece dimension L. The third represents the inherent damping of the matrix material.

At low frequencies, Equation (5) takes the simple form

$$\tan \delta = d_0 + (\gamma/12). \tag{7}$$

Thus a plot of tan δ against the deformation frequency f is predicted to be initially a linear relation with a slope of $\pi\eta L^2/6\phi S_m'K$ and an intercept of d_0.

EXPERIMENTAL DETAILS[5,6]

The theoretical treatment assumes linear viscoelastic behavior. Because of the nonlinear *elastic* behavior of foams in compression,[7] it is only possible to approximate linear behavior at small strain amplitudes of a few percent or less. The experimental arrangement employed for measuring the damping characteristics of foam–air systems at relatively small compressions is described elsewhere;[5] it consisted of a nonresonant forced vibration assembly with facilities for measuring the instantaneous force and displacement applied to the test piece, and hence the dynamic modulus E and loss angle δ. The measurements were carried out at room temperature and atmospheric pressure at frequencies between 0.03 and 30 cps. The deformation amplitude was about 3 percent or less. The measurements were found to be accurately reproducible, and no evidence of deterioration or heating of the foams was observed during the period required to make the measurements.

The test pieces were prepared so as to approximate an infinitely long block of width L, with flow in the L direction only. The top and bottom surfaces were made impermeable by cementing them to rigid plates. When the length of the rectangular test piece was at least four times the width, it was considered equivalent to an infinitely long block. When the length was less than four times the width, the flow path was controlled by sealing two opposite ends of the rectangular test piece with a thin impermeable rubber skin, thus allowing unidirectional flow only. A compounded latex was painted on the surface of the foam and then cured to produce the thin rubber skin. This skin did not significantly change the compressive modulus of the foam. The bulk dimensions of the test pieces were at least 50 times the average cell diameter, to minimize edge effects.

EXPERIMENTAL RESULTS[5,6]

The measured values of tan δ at low deformation frequencies are plotted against the frequency in Figure 3, for a foam sample impregnated with

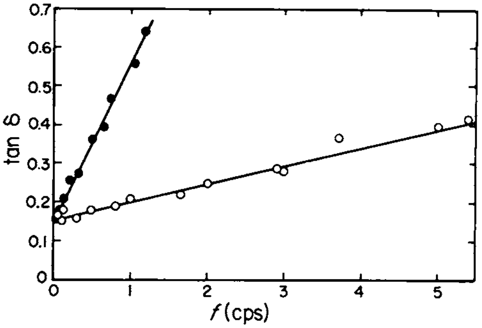


FIGURE 3
Relations between tan δ and the deformation frequency f for a latex foam sample impregnated with water (O) and a glycerol–water (60:40) mixture (●).

water and with a glycerol–water (60:40) mixture. The relations are seen to be substantially linear, in accordance with Equation (7). Moreover, the slopes, 0.42 sec and 0.045 sec, are in the same ratio as the viscosities of the two fluids, about 9.6 at room temperature. On inserting the measured values for the permeability K (2.2×10^{-6} cm^2), the matrix (static) modulus S_m' (0.52 kg/cm^2), the porosity ϕ (0.82), the test-piece width L (2.8 cm), and the viscosities of the fluids η (8.6 cp and 0.90 cp), the values of the slopes calculated from Equation (7) are 0.38 sec and 0.040 sec—in good agreement with the experimental values.

The intercepts of the two relations are equal; they correspond to the inherent damping d_0 of the matrix—about 0.15 in the present case.

Similar results were obtained in all cases. The relations for a sample in four different media are shown in Figure 4, where a logarithmic scale has been employed for the deformation frequency f in view of the wide range. The relations are seen to be approximately parallel and to be displaced by amounts corresponding to the logarithm of the viscosity ratios. In Figure 5, similar relations are shown for samples of different width L, in air. They are displaced in this case by amounts proportional to the logarithm of the ratios of L^2, in accordance with Equation (7). Thus, the measurements at low frequencies are in good agreement with the theoretical treatment. They are described completely by two dimensionless quantities for each

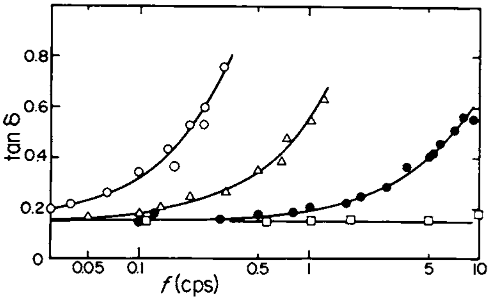
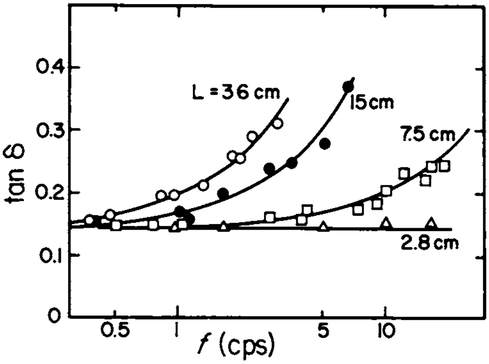


FIGURE 4
Relations between tan δ and the deformation frequency f for a latex foam sample with silicone oil (O), glycerol-water (60:40) mixture (△), water (●), and air (□).

FIGURE 5

Relations between tan δ and the deformation frequency *f* for test pieces of various widths *L* (latex foam, in air).



sample; d_0, a measure of the inherent damping of the matrix, generally lying between 0.1 and 0.2, and γ, given satisfactorily by the theory in terms of the properties of the test piece and the fluid.

At higher deformation frequencies the measured values of tan δ passed through a maximum and then decreased. Typical relations are shown in Figures 6 and 7. The value of the third dimensionless quantity α required by the theoretical treatment was chosen to give the best agreement between the values of tan δ calculated from Equations (4) and (5) and the experimentally determined values over the whole frequency range. The values of α determined in this way for the experimental results shown in Figures 6

FIGURE 6

Relation between tan δ and the deformation frequency *f* for a type I polyurethane foam sample in air. Full curve: theoretical relation.

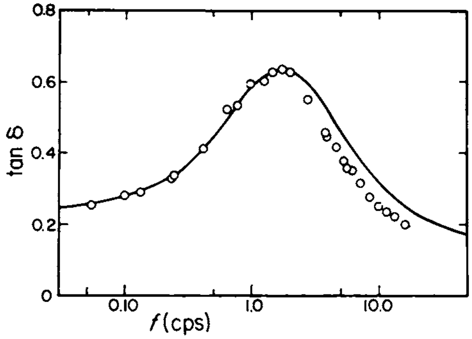
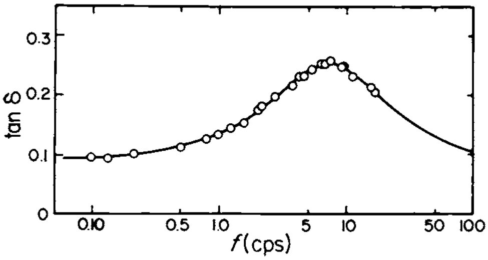


FIGURE 7

Relation between tan δ and the deformation frequency *f* for a latex foam sample in air. Full curve: theoretical relation.



and 7 were 0.52 and 2.0. The corresponding theoretical relations are represented by the full curves in the figures. They are seen to describe the experimental results with considerable success.

Some deviations appear at the highest frequencies, the experimental points lying generally below the theoretical relations in this region. The effect may be due in part to the neglect of inertial-flow-resistance terms which will become increasingly important at high frequencies of deformation, and in part to deformation of the foam samples at right angles to the direction of compression resulting from the outward force exerted by the contained air.

The theoretical values of α for the foams of Figures 6 and 7 were obtained from the relation

$$\alpha = \phi S_m'/S_g,$$

using the measured matrix modulus S_m', porosity ϕ, and the atmospheric pressure for S_g. The values obtained were 0.44 and 1.25, of the same order as the "experimental" values but somewhat lower. Better agreement could be obtained by taking the lateral deformation into account in the theoretical treatment. However, it is clear that in its simplest form the theory predicts the general form of the dependence of the pneumatic damping of foams upon the frequency of deformation quite successfully and gives approximately the correct quantitative relationships in terms of the properties of the foam. More extensive results are given elsewhere.[5,6]

DISCUSSION AND CONCLUSIONS

A theoretical treatment has been presented to describe the pneumatic damping observed in open-cell flexible foams. Data are given which show that the theory successfully relates the observed dynamic behavior of the foam to the properties of the foam and the air, obtained through independent measurements. The agreement between experiment and theory is qualitatively, and to a large extent, quantitatively correct. The theory shows that the pneumatic damping will be significant at low compression frequencies if the air-flow resistance, $1/K$, or if the air-flow path length, L, are large. Furthermore, the extent of the pneumatic damping, i.e., the value of $(\tan \delta)_{\max}$, will be large if α is small. Hence, the external pressure, P, will have a significant effect on the pneumatic damping since α is approximately proportional to $1/P$. As the pressure is decreased, $(\tan \delta)_{\max}$ is decreased. However, since the viscosity of a gas is essentially independent of pressure, the pressure will not have any effect on the frequency f^* at which $\tan \delta$ has a maximum value. The value of $(\tan \delta)_{\max}$ is directly dependent upon the compressive modulus of the foam, S_m'; as the modulus is increased, $(\tan\delta)_{\max}$ is decreased. It is interesting to note that pneumatic damping is relatively insensitive to temperature, since neither S_m' nor S_m'' will be very sensitive to temperature around room temperature, and the viscosity of a gas is relatively independent of temperature.

The theoretical equations presented permit the calculation of both the magnitude of the pneumatic damping and the frequency at which the damping is maximum. This same approach can also be used to analyze damping resulting from liquid flow within an open-cell foam. Thus, a foam–fluid system can be designed to give a desired value of tan δ. By a suitable choice of fluids, high damping can be achieved at relatively low frequencies, without the pronounced temperature dependence shown, for example, by rubbers during the transition to the glassy state.

SUMMARY

Open-cell foams show abnormally large mechanical damping due to the energy dissipated in forcing air in and out of the foam during a deformation cycle. This pneumatic damping has recently been treated theoretically and experimentally. The dependence upon the test-piece dimensions, the frequency of deformation, and the viscosity of the fluid have been shown to be in good agreement with the theoretical predictions. The dominant property of the foam structure is its permeability to fluids. This has also been measured for a number of different foams and related to their structural features by means of a simple model. A review of these developments has been presented.

REFERENCES

1. J. H. Saunders and K. C. Frisch, *Polyurethane Chemistry and Technology, Part I*, Interscience, New York (1962), pp. 255–258.
2. R. E. Jones, P. Hersch, G. G. Stier, and B. A. Dombrow, *Plastics Technol., 5*, 55 (Sept. 1959).
3. C. W. Kosten and C. Zwikker, *Mededel. Rubber-Sticht., 6*, 7 (Feb. 1938); reprinted in *Rubber Chem. Technol., 12*, 105 (1939).
4. A. N. Gent and K. C. Rusch, *J. Cellular Plastics, 2*, 46 (1966).
5. K. C. Rusch, PhD Thesis, University of Akron (1965).
6. A. N. Gent and K. C. Rusch, in preparation.
7. A. N. Gent and A. G. Thomas, *Rubber Chem. Technol., 36*, 597 (1963).

The Role of Surfactants during Polyurethane Foam Formation

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INTRODUCTION

Both chemical and physical processes play an essential part in polyurethane foam production. When leaving aside pure evaporation processes resulting from blowing agents, the physical effects are primarily of a colloidal-chemical nature. They are caused by emulsifying agents and surfactants. These surfactants, as indicated by their name, act on the foam formation as a result of changing the surface properties of the foaming mixtures. In addition, they have an emulsifying action which, in many cases, is sufficient for producing the foams. Thus, the presence of a surfactant is all that is necessary for certain systems of raw materials of which particularly the polyether foams should be mentioned. With other systems, say, in polyester-foam production, this double function of the surfactants is insufficient and, therefore, an emulsifying agent must be included in most cases. This will generally have little, if any, surface-active effect, and it only serves to cause an intimate mixing of the hydrophilic–hydrophobic system, that is, mainly to effect a satisfactory dispersion of the water in the hydrophobic polyol–isocyanate mixture.

The action of the surfactants is a highly complex one. Primarily, they are expected to change the surface properties of the foam during its formation in such a way as to keep it stable until the cell skeleton has sufficient stability of its own because of the chemical reactions proceeding in the ribs. Organic anionic compounds are normally used as foam stabilizers in the production of polyester foams; polyether siloxanes are used for stabilizing polyether foams.

With regard to the solubility of a foreign material in a liquid, it is necessary to make a distinction between the solubility in the volume and the solubility in the surface layer of the liquid. The emulsifying agents and surfactants used in polyurethane-foam production are practically all soluble in the volume. To be surface active, compounds with surfactant action must have a greater solubility in the surface layer than in the volume of the liquid.

PROCEDURE

The surface properties or raw-material mixtures for producing polyurethane foams were determined by using a tensiometer which operates automatically and which records the measured data over an X-Y recorder; this tensiometer (Figure 1) was built at our company.

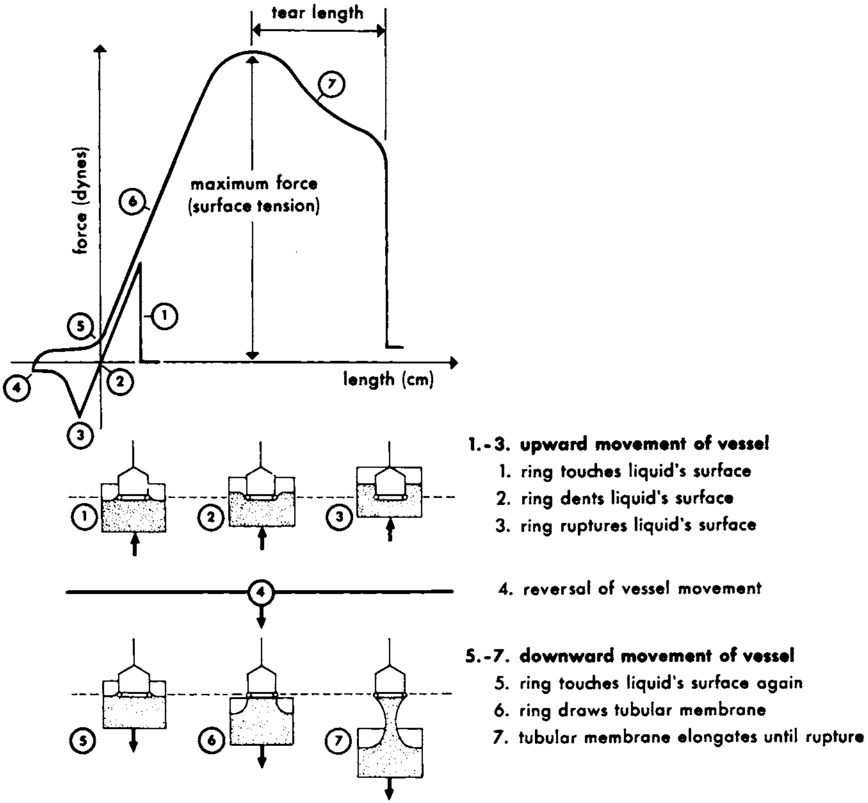


FIGURE 1
Stress–strain behavior of liquid surfaces (Bayer tensiometer).

The measuring instrument operates by the Lecomte de Nouy method, i.e., a dynamic process for determining surface tension. In this method, the forces acting on a ring, which is immersed into and withdrawn from a liquid, are measured. Besides surface tension, the maximum tensile force that the drawn-out lamella of the liquid exerts on the ring, the tear length of the lamella is also determined. The latter is a measure of the viscoelasticity of the surface and indicates the distance by which the lamella can still be elongated, after maximum tensile force has been reached, until it will break. The speed at which the ring was dipped into the surface and withdrawn was constant, 0.5 cm/min.

STARTING MATERIALS

Table 1 lists the surface tension and tear length values of the various starting materials for polyurethane-foam production. It may be seen that with all polyethers, including the polyether prepolymers, the surface tension is between 33 and 40 dynes/cm. Tolylene diisocyanate (TDI), and especially the polymeric 4,4′-diphenylmethane diisocyanate (MDI), have a greater surface tension than the polyethers and even higher values are obtained with the polyesters. The tear length values differ too: polypropyleneglycols have low values; an activation with ethylene oxide causes the tear length to increase and to reach the level obtained with polyethers for rigid-foam production. Polyesters have higher values for tear length than polyethers. A striking difference is noticed between the short tear lengths of TDI and the very high value of polymeric MDI. The extent of the tear length, as a total, is also somewhat influenced by the material's viscosity.

TABLE 1
Surface Tension and Tear Length of Raw Materials for the Production of Polyurethane Foams at 25°C

	Surface Tension, σ (dynes/cm)	Tear Length, l (cm)
Polyether triol (mol. wt. 3,000)	33	0.069
Polyether triol activated (mol. wt. 3,500)	33	0.214
Polyester (mol. wt. 2,500)	52	0.342
Polyether prepolymer (NCO, 8.1%; cps at 25°C, 7,900)	39	0.178
Polyether triol (mol. wt. 450)	37	0.123
Sorbitol polyether (mol. wt. 760)	38	0.214
Tolylene–diisocyanate TDI 80/20	44	0.040
Tolylene–diisocyanate TDI 65/35	42	0.055
Polymeric MDI (200 cps at 25°C)	50	0.498

SURFACE TENSION AS A FUNCTION OF TEMPERATURE

With nearly all organic liquids, the intermolecular forces decrease with increasing temperature, and thus the surface tension drops accordingly. This holds true also for the products used in foam production, as shown by Figure 2.

It will be noticed that the decrease in surface tension as a function of temperature is greater with increased polarity of the compounds; in other words, the decrease is more pronounced with isocyanates and polyesters than with polyethers.

INFLUENCES EXERTED BY VARIOUS COMPONENTS

Figure 3 shows the influence that various components, used to some extent in flexible-polyether-foam production by the one-shot method, exert on the surface tension and the tear length. For these purposes, both characteristics were plotted in the curve versus the additive levels. The components were mixed by hand. From the surface tension versus additive level graph, it is evident that both triethylenediamine and stannous octoate have no surface-active effect, that is, the surface tension remains unchanged with rising additive levels. The same result is also observed with other polyols, say, polyesters or polyethers of low molecular weight when they are used for rigid-foam production. A surface-active effect has never been observed with the usual amines or tin compounds employed in foam production. It follows that with these compounds the solubility in the volume, or the solvation energy, is large. On the other hand, compounds commonly used for stabilizing polyether foams, such as dimethyl silicone fluids and polyether siloxanes, exert a strong influence on the surface tension. With increasing levels of both compounds, the surface tension decreases sharply,

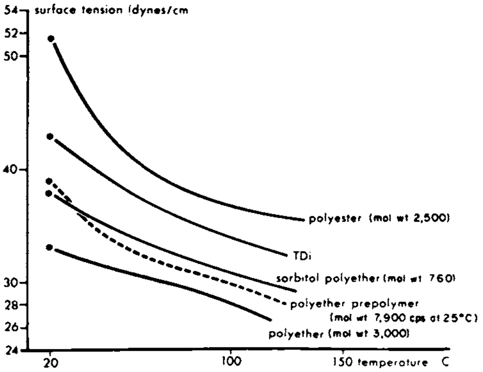


FIGURE 2
Temperature dependence of surface tension.

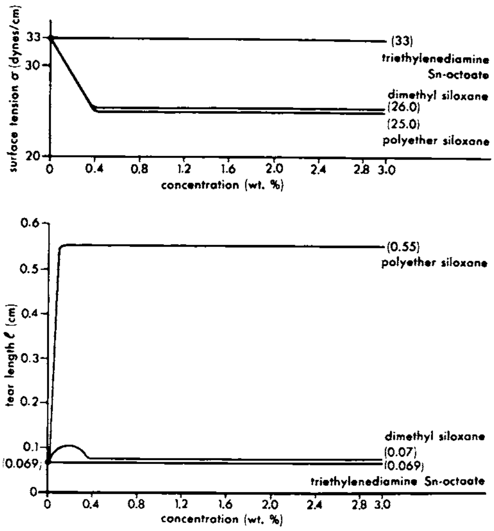


FIGURE 3
Polyether (mol. wt. 3,000): Effect of additives (hand mix) at 25°C.

and starting with a concentration of 0.4 percent by weight, it reaches a constant saturation value independent of concentration and practically identical for both compounds. In this respect, the surface tension observed for the two compounds in a state of saturation is identical to that of the straight products, that is, pure polyether siloxane or dimethyl silicone fluid. The level of concentration, from the point at which the surface tension remains constant, depends on the particular conditions under which the components are mixed. With a mixture blended vigorously in the mixing chamber of foaming machines, it is of the order of 0.8 to 1.0 percent by weight.

The decrease in surface tension of the polyether with increasing dimethyl siloxane or polyether siloxane concentrations results from the fact that both compounds dissolve to a greater extent in the surface layer than in the volume. With increasing levels of these compounds, "two-dimensional" solutions form—so-called surface solutions. As the additives are added, molecular orientation occurs and eventually a saturated surface (completely charged) is obtained—a monolayer surface film. Further addition of the surfactants after attainment of saturation has no effect on surface tension.

The tear length of the polyether remains unchanged by the addition of triethylenediamine and stannous octoate; the same situation is observed with all the other polyols and with polyether prepolymers used for foam production. Dimethyl siloxanes do not change the tear length of polyethers but do shorten the tear length of polyesters. The tear length of the polyethers studied so far by us is, however, greatly increased by polyether siloxanes. In this particular case, an addition as low as 0.1 percent of polyether siloxane causes the tear length to rise to the maximum level of 0.55 cm. Polyether siloxanes and dimethyl siloxanes differ substantially in their influence on the tear length, although both lower the surface tension of the polyether equally.

This behavior, the lowering of the surface tension of polyethers for flexible-foam production with simultaneous increase in tear length caused by polyether siloxanes, is also observed with polyether prepolymers and polyethers used for rigid-foam production. The trend of the relevant curves and their interpretation is the same as described above (see Figures 4 and 5).

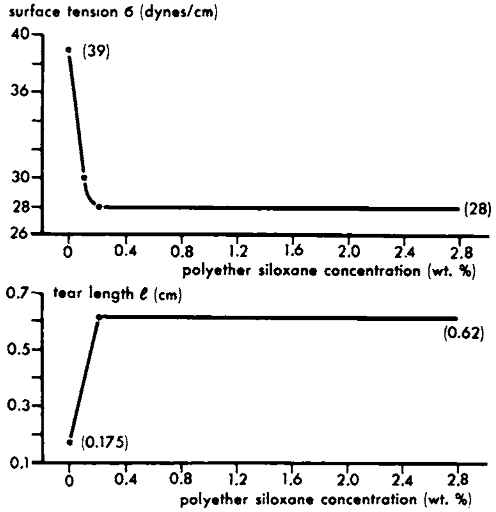


FIGURE 4

Polyether prepolymer (NCO, 8.1%; cps at 25°C, 7,900): Effect of polyether siloxanes (hand mix) at 25°C.

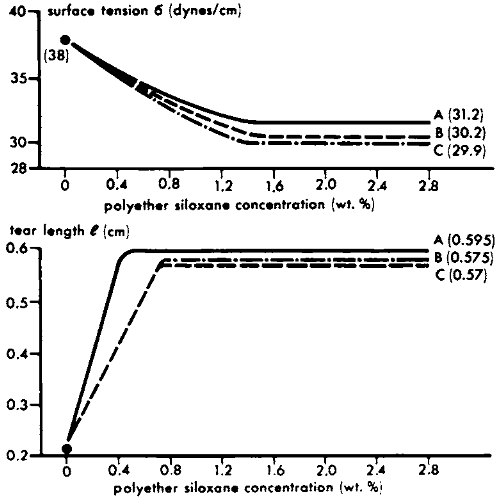


FIGURE 5

Sorbitol polyether (mol. wt. 760): effect of polyether siloxanes (machine mix) at 25°C.

An examination of three different polyether siloxanes is shown in Figure 6. These differ from each other in the composition of the polyether and siloxane portions in the molecule. As may be seen, these siloxanes lower the surface tension of the sorbitol polyether to different extents, while in each case stabilizing the foam formation. During foam formation, finer bubbles are produced when the gas pressure is reduced as quickly as possible with accompanying lowering of the surface tension of the system. Therefore, it would be expected that a foam produced with polyether siloxane C would have finer cells than foams produced with products A and B. This expectation has indeed been borne out by foam production.

Both TDI and polymeric MDI polyether siloxanes (Figure 6) also lower the surface tension, i.e., act as surfactants on these isocyanates. In neither case is there any material change in the tear length.

ACCUMULATION

The effect of time on surface tension (σ) and tear length (l) are shown in Figure 7 for a polyether–polyether siloxane mixture. The samples obtained by hand mixing were evaluated immediately and then after 12 hr.

The tear length versus concentration graph shows only minor differences; the values are somewhat higher now. From the surface tension versus concentration graph, it may be seen that, following standing for 12 hr, the saturation value of the surface tension has been reached at as low a concentration as 0.1 percent of polyether siloxane. These findings should be interpreted as follows: during further standing, polyether siloxane molecules from the volume migrate into the surface layer because of their

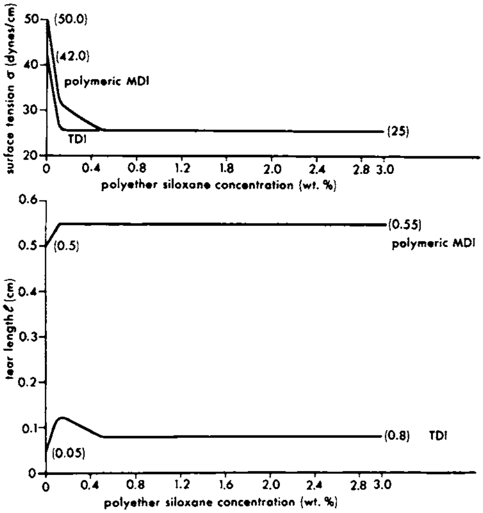


FIGURE 6
Isocyanates: effect of polyether siloxanes (hand mix) at 25°C.

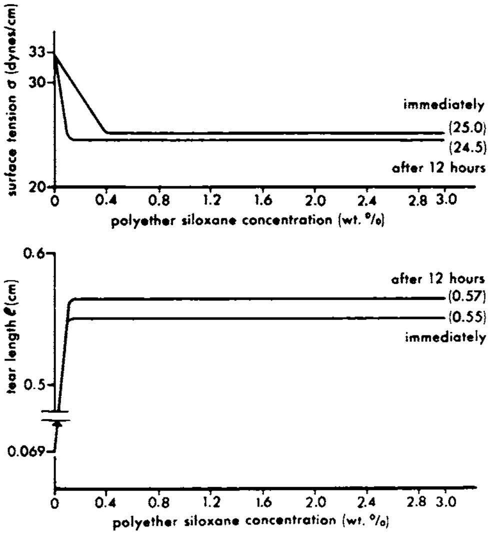


FIGURE 7

Polyether (mol. wt. 3,000)–polyether siloxane mixture: influence of time on σ/l values (hand mix) at 25°C.

greater solubility at the surface. The time period of 12 hr was an arbitrary selection. Figure 8 shows curves illustrating the time-dependent accumulation of polyether and polyether siloxane mixtures from zero time until values of 25 dynes/cm can be recognized. The zero time is the time at which the mixture of the stated composition emerges from the mixing chamber of the foam machine. The time to reach a surface tension of 25 dynes/cm, the saturation value independent of concentration, decreases as the concentration of polyether siloxane increases. With a concentration of 1.0 to 1.1 percent by weight of polyether siloxane, a surface film is formed immediately as the mixture leaves the mixing chamber.

Similar curves are observed for polyethers with lower molecular weight, polyesters, and polyether prepolymers. The time dependence of the accumulation, however, is different because the viscosity of the polyol (which may differ considerably from one product to another) also plays an important part in the migration into the surface layer.

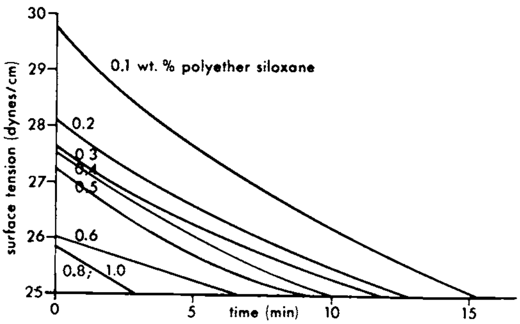


FIGURE 8

Time dependence of polyether siloxane accumulation in PPG–polyether surfaces (machine mix) at 25°C.

As emphasized before, the surface properties of foaming mixtures are determined by the surfactants only. The other additives, e.g., amine or tin catalysts, water, and trichlorofluoromethane, have no surface-active effect. Mixtures of polyols and isocyanates exhibit almost additive values for surface tension and tear length.

Let us explain the relationship between foam stabilization and surface properties of the foaming mixture by resorting to the example of producing a flexible polyether foam (Figure 9).

Measurements had to be taken in the absence of TDI since with TDI the system changed too rapidly, and especially because of the heterogeneous nature of the surface on the onset of the gas reaction. The foam was produced by combining the quantities of the individual components listed in the formulation (Figure 10), while varying the polyether siloxane level, with the requisite quantity of isocyanate (index number 105) in the mixing chamber of a foam machine. From the graphs in Figure 9 it can be seen that the decrease in surface tension and the increase in tear length are independent of the quantity of water in the formulation. In the upper graph the saturation value of the surface tension is of the order of a polyether siloxane concentration of 1.0 percent by weight. As stressed before, this is caused by the intensive mixing in the machine.

The upper graph also illustrates that, when the mixtures are allowed to stand, an additional polyether siloxane accumulation in the surface layer has again been encountered.

The effects of importance in foam production are emphasized by the vertical lines in the graph. Arrows to the left of the lines indicate that a

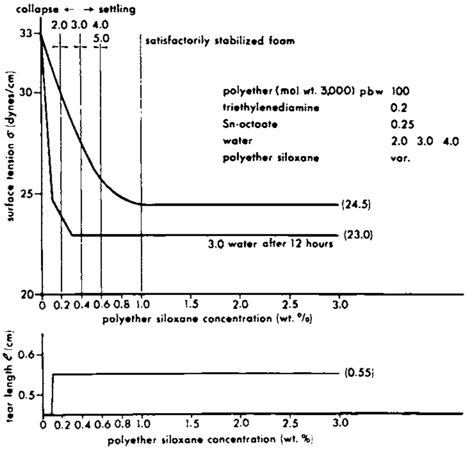
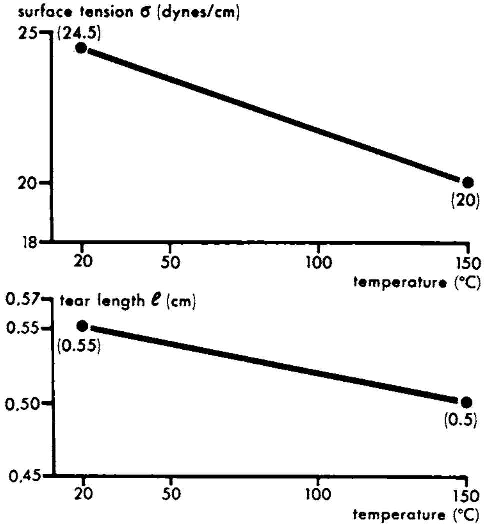


FIGURE 9
Polyethers: relationship between σ/l values and foam behavior (machine mix) at 25°C.

FIGURE 10
Temperature dependence of σ/l values of polyether (mol. wt. 3,000) foam mixtures.



collapse took place up to this polyether siloxane level. Arrows to the right of the lines indicate where the foams settle, to a greater or lesser extent. These effects take place in the range up to 1.0 percent by weight of polyether siloxane. Above this 1.0-percent level, a satisfactorily stabilized foam will always be obtained. The comparison between measurement curve and foam characteristics shows that, to prevent a collapse of the foam when more water is present, the surface tension must be lowered drastically. This may be safely attributed to two things: first, the increasing proportions between surface and volume of the foam; second, the necessity to make available an increasing quantity of polyether siloxane for the more pronounced micelle formation which increases with water content. Satisfactorily stabilized foams will always be obtained when the saturation value of the surface tension is reached, that is, when the mixture has reached its lowest possible surface tension. The tear length always has its maximum no matter whether the foam collapses, settles, or is satisfactorily stabilized.

The results were obtained at a temperature of 25°C. Polyurethane-foam production, however, is accompanied by a pronounced heat generation in the course of which, within a few minutes, the temperatures in the foam may rise to 150°C. This entails a continuous decrease of the measuring characteristics resulting from the general decrease in surface tension with rising temperatures during foam formation. Figure 10 shows the prevailing conditions with the foaming system described.

It may be seen that the surface tension in the region between 20 and 150°C drops from 24.5 to 20 dynes/cm. Similarly, the tear length decreases continuously with increasing temperature (from 0.55 cm at 20°C to 0.5 cm at 150°C) although the decrease is not very great in this case.

The results obtained with a polyether (mol. wt. 3,000) intended for flexible-polyurethane-foam production were also observed with polyethers used for rigid-polyurethane-foam production (mol. wt. 400–800). The stability of the foam system and the fineness of the cell structure increase while the surface tension continues to decrease as a result of the increasing use of polyether siloxane. Here, too, optimum stabilization is obtained with stabilizer concentrations providing the mixture its lowest possible surface tension. In these cases, the tear length is also very large.

In flexible-polyester-foam production using the ordinary organic surfactants, the stabilization of the foam runs parallel to the reduction of the surface tension. The more the surfactant will lower the surface tension, the finer will be the cell structure of the resultant foam. Satisfactorily stabilized foams will always be obtained when the surfactant concentrations are high enough to cause the mixture to reach its lowest possible surface tension. With low surfactant levels, the tear length is large in the polyester system; but, it will then drop to lower values. The reduction lies in the range in which a satisfactory stabilization of the foams is obtained. This behavior has not been fully understood so far. However, it would appear that the higher viscosity of the polyester than that of the polyether plays an important part.

The situation in the foaming of polyether prepolymers is similar to that of the polyesters. Here, too, stabilizers will invariably lower the surface tension, and again optimum stability will be obtained where the system has reached its lowest possible value. Polyether siloxanes give high values for the tear length, and other compounds suitable as stabilizers yield small values. Here again, the difference observed might be attributed to the higher viscosity.

EFFECT OF THE SURFACTANTS

In polyurethane-foam production, surfactants are generally understood to be compounds that are expected to stabilize the cell skeleton about to form, especially during the first phases of foam production. To do so, these compounds must, above all, lower the surface tension of the foaming system because of their higher solubility in the surface layer than in the volume. The effect of the individual products differs in this respect and, in some cases, it is specific for certain polyol systems only. Thus, for example, numerous organic surfactants will lower the surface tension of polyesters but not of polyethers. This means that they act as surfactants only in the polyester system. Considering the surface tension as energy that must be expended to enlarge the surface, a reduction of this value means that the energy of the system must be correspondingly lower to produce a given surface. Conversely, in a given system, the surface produced will be correspondingly larger (the cell structure will be finer) as the surface tension is increased.

Another effect of the stabilizers, beyond the ordinary nonuniform dispersion between volume and surface, is the tendency to accumulate additionally in the surface. Preferably, this effect should occur rapidly during cell growth so that surfactants will diffuse from the ribs to cover as completely as possible the phase interface. During foam production, the minimum concentration of surfactants needed to ensure practically no differences in surface tension between volume and surface, even after intensive mixing of the components, will assist in this covering activity.

Not every compound lowering the surface tension of a polyol system will act as a stabilizer of this system. Besides lowering the surface tension in polyether-based flexible- and rigid-polyurethane-foam production, compounds effective as foam stabilizers must also increase the system's tear length. As pointed out before, this characteristic is proportional to the viscoelasticity. An increased tear length means that the cell walls will be more able to withstand the gas pressure generated during foam formation since the walls have improved elasticity and thus cannot be prematurely torn. The increased strength of the cell walls, furthermore, reduces the drainage of the interlamellar liquid, an additional stabilizing effect on the system. For producing flexible polyurethane foams from the relatively low-viscosity polyethers, a large tear length is absolutely essential for stabilization. Where this is not the case, a boiling of the foam mixtures or a collapse of the foam will invariably be encountered. In such systems, the large tear length is caused only by polyether siloxanes; consequently, only these compounds will act as foam stabilizers. In systems of higher viscosity, say, when foaming polyesters or polyether prepolymers, a high tear length does not appear to be absolutely essential, since a stabilization of the foam has been observed even under conditions of relatively short tear lengths. The reason for this stabilization appears to be due to the higher viscosity which, while decreasing the rate of cell growth, also lowers their rate of breakdown. As a result of the higher viscosity there is a greater resistance to the gas pressure, and thus to a tearing of the cells. However, when foaming polyether prepolymers, especially those types which have a relatively low viscosity, it is advantageous to have a large tear length, and this means that polysiloxanes should also be used in these cases as foam stabilizers.

Our study was undertaken to obtain a better understanding of the effects of surfactants in polyurethane-foam production. It will take further experiments to grasp and interpret all the surface phenomena that are important in foam production.

Panel Discussion

Question Dr. Gent, is it possible to change the resonant frequency of a foam-mounted system through varying something such as the physical dimensions of the foam supports?

Gent Yes, that was one point of my talk.

Question You dealt with absorption of energy, but are you saying that the resonant frequency of the entire system could be changed?

Gent Quite correct, but only insofar as the resonant frequency itself is dependent upon the energy absorption. In a mass–spring–dashpot system, the resonant frequency is dependent upon the characteristics of the dashpot, but not to a great degree. It is easily calculated. Whether it is technically worthwhile, that is, whether it is a valuable effect, I couldn't say.

Question Dr. Gent. have you by any chance carried out a correlation with stress-relaxation experiments, to tie in possibly with any of the relationships which you established on the characteristics of your foam?

Gent The basic mechanism for energy absorption is an impelled motion of the fluid. If stress relaxation is defined as the decay in stress at a fixed deformation, then it would not occur in our model. However, I have been wondering along the following lines: It is possible to get closed flow loops; for example, if you run a ball over a sample of foam, it may not be necessary for the contained fluid to flow to the exterior, but rather in a closed path in the interior. It is possible that there would be some interesting energy absorption properties in these circumstances.

Question I wonder if Mr. Winer could give us some additional information on the foam systems that were used in raising the sunken ships—if there was anything peculiar about the level of catalysis or anything of that sort?

Winer The type and level of catalysis is considered proprietary information by the contractor. It is, however, known that the frothing process was employed and involved the use of both fluorocarbon 11 and 12.

Floor I have the feeling that as you go deeper and deeper in the water we have to operate the pumps at greater and greater pressures, and that we have sort of a knock-off point with this Freon system or the polyurethane system itself.

Winer We are presently trying to determine what the depth limitations are for the urethane frothing systems.

Question Do you think you can go to deeper depths?

Winer Yes. However, we probably will have to go to buoyancy systems other than gaseous expanded urethanes.

Floor The reason I say that is that I believe you are operating around 2,000 psi.

Winer No, not that deep. Our initial objective is to develop a buoyancy system operational to 600 ft.

Question What is the water pressure at 600 ft?

Winer 264 psi.

Question Has foaming in a plastic bag been tried?

Winer Yes. This was done commercially by a contractor while salving a sunken barge off the coast of California.

Question Has any consideration been given to the use of foaming before a flooded condition occurs?

Winer This possibility has been discussed. Various problems would first have to be worked out, such as space limitations for storage of foam ingredients and long-term storage stability of ingredients.

Question What effects do fillers have on the properties of cellular materials?

Einhorn The parameters governing the effects of fillers on film properties are geometrical configuration, loading volume, filler density, specific heat, and chemical composition. If lamellar fillers such as flake glass or mica are used, orientation and settling may be encountered. This may lead to unstable raw material systems. As I have shown in an earlier paper [I. N. Einhorn, *J. Cellular Plastics, 1* (No. 1) (1965)], the incorporation of moderately large spherical fillers of inorganic composition greatly improves the flammability characteristics of cellular plastics. It is desirable to obtain closest packing (72 percent by volume) for perfect spheres of uniform diameter. It may be necessary to modify the foam formulation, as incorporation of a filler will restrict the path of foam rise and lead to higher densities.

Question Are you using this for airplanes?

Winer The Bureau of Naval Weapons has technical cognizance for these materials on aircraft. They may be working with this system.

Question What was the composition of the cellular pellets?

Einhorn The pellets used were cellular glass. Similar pellets may be obtained by producing glass microballoons using a suitable silicate as a binder.

Question Can you tell us something about the project for filling life rafts with foam?

Winer You probably are referring to the instant boat concept. Yes, it is effective when the reaction goes to completion and the foam fully expands. However, when subjected to an extreme range of environmental operating temperatures, variable results occur. Additional development work is necessary to make this system fully operational.

Lloyd Prof. Einhorn speaks of cellular plastics extended with glass pellets, flake glass, or mica. These sound like rather expensive fillers. Have any really inexpensive fillers like rock wool been used with satisfactory results to extend cellular materials?

Einhorn Numerous low-cost fillers have been evaluated as extenders for cellular plastics. These include popcorn, lava, scrub foam, polystyrene beads, sawdust, rock wool, glass fiber, and the by-products of natural materials such as tall oil, lignin, and Vinsol. The early results have been obtained and some systems are available commercially at this time.

Frisch I would also like to comment that there are quite a few other fillers which are being used to lower costs with more or less success including Vinsol and other types of fillers, some of them as low as 5¢ a pound. Of course, you always have to watch out with fillers with regard to their effect on the over-all density of the filled foam, whether you actually gain very much as far as cost reduction is concerned, and, of course, the effect of the filler on the foam properties.

Einhorn Some low-cost extenders possess reactive sites. For example, tall oil has a hindered hydroxyl group. The information presented in recent literature questions the availability of this site for reaction. Generally, more favorable structure is obtained if the extender is bonded to the polymer backbone.

Frisch I think Dr. Saunders has done extensive work in this area, and maybe he would like to comment.

Saunders One of the better types of materials that we have seen is an ethylene oxide-modified Vinsol available from Hercules. This type of material has quite a lot of cyclic structure in it, so that in addition to reducing the cost of the raw materials by perhaps 20 percent, it makes these systems somewhat easier to make flame-resistant by the normal test. The extra cyclic structure is quite helpful in that respect.

Frisch I would like to ask Dr. Heaston how the programs on foamed plastics shelters are developing.

Heaston I think that probably someone in the audience could answer that one.

S. B. Swenson (Engineer R &D Labs., Fort Belvoir) We have been working about 5 years on such a program, and it is coming to a point where we think we will have something to take into the field. During the month of February we set up one building in Vietnam, and it seems to be working out very well. Our intention is to try to fabricate the building completely in the field, although in this particular case, because of the circumstances, we erected a building that had been prefabricated at Fort Belvoir. I believe that the program is getting along pretty well, and within the next, say, 6 months, we ought to have something quite promising.

G. R. Thomas (Natick Labs.) Also in response to Dr. Frisch's inquiry, the Canadians have done a considerable amount of work for the U.S. Army Natick Laboratories on a self-propagating foam. The preliminary work was reported in the previous conference on cellular materials. This work has progressed to the point that we are now ready to build prototypes of shelters, covers, and other items for field evaluation.

Question Is the system superior to a metered liquid system?

Thomas Yes, this system has the advantage of solving the problem of the low-temperature requirements for foaming reactions. We have not solved in the laboratory the problems associated with the low-temperature requirements, say, −65°F, to obtain a good structural element. I do not know whether Belvoir has solved that one either. [Negative indication from Dr. Howard of Belvoir.] But this foaming sheet, in which you have a propagating exotherm traveling along the surface, does solve that problem. We can foam these sheets at −65°F.

Einhorn The research project at the University of Michigan investigating the use of cellular plastics in the construction of low-cost housing for developing nations has been sponsored by the Agency for International Development for several years.

Comments and question from the floor.

Lloyd When the first results began to come out of this program, we made contact with the Army Research Office and have been in continuous touch with them ever since. They, of course, have a much broader contact with the Department of Defense organizations and have been able to transfer the information which they have considered necessary. They now have a very live program which, I believe, they expect to see develop into projects that will be quite significant for their purposes and, of course, we in AID hope to get a lot of benefit out of the work they do.

Question Can foamed plastics possibly compete with cotton duck or cotton duck sprayed with polyester or anything else as shelter material?

Lloyd We are effectively promoting foamed plastics as a material for the production of structures in developing countries. Cotton ducking appears to be in the nature of tentage. Tentage has never been satisfactory for permanent or semipermanent structures. From that point of view, therefore, I am certain the Agency could not be persuaded to investigate that material for the kinds of uses that it has in mind. Therefore, the foamed plastics will be investigated until its possibilities give a yes or no answer. We have not yet arrived at that point.

Einhorn Consideration must be given to the term "permanent structure." If one considers the typical high-rise building constructed in 1966, it is expected that the normal service life will approach a minimum of 30 or 40 years. Thus the cost per unit area (square foot of occupancy) must be amortized over this period of time. This structure, erected in 1966, may be totally obsolete for the purposes for which it was erected within 5 or 10 years after it was built. Certain features installed in the building are included in the mortgage, and payment continues even if these are removed and replaced. Cost of demolition may be excessive, thus the building may be modified as a last resort. On the other hand, it may be just as permanent in the total cost picture, if a structure is erected for $1 to $3 per square foot, and is required to last only 4 to 5 years. I think that this is a whole new concept that one must consider in the design of structures. When construction is considered for developing or emerging nations, separate factors must be investigated, and therefore, though these nations may be rich in certain natural resources, they may not have the necessary capital to sponsor development at this time. It is worthy to note that several nations have established regulations that require the use of their natural resources and raw materials in new ventures such as construction. In certain nations, it is not feasible to consider the total structure. The people may not, at the present time, have a roof over their heads, so you start out with a consideration of a partial structure. This, along with better sanitary conditions, is, in itself, a great step forward. If the actual per capita income on a yearly basis is less than $50 to $70 per year, the nation may not be prepared to receive and participate in these new development ideas.

Question What can be done to make cellular plastics with surface temperatures above 300°F?

Einhorn Well, Dr. Frisch is going to comment on this also. There has been continual work in this area, and, I might also report, not only in the area of foams. Just 2 or 3 weeks ago at the International Conference on Elastoplastics, some very interesting work was described regarding the use of isocyanurate elastomers as potting compounds in capsulation materials, so there is work going on in the general area. One of the problems that Pickless and Gmitter had run into was the degree of reaction and they were looking at other systems. I have a feeling that a lot more has been done on the subject than has been reported because of the patent situations here and it takes time for some of this to come through.

Question Which catalysts are used to promote isocyanurate formation?

Einhorn Pickless and Gmitter had used both. In fact, in their paper they reported on both and they had TGA and DTA analyses on both.

Frisch There has been a fair amount of work; some of it has been published, some not, some of it has been done under certain contracts which are not readily available. However, in a recent paper by Beitchmann, a catalyst system was disclosed consisting of combinations of triethylenediamine, better known as Dabco, and propylene oxide or triethylenediamine–ethylenimine or a substitute of ethylenimine combinations, all of which are fairly good trimerization catalysts. That type of catalyst is not entirely new; similar systems have been reported previously.

Einhorn I did not mention in my presentation the use of foam polyimides. These materials, of course, result in intractable tars. But there are a limited number of polyimides that lend themselves to foaming with rather exotic foaming agents. While these materials are still in the high-priced category, they offer quite a high degree of temperature stability, and I think that there might be some specialized application developed in this area.

Lloyd I noted that much has been said about new compounds, new formulations, and their potential uses, but no one has put a dollar figure against any of these. Certainly they are being compared with other materials in the applications for which they are proposed. There must be some cost figures in the minds of those who promote this research. Now, in our business, the dollar is an important figure for the reasons that I attempted to communicate this morning. This is what I would like to hear now: What materials are on the horizon that promise low cost for specific applications and how do they compare with other materials?

Question What do you consider low?

Lloyd Well, it's not so much *low*, but we want to compare it with the materials that *you* have in mind.

Question How expensive is foamed polystyrene?

Einhorn Certain types of foam polystyrene, usually based on beet stock, are selling for approximately 4½¢ a board foot in Europe. Basically, I think, to look at the price per pound of cellular plastics is wrong. One must look, however, at the price installed. During the past 5 years, the urethane foams, for example, have encountered a considerable cost reduction. Essentially, this industry is operating at commodity prices in a noncommodity market value. This has lead to somewhat of a decrease in the research and development at a time when expansion of this effort is called for in order to insure greater market penetration. Many of the cellular plastics have been used for insulation purposes alone, and as insulation materials, on a cost per unit of k factor, these materials present an interesting economic profile. The *in situ* applied materials look even more interesting than slabstock for insulation of homes. In several cases, residential homes have been insulated by the spray technique. Most of the units insulated in this manner were not redesigned to take advantage of the structural properties of the cellular plastics. At one time there was a great surge of interest to compare the insulating values of a spray-applied urethane insulation with conventional fiberglass insulation. It is known that the fiberglass can be installed for approximately 2½¢ per board foot material cost, and 1¢ per board foot labor cost. On the other hand, if you consider that we have 3⅝ in. of stud space to fill with fiberglass, and that if we overinsulate or begin to compact the material, the k factor actually rises because of the increased density. Comparisons have been made using urethane only on an equal k factor basis, which would mean that approximately half the thickness of the stud space will be filled with foam. If, however, one were to utilize fully the insulation and fill the entire void space with foam, the structure would be theoretically twice as well insulated as that insulated with conventional materials. While foams cannot compare directly on a cost per k factor basis with fiberglass, in the base market, if design factors are considered, it may be possible that a home that is both electrically heated and air conditioned will offer a substantial advantage when insulated with foam.

Frisch I think that this is a rather important point which Prof. Einhorn has pointed out; namely, that not only raw material costs as well as installed cost, but also cost-to-performance ratio must enter into the overall picture as far as savings are concerned.

If there are no further questions, I would like to thank the speakers this afternoon for their excellent presentations, and I would likewise like to thank the members of the panel who participated in this afternoon session. Thank you. Session is adjourned.

SESSION 3

Chemistry and Physics of Cellular Materials (continued)

Chairman, GEORGE R. THOMAS
U.S. Army Natick Laboratories

The Effect of Chemical Structure on Environmental Properties of Polyurethanes

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INTRODUCTION

The relationships between chemical structure and physical properties of polyurethanes have been the subject of several recent investigations.[1–11] Of particular interest has been the influence of chemical composition on the heat stability of these polymers under various environmental conditions.

The behavior of polyurethanes at elevated temperatures has been studied by many investigators, notably Saunders,[12] Dyer and co-workers,[13–16] Ingham and co-workers,[17–19] Engel *et al.*,[20] and Beachell and Ngoc Son.[21]

These investigators have shown that the heat stability of polyurethanes depends upon the chemical structure of the polymer and the presence of catalysts or reactants, as well as upon various environmental factors such as humidity and the presence or absence of air or oxygen. Likewise the degradation of the urethane polymers may take place at different temperatures and via different routes depending upon the chemical nature of the substituted urethane groups in the polymer chain.

The present study deals specifically with polyurethane films and foams of high crosslink density. By using films, prepared from the same polyols as those used in rigid foams, for many of these investigations, it was hoped to eliminate mechanical and process variables introduced during the preparation of foams. Darr and co-workers[7] have previously characterized solid rigid polyurethanes of high crosslink density by means of Vicat softening point, Rockwell hardness, Izod impact strength, and Clash-Berg torsional modulus measurements, and correlated these data with chemical structure.

The prime purpose of this investigation was to study the effect of the structure of polyether polyols and di- and polyisocyanates on the retention of properties of the resulting polyurethanes under selected environmental conditions. In addition, differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were carried out. Thermal data on polyurethanes by means of DTA and TGA had previously been reported by a number of investigators.[20,22–26]

The effects of crosslink density and type of polyether and isocyanate, as well as the isocyanate index (ratio of [NCO]/[OH] × 100) on the methylene chloride absorption of the polyurethanes, were also determined.

The polyether polyols used in the preparation of the polyurethane films and foams are listed in Table 1.

TABLE 1
Polyether Polyols Used in Polyurethane Films

Designation	Composition, Poly(oxypropylene) Adduct of
Diol 686[a]	Propylene glycol
Triol 426	Trimethylolpropane
Triol 702	Trimethylolpropane
Tetrol 416	Pentaerythritol
Tetrol 528	Pentaerythritol
Tetrol 620	Pentaerythritol
Hexol 510	Sorbitol
Hexol 684	Sorbitol
Cyclic Tetrol 500	α-Methyl glucoside
Cyclic Octol 1040	Sucrose

[a] The number in the designation is the experimentally determined average molecular weight.

RESULTS AND DISCUSSION

Heat Resistance of Polyurethane Films

The heat resistance of polyurethane films at high temperatures (140 and 195°C) in an atmosphere of air and oxidation at 100°C in an oxygen atmosphere at 126 psi were determined by measuring the changes in tensile strength. The principal aim was to compare the data from these various environments in order to arrive at general conclusions about the effect of polyurethane structure on heat stability.

Coatings of 8–10 mils thickness were prepared from toluene or toluene–acetone solutions on aluminum and glass panels. Polyether polyols were reacted with di- or polyisocyanates in the presence of 0.05 percent dibutyltin dilaurate (based on polyol equivalent weight) at an isocyanate index of 110. Curing was carried out for 18 hr at 100°C. The stripped films were tested as described.

Heat Resistance at 195°C in Air

The resistance of polyurethanes to degradation at 195°C, in an air atmosphere, was determined by the retention of breaking tensiles of films exposed to these conditions for 24 and 72 hr.

Initial work was carried out to obtain data on the effect of urethane crosslink density. Polyols of various functionalities were reacted with isocyanates, and the results obtained are shown in Table 2. Tensile specimens were prepared by the use of 1/8-in. dies; results shown are the averages of multiple determinations. It was noted that films made from polyols with functionalities higher than 4 were too brittle to allow the preparation of satisfactory tensile samples. To increase the flexibility of the specimens, films were made using blends with 80 percent of the hydroxyl groups coming from the polyols and 20 percent from Diol 686; the inclusion of the diol resulted in more suitable samples. The crosslink densities of these films were, of course, reduced.

TABLE 2
Effect of Crosslink Density on Heat Resistance (195°C) of Polyurethane Films

Polyol	Theoretical Equiv. Wt.	Di- or Polyisocyanate	Polyurethane		
				Retention of Tensile, %	
			$\overline{M}_c$	24 hr	72 hr
Triol 426	142	TDI	1145	20	—
Triol 426	142	MDI	1335	38	—
Triol 426	142	PAPI	886	52	—
Tetrol 416	104	TDI	573	83	—
Tetrol 416, 80%;[a] Diol 686, 20%	152	TDI	833	69	—
Tetrol 416, 80%; Diol 686, 20%	152	MDI	973	89	49
Hexol 684, 80%; Diol 686, 20%	160	TDI	554	74	62
Hexol 684, 80%; Diol 686, 20%	160	MDI	639	91	68
Hexol 684, 80%; Diol 686, 20%	160	PAPI	586	—	78

[a] Proportions are in equivalent weight percent.

TABLE 3

Resistance of Polyurethane Films to Heat Aging at 140°C

Polyol	Theoretical Equiv. Wt.	Diisocyanate	$\overline{M}_c$	Tensile Strength, psi				Elongation, %			
				Original	11 Days	35 Days	56 Days	Original	11 Days	35 Days	56 Days
Cyclic Octol 1040, 80%; Diol 686, 20%	173	MDI	546	10,900	10,700	12,800	—	3.9	3.3	4.0	—
Cyclic Octol 1040, 80%; Diol 686, 20%	173	TDI	477	10,700	10,000	10,800	—	4.2	3.8	3.5	—
Hexol 510, 80%; Diol 686, 20%	137	MDI	590	10,500	13,200	13,700	—	4.0	4.2	3.8	—
Hexol 510, 80%; Diol 686, 20%	137	TDI	504	9,500	9,700	9,600	—	3.9	4.2	4.1	—
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	MDI	1,029	9,100	10,500	13,800	13,900	4.0	4.0	3.2	—
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	TDI	896	8,900	7,800	7,100	6,800	4.2	4.9	4.3	—

The results indicate that the pentaerythritol-based polyol (Tetrol 416) produces urethane films with greater retention of tensile than could be formed from the trimethylolpropane-based polyol (Triol 426); when 20 percent Diol 686 was mixed with Tetrol 416, a decrease in heat resistance was obtained. Urethanes from the hexafunctional sorbitol-based polyol (Hexol 784) showed a slight increase in resistance to aging at 195°C. These comparisons are true for urethanes from either 4,4′-diphenylmethane diisocyanate (MDI) or an 80/20 mixture of the 2,4- and 2,6-isomers of tolylene diisocyanate (TDI); there are indications that the products from the former isocyanate are more heat resistant. The effect of average molecular weight per crosslink, $\bar{M}_c$ (as an indication of crosslink density), on the heat resistance at 195°C for polyurethanes is also shown in Table 2. $\bar{M}_c$ was determined by means of the method of Sandridge *et al.*[27] using a modified expression as follows:

$$\bar{M}_c = \frac{\bar{F}}{\bar{F} - 2} (\bar{E}_P + \bar{E}_I),$$

where $\bar{F}$ is the average functionality of the reactants (polyols and isocyanates), $\bar{E}_P$ is the average equivalent weight of polyol(s), and $\bar{E}_I$ is the average equivalent weight of di- or polyisocyanate. No corrections were made for the presence of unsaturation in polyols or any possible side reactions of the isocyanate groups. It is apparent that resistance to degradation is improved with decreasing values of $\bar{M}_c$.

A comparison of films prepared from TDI, MDI, or PAPI (Upjohn's trade name for polymethylene polyphenylisocyanate, obtained by phosgenation of aniline–formaldehyde condensation products with an average functionality of 2.8) indicated that urethane films from PAPI exhibited the best resistance to decomposition. The films from MDI exhibited better heat stability than those from TDI (despite lower crosslink densities due to higher equivalent weights), but not as good as the films derived from PAPI. The good stability of the MDI films was due to higher aromaticity, as compared with TDI. The samples from PAPI had a higher aromaticity than those from the other two isocyanates; they also had a higher functionality (2.8).

Heat Resistance at 140°C

The heat stability of polyurethane films at 195°C in an air atmosphere is dependent on their ability to resist oxidation and also on cleavage of the urethane bond. This latter type of decomposition is known to occur at temperatures above 150°C. An attempt was made to eliminate this type of cleavage and restrict decomposition to the oxidative type by studying the loss of tensile of films at 140°C in an atmosphere of air. Data in Table 3 indicated that urethanes from a sucrose-based polyol (Cyclic Octol 1040,

TABLE 4

Effect of Isocyanate Structure on Resistance of Polyurethane Films to Heat Aging at 140°C

Polyol	Theoretical Equiv. Wt.	Di- or Polyisocyanate	$\overline{M}_c$	Tensile Strength, psi				Elongation, %			
				Original	2 Days	11 Days	35 Days	Original	2 Days	11 Days	35 Days
Tetrol 416, 80%; Diol 686, 20%	152	MDI	970	10,800	—	10,300	11,000	3.6	—	3.1	3.4
Tetrol 416, 80%; Diol 686, 20%	152	TDI	837	10,700	—	10,800	10,300	3.7	—	3.6	3.9
Tetrol 416, 80%; Diol 686, 20%	152	XDI	861	6,700	7,300	9,700	[a]	114	87	2.7	[a]
Tetrol 416, 80%; Diol 686, 20%	152	PAPI	760	10,900	11,300	11,600	12,100	3.2	3.1	2.8	2.6

[a] Degraded.

containing 20 percent of Diol 686) reacted with TDI or MDI to produce urethane films that showed neither tensile loss nor loss in elongation after 35 days of aging; this was also true for urethanes from the reaction of Hexol 510 (containing 20 percent of Diol 686) with TDI or MDI. It can be noted that the films from MDI even showed increases in tensile strength after aging at 140°C. The aging period was increased to 56 days for films prepared from an α-methyl glucoside-based polyol (Cyclic Tetrol 500), and containing 20 percent of Diol 686. The data showed that tensile loss was obtained with films made from TDI, but no degradation was observed with films from MDI; the latter films even exhibited a significant increase in tensile strength after 56 days of aging. The small change in elongation would indicate that this was not due to continued curing during the aging period.

The evaluation of the influence of isocyanate structure on heat aging at 140°C was extended to include PAPI and XDI (*m*-xylylene diisocyanate). Data for films prepared from Tetrol 416 containing 20 percent of Diol 686 are shown in Table 4. It was again observed that no tensile loss occurred in urethane films from TDI or MDI; this was also found to be true for the product from PAPI. An increase in the tensile strength of the latter samples was noted after 35 days. Of interest were the results obtained with urethane films prepared from XDI; an increase in tensile was observed after 11 days, but by 35 days the samples were completely degraded and distorted. Of additional interest was the high initial breaking elongation of the XDI film; reductions in elongation were obtained with aging, and by 11 days data similar to films from other isocyanates were obtained.

Heat Resistance at 100°C in Oxygen

A further effort was made to obtain completely oxidative degradation of polyurethane films by heat aging in an oxygen atmosphere at 100°C. This was carried out in a pressure vessel at 120 psi. These data are shown in Table 5. Urethane films prepared from the α-methyl glucoside polyol (Cyclic Tetrol 500) and TDI degraded to about 35 percent of their original tensile after 8 weeks; films from XDI oxidized more rapidly and by 5 weeks were completely degraded. MDI produced films with considerably better resistance to oxidation which exhibited no tendency to decompose after 8 weeks. These data confirmed previous results that indicated urethane films from XDI to be the least heat-stable, followed by TDI and MDI in ability to resist degradation.

Similar data were obtained for films prepared from Hexol 510. Again, urethanes from XDI exhibited the poorest stability, followed by TDI and MDI; the latter films showed no evidence of oxidation after 8 weeks. It can be noted that the more highly crosslinked films from Hexol 510 exhibited better stability than those from the α-methyl glucoside tetrol

TABLE 5

Effect of Diisocyanate on Resistance of Polyurethane Films to Aging in Oxygen at 100°C

Polyol	Theoretical Equiv. Wt.	Diisocyanate	$\overline{M}_c$	Tensile Strength, psi			Elongation, %		
				Original	5 Weeks	8 Weeks	Original	5 Weeks	8 Weeks
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	MDI	1,029	10,100	10,300	10,200	6.7	5.7	5.3
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	TDI	896	8,800	8,800	2,855	5.0	4.3	12.2
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	XDI	921	4,500	completely degraded		87.0	completely degraded	
Hexol 510, 80%; Diol 686, 20%	137	MDI	590	10,600	10,400	10,200	4.0	3.6	3.2
Hexol 510, 80%; Diol 686, 20%	137	TDI	504	9,400	9,300	6,400	4.2	4.0	3.7
Hexol 510, 80%; Diol 686, 20%	137	XDI	520	5,600	completely degraded		31.0	completely degraded	

(based on TDI films), which is further evidence of the beneficial effects on heat resistance of polyurethanes resulting from the use of polyols of higher functionality and lower equivalent weight.

Conclusions from Heat Aging of Polyurethane Films The results reported above are concerned with the resistance of polyurethane films to high (195°C) and intermediate (140°C) temperature in an atmosphere of air and to 100°C in an oxygen atmosphere. It should be noted that the resistance to oxidative and thermal degradation is primarily indicative of the ability of ether and urethane structures to withstand cleavage.

The data indicate the following conclusions on the effect of chemical structure on heat and oxidative stability of urethane films: (1) Higher crosslink densities in urethane structures result in improved stabilities. (2) Use of polyisocyanates with higher aromaticity (MDI, PAPI) results in increased stability. (3) Use of benzyl-type isocyanates (XDI) produces poorer stability under the conditions employed.

Differential Thermal Analysis and Thermogravimetric Analysis

DTA and TGA data were obtained on a number of polyurethane samples. The equipment used in this work was designed and built at the Wyandotte Chemicals Research Laboratories. The DTA unit utilized a Leeds and Northrup Speedomax Recorder, an F & M Model 240 temperature programmer, and an ARA model 4SI dc amplifier. A tube furnace was used as the heater. Glass capillary cells were employed in an air atmosphere; the samples were ground to 80 mesh size. Glass beads, 80–120 mesh, were used in the reference cell. The heating rate was 10°C/min.

The TGA apparatus* used the F & M Model 240 programmer connected to a furnace. A standard analytical balance was modified into a recording balance. This was done by using a dc differential transformer as a position-sensitive transducer. The signal from the transducer was fed to an operational amplifier; the output supplied current to a solenoid-type balancing coil, the core being a permanent magnet. The IR drop of a resistor, in series with the balancing coil, was used to drive a Brown Electronik recorder.

Typical DTA and TGA thermograms are presented in Figure 1 for a polyurethane film from Triol 702 and TDI. The DTA thermogram showed an endothermic change at 110–115°C that corresponded with the softening point obtained (115°C) on a thermal gradient bar. An exothermic oxidation started at 255°C; weight loss started at 260°C and coincided with the oxidation as noted by DTA.

Comparative DTA and TGA data for urethane films are presented in Table 6. Polymer softening temperature (PST) data, as determined on a

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*Designed and assembled by Mr. B. McCabe of Wyandotte Chemicals Corporation.

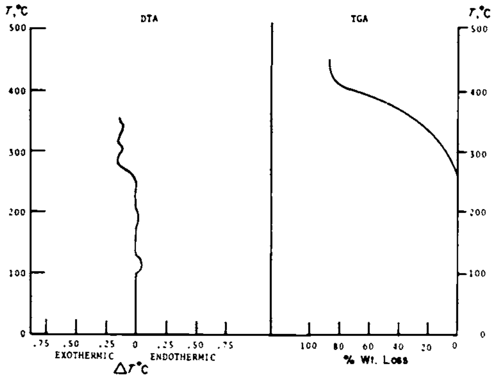

Figure 1
DTA and TGA of polyurethane film from Triol 702 and TDI.

temperature gradient bar similar to the method described by Wittbecker and Katz,[28] are included in this table. Good correlations were obtained between the DTA exotherm and the TGA weight loss temperatures, indicative of oxidative degradation of the polymers. Good agreement was also obtained between the DTA endotherm temperatures and the PST data; in general, they increased with increasing crosslink density. The relationship between crosslink density and oxidation resistance of the polymers was not as clearly defined from the data although the highest decomposition temperatures were obtained for the polymers with the highest crosslink densities (Hexol 510 and Cyclic Octol 1040). It may be of interest to note that the polyurethane based on Cyclic Tetrol 500 and TDI exhibited significant improvement in oxidation resistance as compared with the polyurethane from Tetrol 528 and TDI.

Table 6
DTA, TGA, and PST Data of Polyurethane Films

Polyurethanes from			DTA			
Polyol	Di- or Poly- isocyanate	$\overline{M}_c$	Endo- therm, °C	Exo- therm, °C	TGA,[a] °C	PST,[b] °C
Triol 702	TDI	1,605	110–115	255	260	115
Tetrol 528	TDI	657	135	250	270	130
Tetrol 528	PAPI	644	135	305	305	130
Cyclic Tetrol 500	TDI	636	125	295	287	130
Cyclic Octol 1040	TDI	362	140	305	290	140
Hexol 510	TDI	344	150	305	290	150

[a] Temperature at which weight loss begins.
[b] Polymer softening temperature determined on a temperature gradient bar similar to the method reported by Wittbecker and Katz.[28]

The influence of aromaticity on the oxidation resistance is demonstrated by the polyurethanes prepared from Tetrol 528 and PAPI showing significantly higher stability than the corresponding polymer from TDI.

A comparison was made of DTA data from urethane films and foams. The foams were prepared by blending together the following:

100	parts (by weight) polyol
1.5	parts (by weight) DC 113 silicone
1.0	part (by weight) Dabco
13%	(by weight of total materials) Fluorocarbon-11

To the above blend, 1.05 NCO/OH equivalents of the isocyanate were added and mixed for 35 sec with a motor-driven stirrer. The mixture was poured into a 10 in. × 10 in. × 4 in. box and allowed to rise. The samples were tested after 1 week at 24°C.

DTA data on the foams were obtained after grinding samples to a fine powder, to assure release of blowing agent. The results in Table 7 indicate good agreement in endotherm and exotherm temperatures between film and foam samples, which is evidence that comparable polymer structures were formed in the preparation of film and foam samples.

TABLE 7
DTA Data for Polyurethane Films and Foams

Polyurethane Sample	Endotherm Temp., °C		Softening Point, °C Thermal Gradient Bar	Exotherm Temp., °C	
	Film	Foam		Film	Foam
Triol 702 + TDI	115	110	115	255	265
Tetrol 528 + TDI	135	130	130	250	245
Tetrol 528 + PAPI	135	135	135	305	310
Cyclic Tetrol 500 + TDI	125	125	130	295	300
Cyclic Octol 1040 + TDI	140	140	145	305	295
Hexol 510 + TDI	150	145	150	305	305

Effect of Temperature on Mechanical Properties of Urethane Foams

A number of foams were prepared, using various polyols, in an effort to determine the effect of heat on their mechanical properties.

The data in Table 8 show that the tensile strength of urethane foams can be affected by heating to 100°C. At that temperature, the foams from Tetrol 528 and TDI exhibited a greater loss in tensile (as compared with room

TABLE 8

Effect of Temperature on Tensile Strength of Rigid Foams

Polyurethane	$\overline{M}_c$	Tensile Strength, psi Room Temperature	 100°C	 Change, %
Tetrol 528 + PAPI	644	42.7	39.3	−8.0
Hexol 684 + PAPI	453	30.9	30.3	−1.9
Tetrol 528 + TDI	657	32.6	19.1	−41.4
Hexol 684 + TDI	402	23.4	27.3	+16.7

temperature) than the foam from the same polyol and PAPI. This would indicate a greater resistance to softening of urethane polymers from PAPI than those from TDI; this was true even though there was little difference in crosslink density (or $\overline{M}_c$). Apparently, the greater aromaticity of PAPI was an important factor. It can also be noted that, where significant differences exist, as between foams from Tetrol 528 and Hexol 684, the foam with the higher crosslink density (or lower $\overline{M}_c$ value) exhibited better resistance to heat.

The data in Table 9 are from urethane foams prepared with PAPI and indicate that the effect of elevated temperature on yield strength was similar to that obtained with tensile strengths. Foams with higher crosslink density exhibited greater resistance to loss of yield strength than those with lower concentrations of crosslinks. It is of interest, however, to note that the foam from the Cyclic Tetrol 500 showed a greater resistance to softening than would be expected from its $\overline{M}_c$ value. Other investigators[7] have also reported higher softening points for urethanes from α-methyl glucoside than would be expected from their crosslink densities.

Table 10 shows the results obtained from determination of loss of flexural strength at elevated temperature; the effect of crosslinking density was

TABLE 9

Effect of Temperature on Yield Strength of Rigid Foams

Polyurethane	$\overline{M}_c$	Yield Strength, psi Room Temperature	 100°C	 Change, %
Tetrol 528 + PAPI	644	29.3	17.2	−41
Cyclic Tetrol 500 + PAPI	627	36.6	26.6	−27
Hexol 684 + PAPI	453	35.5	24.4	−31
Cyclic Octol 1040 + PAPI	418	31.3	21.9	−30

TABLE 10
Effect of Temperature on Flexural Strength of Rigid Foams

Polyurethane	$\overline{M}_c$	Flexural Strength, psi Room Temperature	100°C	Change, %
Tetrol 528 + PAPI	644	45.4	36.0	−21
Cyclic Tetrol 500 + PAPI	627	44.2	38.0	−14
Hexol 684 + PAPI	453	41.8	35.4	−15
Cyclic Octol 1040 + PAPI	418	35.7	31.3	−12

similar to that obtained from the other foam data. The greatest loss in flexural strength was obtained in the foam from Tetrol 528; the best retention was obtained in the foam from Cyclic Octol 1040. These foams were all made with PAPI as the polyisocyanate and the use of the Cyclic Tetrol 500 again produced a greater resistance to heat than would be expected from its $\overline{M}_c$ value.

Resistance to Humid Aging

Films

Humid aging tests were carried out on polyurethane films, prepared in the same manner as described above under Heat Resistance of Polyurethane Films (page 76). They were subjected, in an autoclave, to 11 hr at 150°C in excess water at 65 psi. The initial and aged breaking tensiles were determined and the percent retentions are shown in Table 11.

It is apparent that polyurethanes from MDI retained a higher proportion of their original tensiles than did those from TDI. This was true with polyurethanes of lower crosslink density (such as those from Tetrol 416) as well as those of higher crosslink density (such as those from Hexol 510 and the sucrose-based polyol). In most cases, polymers from MDI showed no degradation after the humid aging test. Polyurethanes with higher crosslink densities appeared to resist aging better than those with less crosslinking. Thus, polyols rank in the following order, according to the aging resistance of polyurethane films prepared from TDI: Hexol 510 > Hexol 684 > Tetrol 416. The polyols from sucrose and α-methyl glucoside did not follow this pattern and it appeared that urethane films from these polyols were less resistant to humid aging than would be expected from their theoretical crosslink densities and functionalities. It is probable that the carbohydrate structures of these polyols were responsible for the poorer behavior in this type of aging test. The data in Table 12 indicate that urethanes from XDI exhibited extremely poor resistance to humid aging; none of the films tested showed any tensile strength after aging but were

TABLE 11

Resistance of Polyurethane Films to Humid Aging (11 hr at 150°C)

Polyol	Theoretical Equiv. Wt.	Diisocyanate	$\overline{M}_c$	Retention of Tensile Strength, %
Tetrol 416, 80%; Diol 686, 20%	152	TDI	837	31
Tetrol 416, 80%; Diol 686, 20%	152	MDI	970	98
Hexol 684, 80%; Diol 686, 20%	160	TDI	556	40
Hexol 684, 80%; Diol 686, 20%	160	MDI	641	100
Hexol 510, 80%; Diol 686, 20%	137	TDI	504	70
Hexol 510, 80%; Diol 686, 20%	137	MDI	590	98
Cyclic Octol 1040, 80%; Diol 686, 20%	173	TDI	477	30
Cyclic Octol 1040, 80%; Diol 686, 20%	173	MDI	546	100
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	TDI	896	0
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	MDI	1,029	74

distorted and deformed. The films from PAPI showed aging resistance equivalent to those from MDI.

The following conclusions can be drawn from the above data on polyurethane films: (1) Humid aging resistance can be increased by preparing polyurethanes of high crosslink density. (2) Polyisocyanates of high aromatic content (MDI or PAPI) are to be preferred. (3) Isocyanates with benzyl groups, such as XDI, exhibit poor resistance to humid aging.

Foams

Some of the foams that were used in heat resistance tests were also evaluated for resistance to water immersion. Determination of loss of yield strength after 16 hr immersion in water at 70°C resulted in data that also reflected the beneficial effects of increased crosslink density (Table 13). Tetrol 528 produced foam with the least resistance to water immersing; Cyclic Octol 1040 produced foam with the best resistance, correlating with its lower $\overline{M}_c$ value. The foam from the Cyclic Tetrol 500 exhibited a greater ability to resist water immersion than would have been expected from its $\overline{M}_c$ value.

TABLE 12

Effect of Polyisocyanate on Resistance of Polyurethane Films to Humid Aging

Polyol	Theoretical Equiv. Wt.	Di- or Polyisocyanate	$\overline{M}_c$	Retention of Tensile Strength, %
Hexol 684, 80%; Diol 686, 20%	160	TDI	556	40
Hexol 684, 80%; Diol 686, 20%	160	MDI	641	100
Hexol 684, 80%; Diol 686, 20%	160	PAPI	586	100
Hexol 684, 80%; Diol 686, 20%	160	XDI	572	0
Cyclic Octol 1040, 80%; Diol 686, 20%	173	TDI	477	30
Cyclic Octol 1040, 80%; Diol 686, 20%	173	MDI	546	100
Cyclic Octol 1040, 80%; Diol 686, 20%	173	XDI	490	0
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	MDI	1,029	74
Cyclic Tetrol 500, 80%; Diol 686, 20%	169	PAPI	805	78

TABLE 13

Effect of Water Immersion on Yield Strength of Rigid Foams

		Yield Strength		
Polyurethanes	$\overline{M}_c$	Original	After 16 hr in H_2O at 70°C	Change, %
Tetrol 528 + PAPI	644	29.3	8.9	−70
Cyclic Tetrol 500 + PAPI	627	36.6	20.3	−45
Hexol 684 + PAPI	453	35.3	22.4	−37
Cyclic Octol 1040 + PAPI	418	31.3	21.7	−31

Resistance of Polyurethane Films to Ultraviolet Radiation (Fade-Ometer Tests)

The ability of urethane structures to resist degradation during Fade-Ometer testing has been investigated, with emphasis on a comparison of films from different types of di- and polyisocyanates.

Using Hexol 684 as the polyol, films were prepared and comparisons made of their breaking tensiles before and after 100 hr exposure in the Fade-Ometer. It can be seen from Table 14 that films prepared from XDI were completely degraded; no improvement was noted on the inclusion of Antioxidant 425 (American Cyanamid Company). The best results were obtained from the urethane prepared from TDI; a further improvement was obtained with the inclusion of the antioxidant. The film from PAPI was significantly less resistant to degradation than the TDI-based films.

TABLE 14
Resistance of Polyurethane Films to Ultraviolet Exposure (Fade-Ometer)

Polyol	Theoretical Equiv. Wt.	Di- or Polyisocyanate	Tensile Strength, psi	
			Original	After 100 hr
Hexol 684, 80%; Diol 686, 20%	160	TDI	9,900	8,200
Hexol 684, 80%; Diol 686, 20%	160	TDI + 1% Antioxidant	10,300	10,200
Hexol 684, 80%; Diol 686, 20%	160	XDI	8,000	0
Hexol 684, 80%; Diol 686, 20%	160	XDI + 1% Antioxidant	8,400	0
Hexol 684, 80%; Diol 686, 20%	160	PAPI	10,100	6,300

Effect of Polyurethane Structure on Resistance to Methylene Chloride

Films

Coatings of 8–10 mils thickness were prepared from toluene solutions on aluminum and glass panels. Polyether polyols were reacted with diisocyanates in the presence of 0.05 percent dibutyltin dilaurate (based on polyol) at an isocyanate index of 110. Curing was carried out for 18 hr at 100°C. The stripped films were weighed, immersed in methylene chloride for 3 hr at −3°C and reweighed after drying in air for 1 min.

In an effort to determine the effect of crosslink density on solvent absorption, data were obtained on films from polyols of various functionalities and equivalent weights reacted with TDI, as shown in Table 15. These results and the plot of $\bar{M}_c$ versus absorption (Figure 2) indicate clearly that polyurethanes of higher crosslink density are more effective in resisting solvent swelling. It can be noted that both polyols derived from Sorbitol produced urethane films with no detectable solvent absorption at −3°C. Their behavior on 24-hr immersion in methylene chloride at 23°C is illustrated in

TABLE 15

Effect of Crosslink Density of Polyurethane Films on Absorption of Methylene Chloride

		Polyurethane	
Polyol	Theoretical Equiv. Wt.	$\overline{M}_c$	Absorption, % 3 hr at −3°C
Triol 426	142	1,145	26
Triol 702	234	1,605	49
Tetrol 416	104	573	4
Tetrol 528	132	657	18
Tetrol 620	155	726	23
Hexol 684	114	402	0
Hexol 510	85	344	0
Cyclic Octol 1040	130	362	8
			24 hr at 23°C
Hexol 684	114	402	60
Hexol 510	85	344	0

Table 15; the more highly crosslinked urethane polymer with an $\overline{M}_c$ value of 344 exhibited significant improvement in solvent resistance.

The effect of isocyanate index on methylene chloride absorption was also determined. Polyurethane films used in this investigation were prepared from TDI by reaction with Triol 426; other films were prepared from Tetrol 620. It is apparent from Table 16 and Figure 3 that changes in isocyanate index had an effect on solvent resistance. At an index of 130, reduced resistance to methylene chloride was obtained; at indices between 95 and 110 no effect on absorption was noted. The increased swelling behavior at higher isocyanate content was probably due to a lower crosslink density, caused by the upset of stoichiometry in the presence of larger excesses of isocyanate groups.

The influence of the type of isocyanate was also studied in an effort to determine if increased aromaticity (as in MDI) plays a role in solvent

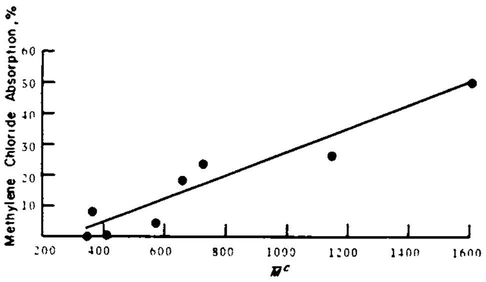

FIGURE 2

Effect of crosslink density on methylene chloride absorption.

TABLE 16

Effect of Isocyanate Index on Absorption of Methylene Chloride

Polyol	Theoretical Equiv. Wt.	Isocyanate Index	Polyurethane Film Absorption, % 3 hr at −3°C
Triol 426	142	95	30
Triol 426	142	100	26
Triol 426	142	103	24
Triol 426	142	106	25
Triol 426	142	110	26
Triol 426	142	130	66
Triol 426	142	150	79
Tetrol 620	155	95	25
Tetrol 620	155	100	28
Tetrol 620	155	103	27
Tetrol 620	155	106	28
Tetrol 620	155	110	23
Tetrol 620	155	130	65
Tetrol 620	155	150	72

resistance. Pure MDI was chosen, rather than PAPI, to effect no change in isocyanate functionality. The results (Table 17) indicate little difference in methylene chloride absorption for urethanes from TDI or MDI. Apparently, in structures with high crosslink density the type of aromatic isocyanate used has little effect on solvent resistance.

The conclusions to be reached from this work on the comparative methylene chloride absorption properties of polyurethane films were: (1) Resistance to swelling was significantly higher for polyurethanes of high crosslink density. (2) Polyurethanes of low isocyanate index (95–110) are preferable

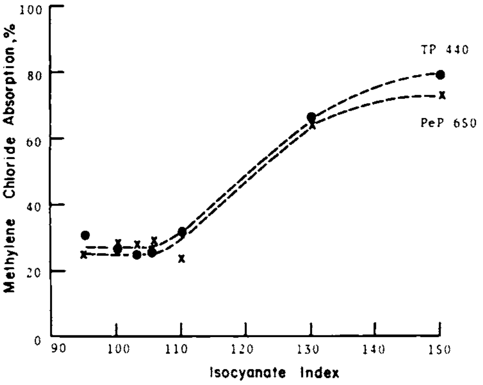

FIGURE 3

Effect of isocyanate index on methylene chloride absorption.

TABLE 17
Effect of Type of Diisocyanate (MDI versus TDI) on Absorption of Methylene Chloride

			Polyurethane Film	
Polyol	Theoretical Equiv. Wt.	Diisocyanate	M_c	Absorption, % 3 hr at −3°C
Triol 426	142	TDI	1,145	28
Triol 426	142	MDI	1,335	25
Tetrol 620	155	TDI	726	26
Tetrol 620	155	MDI	840	22
Tetrol 528	132	TDI	657	18
Tetrol 528	132	MDI	771	19

to those of higher isocyanate content (130 and above). (3) No improvement was obtained with the use of MDI as compared with TDI.

Foams

Foams were prepared, from a combination of polyols and polyisocyanates, of two different crosslink densities. Their $\bar{M}_c$ values were 657 and 773. The procedure used in their preparation was the same as described previously, with the exception that methylene chloride was used as the blowing agent. It was noted that, 0.5 hr after foaming was completed (Figure 4), the foam with the higher crosslink density retained its shape better than the other sample. The latter foam showed a greater tendency to crack and distort. The same comparison could be made of the samples 48 hr after the completion of foaming (Figure 4). It is of interest that the crosslink density of the polymer structure had the same effect on resistance to methylene chloride in the foam samples as had been exhibited in film samples.

SUMMARY

A study of the resistance of polyurethane films and foams to various swelling and degrading environments was carried out. Physical properties of the resulting polymers were correlated with chemical variations in the polyether and isocyanate structures.

Thermal resistance was determined by various techniques, including differential thermal analysis, thermogravimetric analysis, and heat aging. High crosslink density and the use of polyisocyanates of high aromatic content resulted in increased thermal stability.

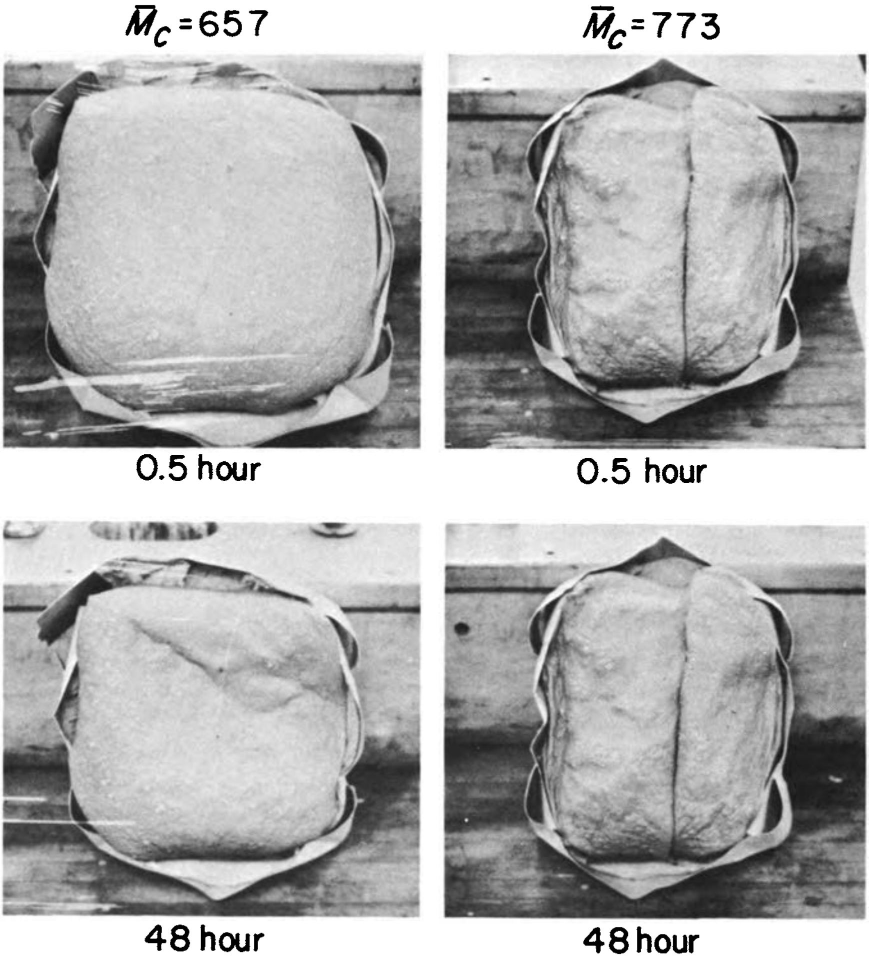

FIGURE 4
Foam samples blown with methylene chloride (0.5 and 48 hr).

Resistance to moisture, at high temperatures, was also found to increase with crosslink density; it was influenced by the type of polyol and isocyanate used in the urethane reaction.

Solvent resistance of polyurethane structures increased at higher crosslink densities, appeared to be unaffected by the type of aromatic diisocyanate, and was reduced with the use of a large excess of isocyanate.

The ultraviolet resistance of films prepared from various isocyanates decreased in the order: tolylene diisocyanate (TDI) > polyphenyl polymethylene polyisocyanate (PAPI) > xylylene diisocyanate (XDI).

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REFERENCES

1. J. H. Saunders, *Rubber Chem. Technol.*, *33*, 1259 (1960).
2. T. Tanaka and T. Yokoyama, *Rubber Chem. Technol.*, *35*, (No. 4), 106 (1962).
3. J. H. Saunders and K. C. Frisch, *Polyurethanes, Part I, Chemistry*, Interscience-Wiley, New York (1962), pp. 261–344.
4. J. H. Saunders and K. C. Frisch, *Polyurethanes, Part II, Technology*, Interscience-Wiley, New York (1964), pp. 722–729.
5. O. Bayer and E. Mueller, *Angew. Chem.*, *72*, 934 (1960).
6. E. F. Cluff and E. K. Gladding, *J. Appl. Polymer Sci.*, *3*, 290 (1960).
7. W. C. Darr, P. G. Gemeinhardt, and J. H. Saunders, *Ind. Eng. Chem. Prod. Res. Develop.*, *2*, 194 (1963).
8. K. C. Frisch, *J. Cellular Plastics*, *1*, 321 (1965).
9. T. L. Smith and A. B. Magnusson, *J. Polymer Sci.*, *42*, 391 (1960).
10. T. L. Smith and A. B. Magnusson, *J. Appl. Polymer Sci.*, *5*, 218 (1961).
11. A. J. Havlik and T. L. Smith, *J. Polymer Sci.: Part A*, *2*, 539 (1964).
12. J. H. Saunders, *Rubber Chem. Technol.*, *32*, 337 (1959).
13. E. Dyer and G. E. Newborn, *J. Am. Chem. Soc.*, *80*, 5495 (1958).
14. E. Dyer and G. C. Wright, *J. Am. Chem. Soc.*, *81*, 2138 (1959).
15. E. Dyer and R. E. Read, *J. Org. Chem.*, *26*, 4388 (1961).
16. E. Dyer and R. J. Hammond, *J. Polymer Sci.: Part A*, *2*, 1 (1964).
17. J. D. Ingham and N. S. Rapp, *J. Polymer Sci.: Part A*, *2*, 4941 (1964).
18. N. S. Rapp and J. D. Ingham, *J. Polymer Sci.: Part A*, *2*, 689 (1964).
19. R. Simha, J. D. Ingham, N. S. Rapp, and J. Hardy, *J. Polymer Sci.: Part B*, *2*, 675 (1964).
20. J. H. Engel, Jr., S. L. Reegen, and P. Weiss, *J. Appl. Polymer Sci.*, *7*, 1679 (1963).
21. H. C. Beachell and C. P. Ngoc Son, *J. Appl. Polymer Sci.*, *8*, 1089 (1964).
22. C. M. Cusano, E. P. Dunigan, and P. Weiss, *J. Polymer Sci.: Part C, No. 4*, 743 (1963).
23. P. E. Slade, Jr., and L. T. Jenkins, *J. Polymer Sci.: Part C, No. 6*, 27 (1964).
24. J. K. Backus, W. C. Darr, P. G. Gemeinhardt, and J. H. Saunders, *J. Cellular Plastics*, *1*, 178 (1965).
25. L. Nicholas and G. T. Gmitter, *J. Cellular Plastics*, *1*, 85 (1965).
26. W. C. Darr, P. G. Gemeinhardt, and J. H. Saunders, paper presented before the Division of Organic Coatings and Plastics Chemistry, American Chemical Society, Detroit, Mich., April 1965.
27. R. L. Sandridge, A. S. Morecroft, E. E. Hardy, and J. H. Saunders, *J. Chem. Eng. Data*, *5*, 495 (1960).
28. E. L. Wittbecker and M. Katz, *J. Polymer Sci.*, *40*, 367 (1959).

Outgassing Rates in Polymeric Foams*

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INTRODUCTION

Currently, there is considerable interest in the possibility of using polymeric foams as lightweight encapsulants for electronic components on spacecraft. Very little is known, however, about the electrical breakdown behavior in foams, when an important parameter is the pressure of the blowing gas within the foam cells; in particular, in the ionization region for the gas. Therefore, a study was undertaken of the diffusion of the blowing gas from foams when placed in high vacuum. The fundamental aspects of this process are of importance to the general problem of transport properties of heterogenous synthetic or natural polymeric systems.

The purpose of this report is to present (1) a relationship that was developed to relate the diffusion constant for a foam to its density and the permeation constant of the bulk polymer, (2) a description of the experimental techniques used for this study, and (3) experimental results obtained on closed-cell polyurethane foams.

DIFFUSION EQUATIONS

Diffusion equations for polymeric foams were developed using, as a simple, but physically reasonable model, a three-dimensional array of cubical cells

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having walls of uniform thickness and permeable to gases. Here, only one-dimensional diffusion is considered, although extension to the three-dimensional case is straightforward.

The general relation for the flux J at which a gas permeates through a membrane is

$$J = \frac{dw}{dt} \frac{P_e A}{L} \Delta P, \tag{1}$$

where

w = weight of gas,
P_e = permeation control,
A = area,
L = thickness of membrane,
P = pressure difference across the membrane,
t = time.

The net flux for the nth layer of cells is given by

$$dw_n/dt = J_{n+1} - J_{n-1}, \tag{2}$$

which, upon substituting for J, yields

$$\frac{L}{P_e A} \frac{dw_n}{dt} = P_{n+1} - 2P_n + P_{n-1}. \tag{3}$$

From the perfect gas law,

$$w_n = P_n(VM/RT), \tag{4}$$

which can be substituted into Equation (3) to yield the following differential equation:

$$\frac{LVM}{P_e ART} \frac{dp_n}{dt} = P_{n+1} - 2P_n + P_{n-1} \tag{5}$$

for the pressure P_n in the nth layer of cells.

Thus for a system of N layers, we have a set of N linear homogeneous equations. For the boundary condition that the external pressure is always zero, along with the initial condition that for zero time the pressure P_0 in all layers is uniform, the following relationship is obtained:

$$\frac{P_n(t)}{P_0} = \sum_{k=1}^{N} \alpha_k \left[\sin \frac{\pi n(2k-1)}{2N+1}\right] \times \exp\left\{-\left(\frac{P_e ART}{LVM}\right)\left[2 - 2\cos\frac{\pi(2k-1)}{2N+1}\right]t\right\}. \tag{6}$$

For the limiting case of $N \to \infty$, the coefficients α_k's can be readily evaluated, and the solution becomes

$$\frac{P_n(t)}{P_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin\left[\frac{\pi(2k-1)n}{2N}\right] \times \exp\left\{-\left(\frac{P_e ART}{LVM}\right)\left[\frac{\pi(2k-1)}{2N}\right]^2 t\right\}. \tag{7}$$

If $N > 20$, values of α_k's for the limiting case of $N \to \infty$ can be used without introducing a significant error. Since for a 1-in.-thick foam, N is of the order of a few hundred, Equation (7) is applicable for all cases of interest. Now, if formally we consider the gas as a diffusion process in a medium characterized by a diffusion constant D, the following well-known equation is appropriate:[1]

$$\frac{P_x}{P_0} = \frac{C_x}{C_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin\left[\frac{\pi x(2k-1)}{2a}\right] \times \exp\left\{-\left[\frac{(2k-1)\pi}{2a}\right]^2 Dt\right\}, \tag{8}$$

where

C_x = concentration of gas,
C_0 = initial concentration,
a = thickness of solid,
x = distance in from exposed surface,
D = diffusion constant.

This equation is identical to Equation (7) only at the limit $N \to \infty$. But again, it will be a close enough approximation for large N. Noting that since $n/N = x/a$, the coefficients in both equations are identical and hence the arguments of the exponential for Equations (7) and (8) must be equal; thus,

$$D/a^2 = P_e ART/LVMN^2. \tag{9}$$

As V/A is the length of the side of cell d, we substitute and rearrange Equation (9) to get

$$D = P_e\left(\frac{RT}{M}\right)\frac{a^2}{(NL)\,(Nd)}. \tag{10}$$

As a is the thickness of the foam and NL and Nd are the thickness of the membranes and the cells, respectively, it follows that $a = NL + Nd$. The ratio $a^2/[(NL) \times (Nd)]$ can be readily expressed in terms of the densities of the foam ρ and the bulk polymer ρ_0. For a cube of unit dimensions, i.e., $a = 1$, which contains N^3 cells, the total volume of cells is $(Nd)^3$.

This volume represents the volume fraction of voids and is therefore equal to $1 - (\rho/\rho_0)$. Thus (Nd) is equal to $[1 - (\rho/\rho_0)]^{1/3}$ and, since $(Nd) + (NL) = 1$, (NL) is equal to $1 - [1 - (\rho/\rho_0)]^{1/3}$. Substituting for (NL) and (Nd) in Equation (10) and factoring out ρ_0/ρ, the following expression is obtained:

$$D = P_e \left(\frac{RT}{M}\right)\left(\frac{\rho_0}{\rho}\right)\left\{\frac{1}{[1 - (\rho/\rho_0)]^{1/3}} + 1 + [1 - (\rho/\rho_0)]^{1/3}\right\}, \qquad (11)$$

where

ρ = density of foam,
ρ_0 = density of membrane material.

Equation (11) relates the diffusion constant of a polymer foam to the permeation constant and foam density. The expression

$$\left\{\frac{1}{[1 - (\rho/\rho_0)]^{1/3}} + 1 + [1 - (\rho/\rho_0)]^{1/3}\right\}$$

varies slowly between 3 and 3.05 as ρ/ρ_0 varies between 0 and 0.5. Since most polymer foams are of low density, the variation in this term can be neglected. Thus, for a given family of foams, Equation (11) predicts that the diffusion constant is inversely proportional to the foam density and can be simply represented as

$$D = K/\rho. \qquad (12)$$

The experimental data are obtained by measuring the weight loss of gas Q, from polymer foams in vacuum. The value of D is then calculated by use of the integrated form of Equation (8):[1]

$$Q = Q_\infty - \frac{8Q_\infty}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k - 1)^2} \exp\left\{-\left[\frac{(2k - 1)\pi}{2a}\right]^2 Dt\right\}, \qquad (13)$$

where Q_∞ is the initial weight of gas in the foam. For sufficiently long times, all the exponential terms except the first ($k = 1$) can be neglected. Thus a plot of $\ln(Q_\infty - Q)$ versus time will eventually become linear with a slope of $(\pi/2a)^2 D$.

EXPERIMENTAL

To obtain weight-loss data, foams of 3-in. diameter and 1 in. deep were bonded into aluminum containers, leaving the top surface exposed. The bonding agent was Eccobond 55,* a room-temperature curing epoxy.

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*All foams and the bonding agent were supplied by Emerson and Cuming, Inc.

Weight-loss data at room temperature, 22 ± 1°C, were obtained with an Ainsworth vacuum balance unit.

For elevated temperatures, weight loss was measured with a Cahn RH Electrobalance, which was situated inside a vacuum unit manufactured by the Consolidated Vacuum Corporation. The sample was heated by means of a variac-controlled 250-W bulb. A temperature differential of less than 1° was maintained across the sample by means of a reflecting aluminum shroud.

The following polymer foams were investigated:

1. Eccosil 5000,* a syntactic silicon foam of nominal specific gravity 0.48 prepared by mixing together hollow silicone spheres and a silicon resin.
2. Eccofoam SH,* a nominal 8-lb/ft^3 polyurethane foam filled with CO_2 gas. This material is purchased already blown in 1-in.-thick sheet stock. Actual measured density of the sample is 7.6 lb/ft^3.
3. Stycast 1090,* a syntactic expoxy foam prepared by mixing together hollow glass spheres and an epoxy resin. System cures hard with a nominal specific gravity of 0.78.
4. Eccofoam FPH/12/2H,* a nominal 2-lb/ft^3 polyurethane foam filled with CO_2 gas. Material prepared prior to test by mixing a resin–catalyst system and allowing the combination to foam and cure. Density of sample was 2.1 lb/ft^3.
5. Eccofoam FPH/12/6H,* a nominal 6-lb/ft^3 polyurethane foam filled with CO_2 gas. Material prepared prior to test by mixing a resin–catalyst system together and pouring into a mold 2 in. deep and 3 in. in diameter. Using an appropriate weight schedule, the foaming reaction would result in about half of the cured material extending above the top of the mold. Samples prepared from the top and bottom halves were found to be 4.5 and 6.4 lb/ft^3, respectively.

The family of rigid, closed-cell polyurethane foams known as Eccofoams FPH are asserted by the manufacturer to be capable of withstanding indefinite exposure to a temperature of 300°C, and even to higher temperatures for short periods of time. These materials are available in the density range from approximately 2 to 10 lb/ft^3.

The initial weights of CO_2 gas (Q_∞, mg) in all foams were calculated using the perfect gas law and 1 atm of pressure.

RESULTS AND DISCUSSION

Weight-loss curves for Eccosil 5000, Eccofoam SH, and Stycast 1090 are shown in Figure 1. The outgassing rates of these materials parallel the

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*All foams and the bonding agent were supplied by Emerson and Cuming, Inc.

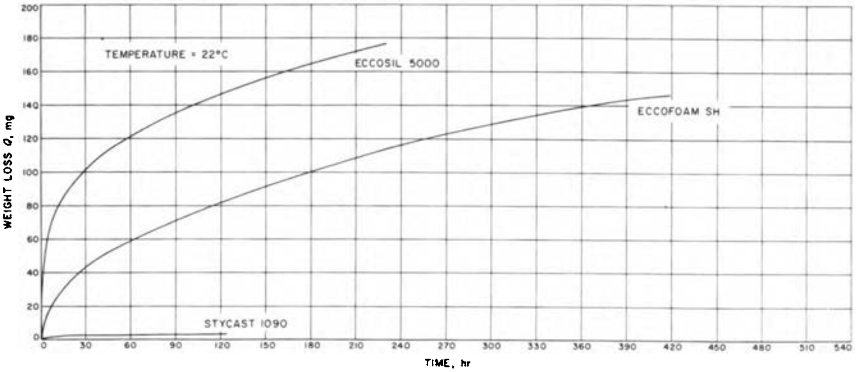

FIGURE 1
Weight-loss curves for three polymer foams at 22°C.

relative order of their respective gas-permeability constants.[2] Eccosil 5000 lost 180 mg of weight in 225 hr, approximately 90 mg more than the calculated CO_2 content of 90 to 100 mg (Q_∞). The additional weight loss presumably results from volatile impurities or volatile components that were not consumed in the curing reaction.

The rate of weight loss for Stycast 1090 is extremely low, as only 3.5 mg out of a possible 70 mg of gas were removed under vacuum in approximately 130 hr. This is to be expected, because the CO_2 gas is contained inside glass spheres of low permeability. In addition, the high density of this material results in the formation of very thick membranes between the glass spheres.

For the Eccofoam SH, the plot of log ($Q_\infty - Q$) versus time shown in Figure 2 was constructed from the weight loss data (Figure 1) and $Q_\infty = 184$ mg. Using Equation (13) and the slope of the linear portion of the curve ($t > 120$ hr), a diffusion coefficient of 2.40×10^{-6} cm²/sec at 22°C was calculated.

Weight loss curves at 22°C for three Eccofoam FPH systems of densities 2.1, 4.5, and 6.4 lb/ft³ are shown in Figure 3. Using these data, plots of log ($Q_\infty - Q$) versus time were obtained (Figure 4), and the diffusion coefficients were found to be 6.2×10^{-7} cm²/sec for the 2.1-lb/ft³ foam, 1.76×10^{-6} cm²/sec for the 4.5-lb/ft³ foam, and 1.24×10^{-6} cm²/sec for the 6.4-lb/ft³ foam. The values used for Q_∞, which were calculated with an assumed initial gas pressure of 1 atm, were, respectively, 203 mg, 194 mg, and 188 mg of CO_2.

From Equation (11), the diffusion coefficient should be inversely proportional to the density. This relationship holds true for the 4.5- and 6.4-lb/ft³ foams, but not for the 2.1-lb/ft³ foam, which in fact has the lowest diffusion coefficient of the three. However, this is inconsistent with the faster initial

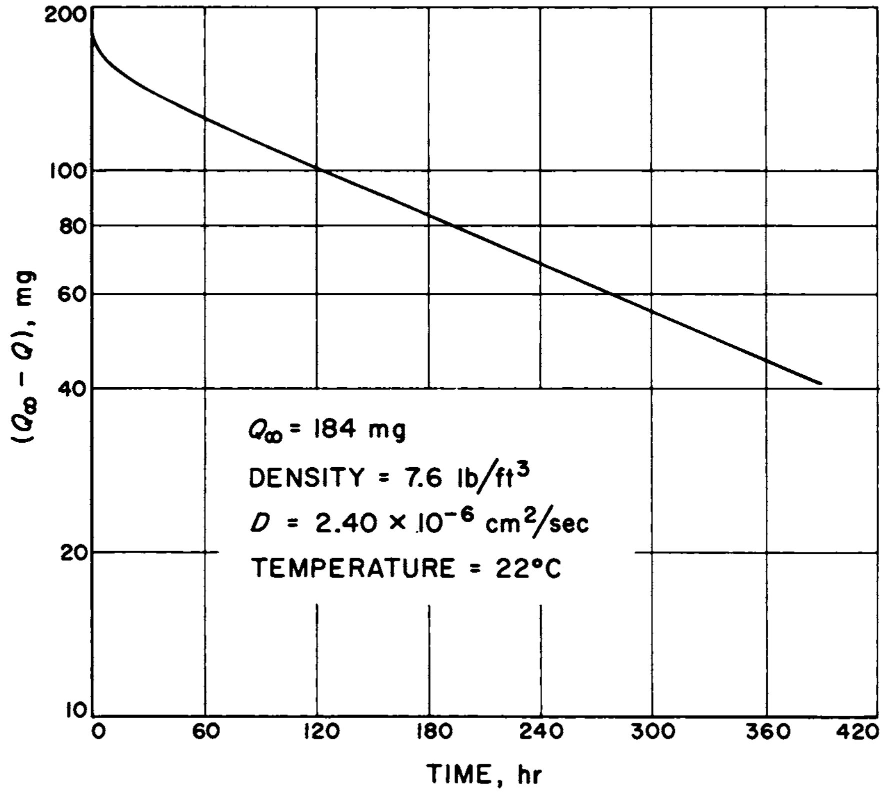

FIGURE 2
Log ($Q_\infty - Q$) versus time for Eccofoam SH at 22°C.

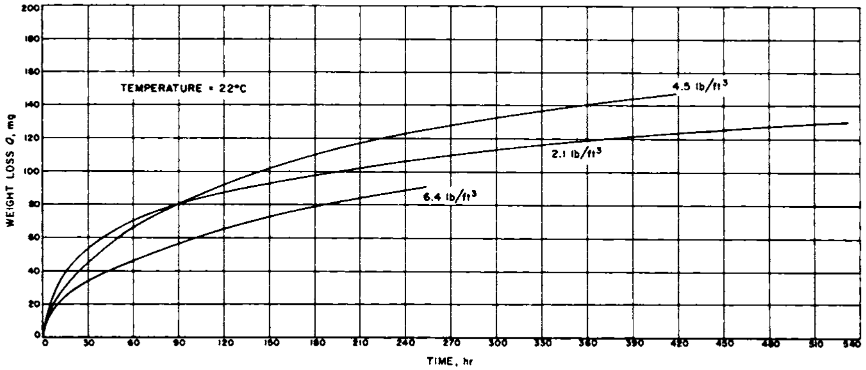

FIGURE 3
Weight-loss curves for Eccofoam FPH foams at 22°C.

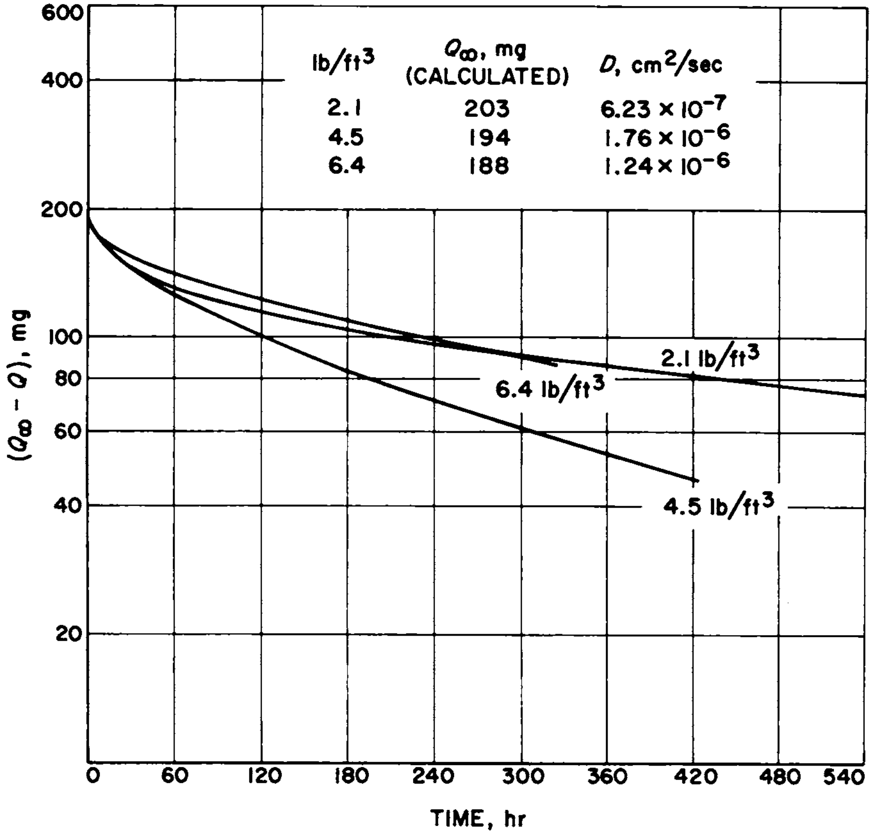

FIGURE 4
Log ($Q_\infty - Q$) versus time for Eccofoam FPH foams at 22°C.

outgassing rate observed for the 2.1-lb/ft³ foam. This discrepancy can arise from an incorrectly chosen value of Q_∞. Equation (13) shows that D is inversely proportional to Q_∞. Thus a higher value of D can be obtained from the log ($Q_\infty - Q$) plots by using a lower value of Q_∞. Support for the use of a lower value of Q_∞ can be seen from Figure 3, where the weight loss curve for the 2.1-lb/ft³ foam is apparently approaching an asymptotic value of Q_∞ that is considerably less than the calculated value of Q_∞. From Equation (12) and the diffusion coefficients for the 4.5- and 6.4-lb/ft³ foam, a value of 3.76×10^{-6} cm²/sec is predicted for the 2.1-lb/ft³ foam. Using the latter value for the diffusion coefficient, and the weight-loss data (Figure 1), a trial-and-error procedure yielded a value for Q_∞ of 148 mg. Figure 5 is a plot comparing the log ($Q_\infty - Q$) plots for Q_∞ values of 203 and 148 mg. Figure 6 is a normalized plot of Q/Q_∞ versus time for all three

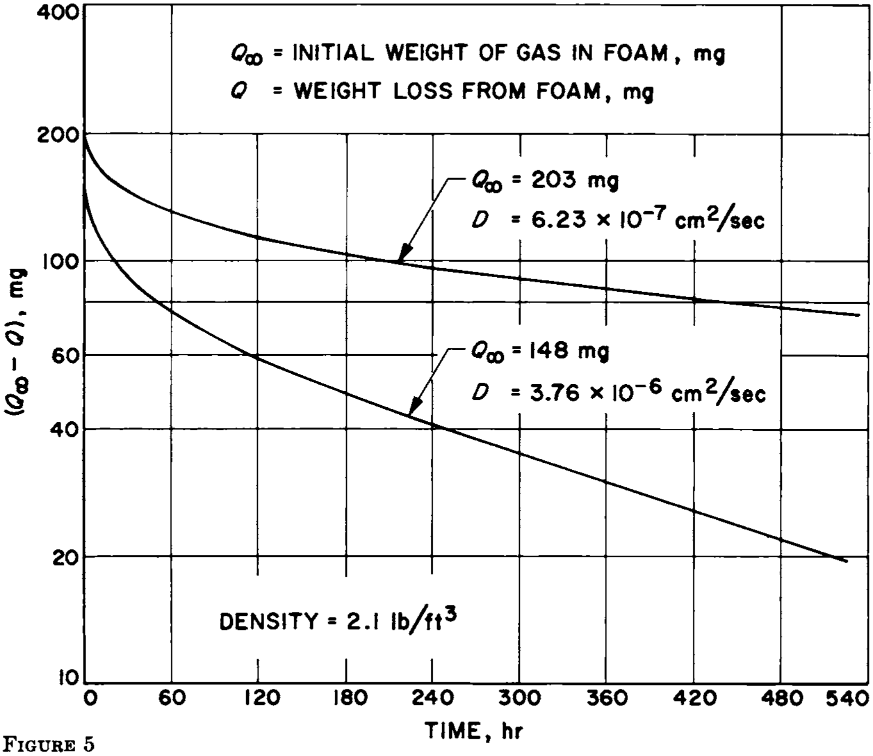

Figure 5
Log $(Q_\infty - Q)$ versus time for Eccofoam FPH/12/2H at 22°C.

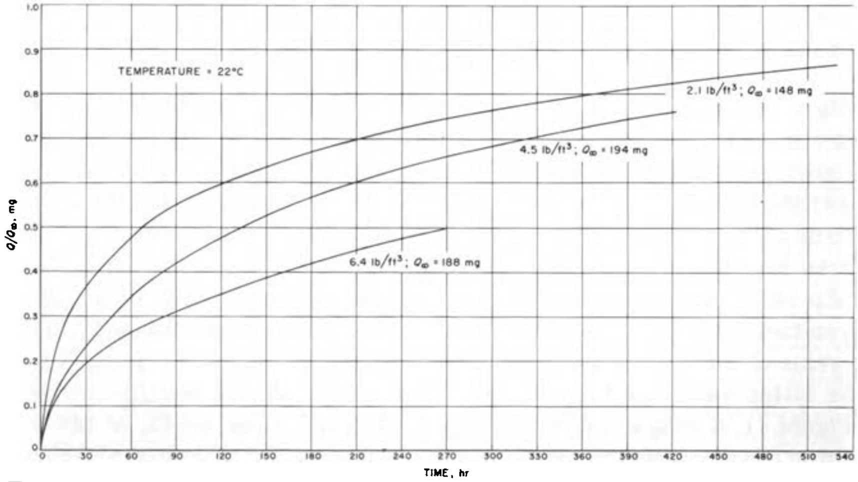

Figure 6
Q/Q_∞ versus time for Eccofoam FPH foams at 22°C.

Eccofoam FPH foams, and it can now be seen that the weight-loss curve for the 2.1-lb/ft^3 foam has assumed its expected relationship in relation to the other two foams.

It should be pointed out that extrapolation to zero time of the linear portion of plots of log $(Q_\infty - Q)$ versus time should intercept at a value of log $(8Q_\infty/\pi^2)$ [Equation (13)]. Thus, if the diffusion coefficient is independent of concentration, the diffusion equations will predict the value of both Q_∞ and D for a given set of weight-loss versus time data. It was found that for the 6.4-lb/ft^3 foam the calculated value of Q_∞ coincided with that obtained by back-extrapolation, justifying the use of the perfect gas law to calculate Q_∞.

However, extrapolation of the log $(Q_\infty - Q)$ plot for the 4.5-lb/ft^3 foam did not yield the calculated value of $Q_\infty = 194$ mg. Inspection of the log $(Q_\infty - Q)$ plot for this foam shows that there is a greater drop in the initial portion of the curve than that observed for the 6.4-lb/ft^3 foam. For the 2.1-lb/ft^3 foam, which also failed to satisfy the equations, the drop in the initial portion of the log $(Q_\infty - Q)$ curve is greater yet. This behavior is most readily attributed to a pressure dependence of the diffusion coefficient, which becomes more pronounced with decreasing foam density. If for a polymer foam the initial diffusion coefficients are higher, then the initial portion of the log $(Q_\infty - Q)$ would drop more rapidly and then, after a long time, the asymptotic diffusion coefficient can be obtained from the linear portion. But because of the initial larger drop, back-extrapolation will yield a lower value of log $(8Q_\infty/\pi^2)$, and this is observed for the 4.5- and 2.1-lb/ft^3 foams.

The foregoing has shown that the initial gas contents of polymer foams of densities greater than 4.5 lb/ft^3 can be determined from the perfect gas law. Also, there seems to be little, if any, dependence of the diffusion coefficient on pressure for densities greater than 6.4 lb/ft^3, and thus both weight loss and pressure distributions can be predicted employing a single diffusion equation and the diffusion equations for a homogeneous solid.

Using the diffusion coefficients for the 4.5- and 6.4-lb/ft^3 foams, it was possible to calculate the value of the constant K in Equation (12). This equation for the Eccofoam FPH polyurethane foams is

$$D = \frac{7.9 \times 10^{-6}}{\rho},$$

where D is in units of cm^2/sec and ρ in units of lb/ft^3.

The permeation constant of the bulk polyurethane polymer constituting the foam material can now be calculated from Equation (11), using the experimentally obtained diffusion coefficients. This procedure yielded a value of P_e equal to 5.1×10^{-9} (cc STP) mm/sec/cm^2/cm Hg, which can be compared with a value of 12×10^{-9} reported for rubbery polyurethanes.[2]

However, a lower P_e value for the rigid foam material would be expected in comparison with the equivalent rubbery material.[2]

TEMPERATURE DEPENDENCE

Outgassing rates for a 4.5-lb/ft^3 foam were determined at 22, 41, 61, and 81°C. The tests were conducted by first heating the samples in air to the desired temperature and then subjecting them to a vacuum. It was found, however, that the samples heated in air would lose an amount of CO_2 which increased with increasing temperature. It became a practice therefore to start recording the weight loss in air during heating. When the desired temperature was reached and the weight loss rate slowed significantly, vacuum was applied. The results of the tests are given in Figure 7, which shows weight loss both in air and in vacuum with zero time taken as the point when vacuum was initiated.

The curves in Figure 7 show a dramatic increase in the rate of gas removal with increasing temperature. The largest change occurs between 22 and 61°C. Above 61°C the changes are small. It is instructive to observe that at the higher temperatures, the weight-loss asymptote appears to be the value of $Q_\infty = 194$ mg, which was calculated from the perfect gas law. This further justifies the use of this value in determining the diffusion coefficients from plots of log $(Q_\infty - Q)$. Using the same value of $Q_\infty = 194$ mg, it is seen that this foam has lost approximately 97.5 percent of its gas content in 180 hr at 61°C and higher, whereas only 57 percent of the gas content was lost in 180 hr at 22°C.

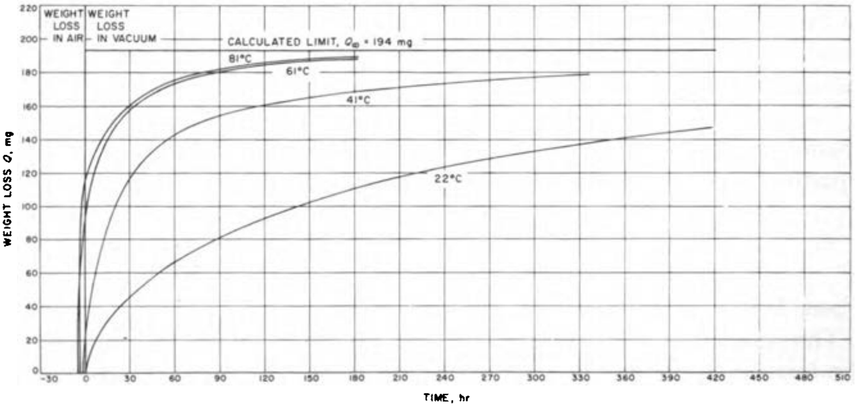

FIGURE 7

Temperature dependence of the outgassing rate for an Eccofoam FPH/12/6H foam of density 4.5 lb/ft^3.

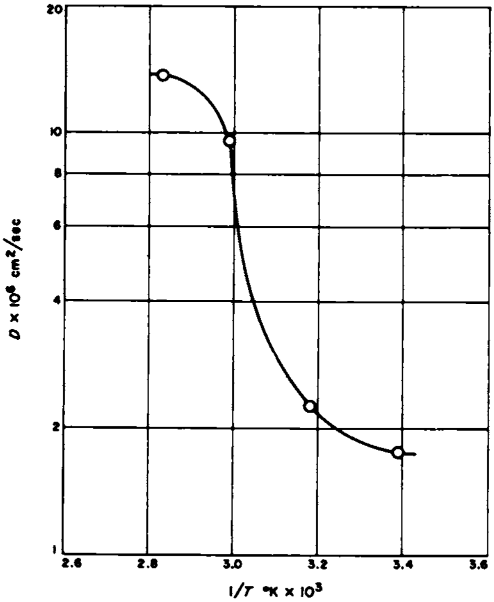

FIGURE 8
Log D versus $1/T$ °K for an Eccofoam PFH/12/6H foam of density 4.5 lb/ft³.

The diffusion coefficients obtained at the various temperatures are plotted in Figure 8 as log D versus $1/T$ in °K. The general appearance of this curve is sigmoidal and indicates that the largest changes in the diffusion coefficient occur between 22 and 81°C, above and below which there appears to be only a gradual dependence of log D on $1/T$.

SUMMARY

Diffusion rates for carbon dioxide were determined on closed-cell polyurethane foams of varying densities by monitoring, for 2 to 3 weeks, the loss of weight from specimens suspended in a vacuum of 10^{-7} mm Hg. The experimental data were used to calculate diffusion coefficients for these materials, which were found to be of the order of 10^{-6} to 10^{-5} cm²/sec between 22 and 81°C.

The solution of the diffusion equation for an idealized model for a foam yielded the following expression for the diffusion coefficient:

$$D = P_e\left(\frac{RT}{M}\right)\left(\frac{\rho_0}{\rho}\right)\left[\frac{1}{(1-\rho/\rho_0)^{1/3}} + 1 + (1-\rho/\rho_0)^{1/3}\right],$$

which relates the diffusion coefficient D to the foam density ρ and to the permeation constant P_e and the density ρ_0 of the bulk polymer; R is the gas constant, T the temperature, and M the molecular weight of the gas.

Using this equation and experimentally obtained values of D, a P_e of 5.1×10^{-9} (cc STP) mm/sec/cm^2/cm Hg was calculated for the polyurethane material constituting the foam, which agrees within a factor of 2 for reported P_e constants for polyurethane.

REFERENCES

1. J. Crank, *The Mathematics of Diffusion,* Oxford University Press, New York (1956).
2. C. E. Rogers, "Permeability and Chemical Resistance," Chapter 9 in *Engineering Design for Plastics*, sponsored by the Society of Plastics Engineers, Inc., E. Baer, ed., Reinhold Publishing Corp., New York (1964).

A Method for Determination of the Cellular Gas Content of Rigid Urethane Foams and Its Relationship to Thermoconductivity

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One of the outstanding applications of expanded plastics, and of rigid urethane foams in particular, is in the field of thermal insulation. Today, rigid and semirigid foams are being used for insulation in the transportation industry, in the appliance field, in clothing, in the construction field, and in many other areas. The most important physical property, the basis for the insulative use of these foams, is thermal conductivity. It must be evaluated and controlled. The thermal conductivity of a material such as urethane foam is expressed in terms of a k factor or a k value and has the dimensions of Btu/(hr) (ft^2) (°F/in.). Many natural and synthetic insulants contain gases trapped in a matrix. These gases act as poor conductors of heat and consequently cause the materials to be good insulators.

Table 1 shows the relative thermal conductivities of several gases and vapors. You will notice the tremendous difference in conductivity between trichlorofluoromethane and the other gases.

In the early days of rigid-foam technology, carbon dioxide was used to expand the reacting polymer. The source of CO_2 resulted from the reaction of isocyanate with the water added to the formulation for this purpose. These foams are more expensive to produce than present foams utilizing fluorocarbons because of the consumption of isocyanate to afford CO_2. Moreover, the resulting thermal conductivity of the present foams is much higher. They usually exhibited an initial heat conductivity of about 0.16 k-factor units that rapidly increased with age to about 0.24 k-factor units. However, CO_2-blown foams were far better with respect to k factor than many insulating materials then available. Table 2 has comparative k values of several available insulants and shows that the CO_2 foams are better

TABLE 1

Thermal Conductivity of Gases and Vapors[1]

Substance	°F	k^a
Air	32	0.168
Carbon dioxide	32	0.102
Trichlorofluoromethane	32	0.058
Nitrogen	32	0.168
Oxygen	32	0.170
Water vapor	115	0.144

[a] k = Btu/(hr) (ft^2) (°F/in.).

than all except the fluorocarbon-blown foams, which are superior. The use of a volatile material such as trichlorofluoromethane in the foam formulations is far simpler and easier to control than CO_2 as a blowing agent. The heat of reaction from the isocyanate–resin reaction is sufficient to cause the generation and release of the fluorocarbon gases. The fluorocarbon does not enter into a chemical reaction with the other components of the system and therefore affords much greater control of the eventual foam properties. Urethane foams prepared using fluorocarbon blowing agents are in great demand today because of their extremely low k factor. This demand has to some extent put pressure on foam producers to guarantee a low k-factor

TABLE 2

Thermal Conductivity of Some Building and Insulating Materials[1]

Material	Density lb/ft^3	°F	k^a
Asbestos	29.3	32	1.08
Aluminum foil, 7 air spaces/2.5 in.	0.2	100	0.300
Cork board	10	86	0.300
Felt, wool	20.6	86	0.48
Fiber insulating board	14.8	70	0.336
Fiberglass[3]	0.5	75	0.29
Mineral wool	9.4	86	0.270
Mineral wool	19.7	86	0.288
Polystyrene, rigid foam[4]	1.8	40	0.25
Polyurethane, CO_2-blown	2.3	75	0.24
Polyurethane, CCl_3F-blown (cut samples, initial)	2.1	75	0.110
Slag wool	12	86	0.262
Wallboard, insulating type	14.8	70	0.336
Wool, animal	6.9	86	0.252

[a] k = Btu/(hr) (ft^2) (°F/in.).

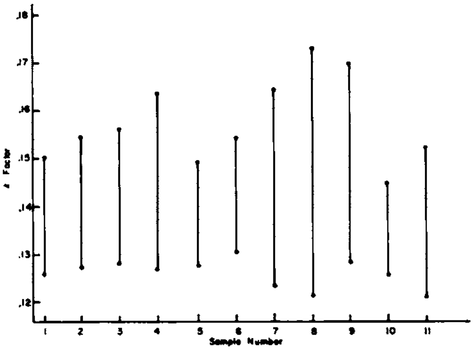

FIGURE 1
k Factor, initial and aged, 10 days, 140°F.

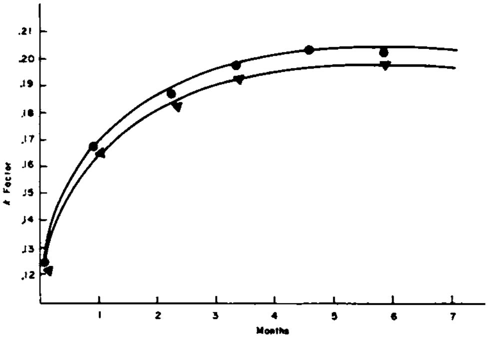

FIGURE 2
k Factors of two formulations over 6 months.

value to the consumer. It is this fact that has caused us to have an interest in the contributions to thermoconductivity of rigid foams.

The now well-known observation that all urethane foams, irrespective of the blowing agents utilized, have initial *k* values that are lower than the value obtained after the foams have aged, strongly suggests that diffusion of air and CO_2 occurs within the closed cells. This has been substantiated by the works of Harding and James,[2] Skochdopole,[3] and others.[4,5] Having a larger molecular diameter and molecular weight than carbon dioxide, trichlorofluoromethane would be expected to diffuse more slowly or not at all and hence give rise to equilibrium *k* values that remain low after aging—giving these foams additional advantages. This pattern has been observed by Doherty *et al.*,[6] as well as in our laboratories. Figure 1 shows both initial and aged *k* factors on cut specimens determined for a variety of foam systems based on various resins and ratios of PAPI.* These samples were aged for 10 days at 140°F. It is apparent that the *k* factor for each foam has increased in value. Figure 2 shows *k* factors for two of the formulations shown in Figure 1 for a period of 6 months. These data

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*Upjohn's registered trade name for polymethylene polyphenylisocyanate (the polyisocyanate derived from an aniline–formaldehyde condensation product).

merely confirm for our systems what has been observed in the field. These findings pointed out the need for quantitative knowledge of the cellular gas composition, which shed light on the relationships of thermoconductivity with blowing agents, the diffusion of air and CO_2 upon aging, and, to some extent, the influence of cell structure. Thus, a good method for the determination of cellular gas content of urethane foams was desired —this is the subject of this paper.

A brief review of the literature revealed that others had wrestled with this problem. A procedure based on mass spectrometric analysis of the gases released when a polymer was destroyed in vacuum with sulfuric acid has been reported by Williams[7] to Doherty[6] in a private communication. From what could be obtained about the method and their results, it can be concluded that they were able to show increases in nitrogen content of the closed cells of urethane foam after 7 days of aging, while the trichlorofluoromethane concentration remained essentially constant. Carbon dioxide was not reported, but almost certainly was present. I assume that, under the conditions of analysis, CO_2 would be held in the sulfuric acid solution. Lyon and co-workers[5] also utilized the mass spectrometer and employed a novel apparatus for crushing the urethane sample under an atmosphere of argon. Their data reported $N_2 + O_2 + CO_2$ as air and the difference between their value for air and 100 percent as the trichlorofluoromethane concentration.

An analytical method for the determination of cellular gas composition in urethane foams was developed by Bauer[8] and presented at the Wayne State Polymer Conference series last year. In Bauer's method, a sample of foam is inserted into a collapsible tube, such as a toothpaste tube, sealed, and fitted with a valve. The tube is evacuated and then immersed in Fluorocarbon-22 refrigerant, to embrittle the foam. The contents of the tube are then crushed, thereby releasing the gases contained in the cells. He then connected the assembly to a gas chromatograph where the contents of the tube was separated and analyzed. With this apparatus, Bauer was able quantitatively to assay gaseous compositions of urethane foams.

All the methods that had been tried seemed to us to contain inherent difficulties: the sulfuric acid method did not appeal to us because there was no guarantee that the gases contained in the foam would not be changed by the sulfuric acid treatment. Possibly nitrogen is generated during the degradation. Analysis by the mass spectrometer employed by both Williams and Lyons was felt to be more complex than necessary. Gas chromatography is a more suitable analytical tool, since it allows for both separation and analysis and is more convenient to use. Prior to knowledge of Bauer's work, we also had tried crushing a core of rigid urethane foam in a collapsible tube that was fitted with valves so that connection to a gas chromatograph could be made for analysis. This system worked well except that we did not use the right kind of collapsible tube. We used a heavy-walled polyvinyl chloride tubing which absorbed some of the liberated gases. This problem perhaps does not occur when employing a toothpaste tube since the latter is fragile and may develop small holes during the crushing of the foam. This problem was obviated by Bauer by immersing the tube in Fluorocarbon-22 immediately after crushing, whereby the tube filled with this material and prevented further infusion of air if a leak had developed. This is a good approach, but was considered difficult for some of our objectives and somewhat prone to error for air analysis.

During the course of our investigation, we found that one could very easily obtain a representative sample of the cell gas by merely inserting the needle of a hypodermic syringe into the matrix and withdrawing a sample. The sample, which contained air and cellular gases, was then injected directly into a gas chromatograph. The only difficulty with this method was that air could not be excluded. However, the technique is very simple and much information about the blowing-agent concentration can be obtained. Certainly ratio data can be obtained in this manner.

We developed an apparatus that enables us to use the syringe technique and yet allows for quantitative air determination. The apparatus embodies criteria which we feel will make it useful to others in the field.

1. The method does not change the composition of the gas. The gas is obtained at room temperature and is released by physical action.
2. The method employs gas chromatography, which is simple to use and readily available.
3. Multiple analysis can be obtained rapidly on the same identical sample. This cannot be done by other methods.
4. The procedure can be applied and used in the field without extensive laboratory equipment.
5. The apparatus is novel and can be used as an analytical gas sampler.

The apparatus is shown in Figure 3, where it is seen as an attachment to a gas chromatograph. To operate the gas sampler, a core of foam, which is conveniently obtained from bun stock with the aid of a sharpened cork borer, is inserted into the larger portion of the sampler after the spring is in place. The spring functions only to hold the foam sample secure while sampling. The second half of the apparatus is joined to the main body and clamped in place with a laboratory U-type pinch clamp. The rubber O-ring seal provides for adequate tightness. A hypodermic syringe fitted with an 8-in. No. 22 gauge needle is inserted through the entrance system but not allowed to enter the foam sample. At this point, the chamber of the apparatus is alternately evacuated and flushed with helium gas by manipulation of the appropriate valves. This is done three times. With the chromatograph ready for the sample, the syringe needle is pushed through the sample slowly; simultaneously, the plunger is withdrawn so that by the

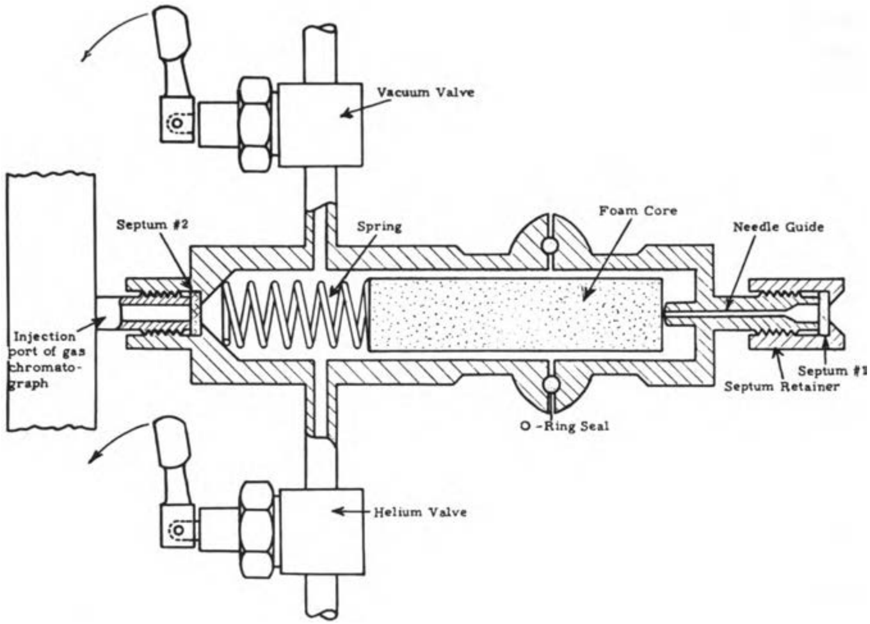

FIGURE 3
Gas sampler.

time the needle has completely passed through the sample foam core the plunger has been withdrawn to about a 3-ml volume. The needle to the syringe is then pushed further until it engages the silicone rubber septum of the chromatograph and through it into the chromatograph sample chamber. At this point, the sample is expelled. The entire operation takes about 2 to 5 min. Figure 4 shows an exploded view of the apparatus.

The gas-chromatographic conditions employed for the separation of nitrogen (air), carbon dioxide, and trichlorofluoromethane are given in

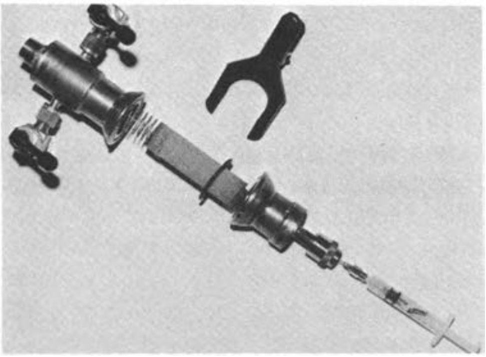

FIGURE 4
Gas sampler, exploded view.

TABLE 3

Conditions for the Gas-Chromatographic Analysis of Released Gas

Apparatus	F &M Model 810 programmed-temperature gas chromatograph
Column	3 in. × 3/16 in. id stainless steel tubing which had been activated at 100°C
Column support	Silica gel 80/90 mesh
Column temperature	Programmed 118 to 222°C at 50°C/min
Dector	Thermal conductivity
Injection port temperature	180°C
Detector block temperature	260°C
Carrier gas	Helium 70 ml/min
Sample size	3-ml gas sample from foam

Table 3. In actuality, these conditions are not critical. There are many different gas-chromatographic conditions that will work for the separation. It may also be possible to obtain the separation without temperature programming. Figure 5 is a typical chromatogram obtained showing the cellular gas composition. One of the difficulties with the first model of this apparatus was that only one sample of gas could be obtained from any core of foam. There was no apparent way to insert the needle through the core with assurance that one would engage new closed cells. On the average, about 100–150 cells are broken in the operation. We solved this problem with our present model by merely allowing the foam core to set on a grooved support within its sample chamber; this places the core eccentric to the axis of the sampler. Now the core is off to one side of the sample. A repeat analysis only requires that the sample be rotated 90°. It is very important to be able to check the results of an assay on the same sample, since the cellular gas composition has been found to change throughout the substance of a foam. Several experiments were done to determine reproducibility. Results showing repeatability on the same sample are shown in Table 4. Table 5 shows precision data obtained on a standard gas mixture

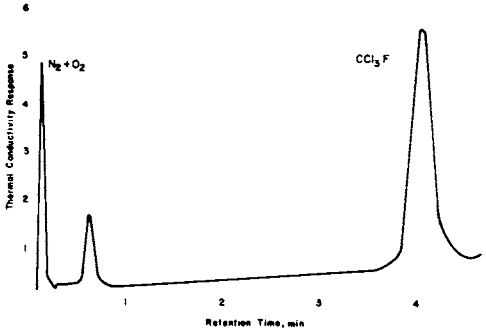

FIGURE 5
Chromatogram of cellular gas composition.

TABLE 4

Mole % of Cellular Gases Found on Single Core Using Modified Apparatus

Samples from One Bun 7 in. × 7 in. × 12 in.			Samples from Two Cores		
Air	Freon 11	Carbon Dioxide	Air	Freon 11	Carbon Dioxide
6.2	70	23	(a) 4.2	72	24
4.9	73	22	3.6	70	26
4.7	73	22	3.0	75	22
5.1	72	23			
4.4	72	23	(b) 6.6	71	22
3.1	74	23	4.2	76	20
4.2	72	24	3.2	77	20
6.6	71	22			
5.8	73	22			
10.0	69	20			
7.0	74	19			
7.7	72	20			

TABLE 5

Repeat Analysis on Standard Gas Mixture, Mole %

	Air	Freon	Carbon Dioxide
	15	44	41
	15	54	31
	11	60	29
	14	50	37
	12	54	34
	13	54	33
	13	48	39
	13	49	37
	14	49	37
	20	46	35
	18	47	35
	17	48	36
	16	45	39
Av.	14	50	36
σ[a]	2.63	4.50	3.24
c.v.[b]	19%	9.0%	9.0%

[a] Standard deviation.

[b] Coefficient of variance.

by the gas-chromatographic technique. In another attempt to demonstrate repeatability and reliability of the method, we assayed six samples of machine-prepared urethane foam, in which the analytical sample was taken from the same location of the bun. These results are shown in Table 6. Results obtained without the modification of the grooved support are shown in Table 7. In this case, the data were obtained on machine-prepared

TABLE 6
Cellular Gas Analysis on Rigid Urethane Buns Machine Prepared from the Same Formulation and Identically Sampled

	Cell Gas Composition (Mole %)				
Sample No.	Air	CO_2	CCl_3F	Unknown	*k* value
1	8	34	57	2	0.12 (5)
2	9	27	61	2	0.13 (0)
3	6	31	61	2	0.12 (6)
4	7	32	59	2	0.12 (8)
5	6	30	62	2	0.12 (6)
6	8	28	62	2	0.12 (7)

TABLE 7
Cellular Gas Content of Rigid Urethane Foams Obtained from Random Sampling

	Air (Mole %)	CO_2 (Mole %)	CCl_3F (Mole %)
Sample No. 1			
	16	4	80
	17	5	78
	22	8	70
	25	15	60
	27	16	57
	20	15	65
	21	14	65
	12	18	70
	11	15	74
	14	12	74
	11	16	73
Sample No. 2			
	12	18	70
	14	23	63
	9	20	71
	13	22	65
	10	25	65
	13	26	61

and random core samples of open bun stock. This was done to show maximum deviations. Two different formulations are represented. Sample No. 1 contained slightly less water in the formulation than sample No. 2. The results for CO_2 in the second sample are the *k*-factor values for each sample that was run. These data reflected similar variations. In another experiment, we sampled at several locations across the bottom, the middle, and top of a machine-produced bun. Table 8 shows the ratio of CCl_3F/CO_2 obtained. You will note that there are variations even in going across on a plane of the sample. On the average, there is a distinct difference in ratio of trichlorofluoromethane to CO_2 throughout the bun.

In another investigation, a series of foam samples prepared from formulations having various isocyanate–hydroxyl ratios and added amounts of water were analyzed for gas composition. This was to determine the direct effects of water and NCO/OH ratio on the over-all *k* factor. These results are shown in Table 9. The data have been represented to show that the dependence of the *k* value of CCl_3F/CO_2 ratio on water concentration is greater than on the isocyanate–hydroxyl ratio. This was the expected result. It can also be seen that the *k* value is linearly related to the CCl_3F/CO_2 ratio for any given density material.

We have studied many different urethane systems and found about the same type relationships to hold. We feel that by this simple method one can easily monitor the reproducibility of a foam system, and we can check for excessive water that may be getting into the raw materials. This method offers a convenient tool to study the effects of foam reaction parameters, such as nucleation, temperature of foam components, and blowing agents in general.

The next phase of our work was to attempt to utilize the cellular gas composition to calculate a *k*-factor value. We felt that the understanding

TABLE 8
Variation of CCl_3F/CO_2 Ratio across a Foam Bun

Peak Ratio		
Bottom	Middle	Top
13.3	6.0	7.5
9.1	10.2	5.5
9.2	7.1	7.8
9.3	9.0	7.2
11.3	5.7	—
—	8.4	—
—	6.7	—
Av. 10.2	8.5	7.0

TABLE 9
Variation in Foam Properties and Cellular Gas Composition with Changes in Formulation Parameters

	Ratio NCO/OH			
Water, %	1.05	1.20	1.35	
0.0	12.0	11.6	9.4	Ratio CCl_3F/CO_2
	0.122	0.124	0.123	*k* Value
	1.72	1.86	1.99	Density
0.5	5.8	5.0	5.2	Ratio CCl_3F/CO_2
	0.121	0.131	0.127	*k* Value
	1.53	1.58	1.78	Density
1.0	4.2	3.6	3.8	Ratio CCl_3F/CO_2
	0.126	0.134	0.140	*k* Value
	1.43	1.50	1.66	Density
2.0	2.6	2.4	2.2	Ratio CCl_3F/CO_2
	0.140	0.139	0.141	*k* Value
	1.27	1.34	1.49	Density

of thermoconductivity would be greatly enhanced by this type of determination. If we could separate the contributions to the *k* factor, we would determine not only the *k*-factor value quickly, but could relate reaction conditions and foam properties to the *k* factor more readily. One added advantage is that we could obtain *k* factors on odd-shaped pieces of foam such as pipe insulation.

Skochdopole and Patten[3,4] and McIntire and Kennedy[9] have discussed the relationships between foam properties and the modes of heat transfer and have been able to separate approximately the component parts of the total thermal conductivity of a material into specific heat contributions due to the solid, the gas, and the radiation and convection effects. The expression for this relationship is

$$k = k' \text{ solid} + k' \text{ gas} + k' \text{ radiation} + k' \text{ convection},$$

where *k*, the over-all thermal conductivity of the material, is equal to the thermal conductivity contribution arising from heat conduction through the solid, the contribution from conduction through the gas, and the contribution from radiation and convection effects in the gas. Generally, for urethane foams of about 2 lb density, $k'r$ is regarded to be about 0.03 *k*-value units. As the density increases, this value would decrease due to increased material that would absorb, reflect, or scatter heat. However, radiation effects would be expected to become more significant as the cell size increased. This is primarily due to the decrease in the number of cells and walls to effect scattering, absorption, or reflection.

It has been pointed out and experimentally established by Skochdopole[3] that $k'c$ is of negligible value at cell sizes less than about 4 to 6 mm. Most urethane foams possess cell diameters of less than 4 mm so that it is not necessary to consider this contribution for the purpose of this work. In our foams, the cell diameters are about 0.5 mm. The value of $k's$ for a foam of approximate 2 lb/ft^3 density has been reported to be about 0.04 k-value units.

Since we were attempting to relate the thermal conductivity of the gas as determined by our method and the value of $k's$, $k'c$, and $k'g$ to the over-all k-factor value in much the same way as Skochdopole had in his study, it became necessary for us to determine the $k's$ for our urethane systems.

The determination of thermal conductivity of the solid polymer was made by determining the thermal conductivity of a ½ in. × 6 in. × 6 in. slab of the solid urethane by the modified guarded hot-plate method. The slab of product was prepared in an aluminum mold fabricated for this purpose and involved the reaction of the same essential components of a foam formulation but without trichlorofluoromethane and catalyst. By taking into account density and the relative amount of solid in a 2 lb/ft^3 foam, the value of $k's$ was determined to be 0.03 k-factor units. Therefore, for any given system where $k's$ is known, $k'g$ can be determined and a k factor calculated. We followed this approach and ran several comparative studies to relate the calculated k factor with the actual k factor obtained from the modified guarded hot-plate method.

Calculations of k factor from the determined $k's$ and density of the prepared plate of solid urethane and from the determined $k'g$ were made using the following equation which we developed:

$$k = k_s \left(\frac{D'_f + 0.0716 - d_g}{d_s - d_g} \right) + k_g \left[\frac{d_s - (D'_f + 0.0716)}{d_s - d_g} \right] + C,$$

where

k = k factor,
k_s = contribution due to conduction in the solid,
D'_f = apparent density of the foam,
d_g = true density of the gas,
d_s = density of the solid determined experimentally,
k_g = contribution due to conduction in the gas,
0.0716 = constant for buoyancy convection,
$C = k'_r + k'_c$.

Table 10 shows the k values obtained from our experimental procedure and those obtained with the modified guarded hot-plate method. The

TABLE 10

Thermoconductivity Factors Calculated from Cellular Constants[a] and Found by the Guarded Hot-Plate Method

Sample No.	$k_{(\text{calculated})} - C$	$k_{(\text{found})}$	Δ or C
1	0.1111	0.125	0.0139
2	0.1070	0.130	0.0230
3	0.1063	0.126	0.0197
4	0.1048	0.128	0.0232
5	0.1056	0.126	0.0204
6	0.1069	0.127	0.0201

[a] The density, D_f, of all foams was 2.0716, except for No. 4, which was 1.7716 pcf; d_s (density of matrix) = 76.41 pcf; k_s = 0.924 (determined by guarded hot plate).

data are represented in terms of k value minus C (the contributions due to $k'c$ and $k'r$) in order to show the magnitude of C. The values of C appear to be consistent with the reported value of 0.03 given by Skochdopole. These data were obtained on urethane foams that had small uniform cell structure. Data similar to those shown in Table 10 were obtained on foams having coarse irregular cell structure to determine if the value of C would reflect this change. The k values obtained were not in close agreement with actual k values. The difference in the two k values becomes more significant as the cells become more distorted. It seems apparent from the data that the contributions to thermal conductivity of a urethane foam as originally prepared by McIntire and Kennedy[1] are fairly well represented.

CONCLUSION

We have developed a method for the determination of cellular gas composition in rigid urethane foams. The method may be adapted easily for use with any expanded plastic having closed cells. The cellular gas composition was shown to vary throughout the matrix of the urethane sample, this variance being consistent with the change in k value. The analytical method was shown to be useful in the study of the reaction parameters of urethane foams. In addition, the calculation of k values from the cellular gas composition was demonstrated. Our technique is most applicable to cases where the contributions of cell structure to thermal conductivity can be estimated. It is of interest to point out that the apparatus developed for this method has many practical uses—as an analytical gas sampler or it could be utilized with other analytical instruments, such as the mass spectrometer and the infrared spectrophotometer.

ACKNOWLEDGMENT

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REFERENCES

1. L. R. LaBras, "Recent Developments in Rigid Urethane Foams," paper presented at 16th Annual Technical Conference of SPE, Chicago, Ill., Jan. 1960.
2. R. H. Harding and B. F. James, *Modern Plastics, 39,* 133 (1962).
3. R. E. Skochdopole, *Chem. Eng. Progr., 57,* 55 (1961).
4. G. A. Patten and R. E. Skochdopole, *Modern Plastics, 39,* 149 (1962).
5. K. C. Lyon, V. H. Garrett, D. R. Black, P. H. Applewhite, and L. A. Goldblatt, *Ind. Eng. Chem., 4* (3), 189 (1965).
6. D. J. Doherty, R. Hurd, and G. R. Lester, *Chem. Ind.,* 1340 (1962).
7. A. E. Williams, I.C.I. Dyestuffs Division, private communication.
8. A. W. Bauer, E. I. du Pont de Nemours and Company, private communication (April 1965).
9. O. R. McIntire and R. N. Kennedy, *Chem. Eng. Progr., 44* (9), 727 (1948).

Thermal Degradation and Flammability of Urethane Foams

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INTRODUCTION

The flammability of urethane systems is of broad interest, with practical aspects including intumescent coatings, ablative materials, flexible foams, and especially rigid foams. Numerous papers have appeared giving specific formulations for flame-resistant systems.[1-7] The thermal decomposition of the polymers, which is an integral part of combustion, has also been studied for several model polyurethanes. This aspect of the subject was reviewed in 1959[8] and in 1962.[9]

More recent publications on polyurethanes are reviewed later in this survey. An excellent review of the thermal decomposition of polymers other than urethanes is the book by Madorsky.[10] Certain phases of combustion chemistry have been presented by Dickert and Toone,[11] and an over-all survey has been made by Saunders and Backus.[12]

These results in the polyurethane field may be combined with combustion studies in other polymer systems to present an integrated view of decomposition and combustion of broad usefulness. This paper attempts to do that, with particular emphasis on rigid foams.

GENERAL THEORIES RELATING TO COMBUSTION

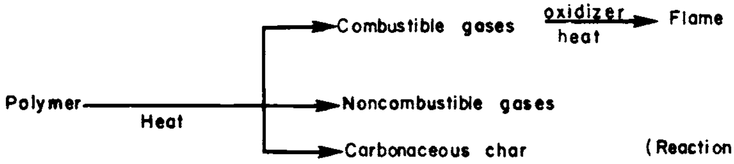
Some of the most extensive research on the flammability of polymers has been conducted in the textile field (see especially reference 13), on cellulosics,[14] especially related to wood, and on intumescent coatings for wood.[15]

A closely related area of interest, ablation, has also received extensive attention in recent years.[16,17]

A simple generalized scheme which is in agreement with all of these areas of study has been summarized by Buck[13] as follows.

In the combustion of any polymer, decomposition first occurs as a result of heat supplied from some source. At the same time, any combustible gases from this decomposition are heated to their ignition temperatures and if an adequate oxidizing agent is present, these gases then ignite. The burning provides additional heat to propagate further decomposition and ignition. The simple requirements for a flame then are heat, a material that will provide combustible gases, and an oxidizing agent.

In addition to combustible gases (hydrocarbons, alcohols, aldehydes, hydrogen, and organic acids, for example) from polymer decomposition, one also usually obtains some noncombustible gases, such as water and carbon dioxide, and a carbonaceous char. The entire process may be summarized by the simple scheme shown in Reaction 1. The combustible gases are obviously the most undesirable products and must be reduced to a minimum if flame is to be controlled to a satisfactory level.



(Reaction I)

The noncombustible gases are not directly harmful, but may cause difficulty by rupturing the polymer mass, exposing new surfaces to destructive temperatures. The char is useful as a relatively stable insulating layer which protects the lower layers of polymer and other substrates from the heat of combustion. The char may glow slowly under certain conditions, but the rates of heat generation and of flame spread from such a glow are very low.

The ablation of polymers is very similar to their combustion except that the oxidizer is essentially absent. Similar decompositions occur and any char may serve to insulate the substrate from high temperatures, as during the re-entry of missiles into the atmosphere. Evaporation of decomposition products helps to keep the temperature of the substrate at a safe level.

In the burning of a polymer, several features of the process are important. A sudden flash of flame along the surface may be disastrous to personnel. This surface flash may occur when the surface is finely divided, a plentiful supply of oxygen is available, and the polymer readily decomposes to give a high yield of easily combustible gases. This situation existed with some early varieties of unprotected acoustic tile and also exists with some unprotected foam types.

The continued burning of the major body of the sample generates destructive quantities of heat and poisonous combustion products—"smoke." When little is left but the carbonaceous char, this char may glow for a long time as carbon is slowly volatilized and burned.

The quantity of heat generated from the burning of a particular polymer is important with regard to the rate of spread of the fire and to the destruction of other materials of construction such as metals.

A detailed analysis of the combustion behavior of any specific system is exceedingly complex in detail and has thus far been beyond complete experimental characterization. In spite of this, the process can be understood in a general way if the above simplified approach is used.

In agreement with this general theory, approaches toward reducing the flammability of a polymer system fall into several general categories:

1. Dilution with materials that will not burn at normal combustion temperatures (2000–3500°F), such as inorganic materials. These may be particularly effective if they can form a protective nonburning layer on the surface of the remaining polymer.
2. Addition of products that will decompose to noncombustible gases when heated. These gases may provide a protective blanket, excluding oxygen, or may dilute the mixture of combustible gases and air below the critical limits for combustion. Ammonium carbonate would be an example of such an additive.
3. The addition of materials that will reduce the formation of combustible gases and/or increase the char formation. These additives are usually catalytic or inhibitory in nature. For example, a bromine-containing flame retardant may serve as a retarder or inhibitor for free-radical chain reactions involved in the polymer decomposition, which produce low-molecular-weight combustible gases. Phosphorus-containing additives and others that may serve as Lewis acids may catalyze carbon formation by a carbonium ion mechanism. Although these various additives may not be catalytic under normal use conditions, during the combustion process they may be converted to active states. Thus the phosphorus-containing material may be converted to a condensed phosphoric acid of known catalytic activity. Halogen compounds may give hydrogen halides or free halogen atoms, known retarders for many free-radical reactions. The role of other effective additives may be interpreted similarly.
4. The design of the total system to provide a significant endotherm on decomposition, as by dehydration of an inorganic hydrate that is a filler in the system. The endothermic reaction cools the system, thus retarding further decomposition. This effect may be achieved with the use of suitable fillers and also with polymer design.
5. The polymer itself may be designed to favor the formation of char and noncombustible gases and give a small volume of combustible gases,

preferably with the absorption of considerable energy required for the decomposition. A low heat of combustion is also highly desirable. Urethanes in particular lend themselves to this approach, and this aspect of the total picture is the subject of this presentation.

The results of any of these approaches to improving flammability are complicated and confused by the nature of the test methods used. In some of the simpler tests, melting and flowing of the polymer away from the flame result in a "self-extinguishing" rating. Such tests have only limited practical significance since in an actual fire the melt cannot usually flow away from the flame. In other tests, the retention of a high melt viscosity during decomposition is desirable so that a dense strong char forms and insulates the materials below. A further complication is the effect of the physical state of the material. The more finely divided the solid phase, the more readily it will burn (e.g., low-density foam normally burns much more readily than high-density foam). In addition, flaws in a foam, such as striations and fissures, may alter the burn-through time considerably in tests utilizing a high-velocity flame such as a blow torch.

For good commercial success of intumescent coatings and foams the objective must be systems whose actual performance in a burning building will be satisfactory, regardless of variations in temperature from about 2000 to 3500°F, of air currents, of the surface exposed, and of minor imperfections in the application of the polymer system. One report of the performance of rigid urethane foam during a fire on a ship indicates that this is today an achievable goal.[18] Further improvements may be expected.

In this paper, recent data related to polyurethane decomposition and combustion are surveyed and interpreted based on these general theories concerning flammability. In much of this research the analytical tools of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been used. These provide an excellent insight into the reactions that are taking place as a sample is heated at a standard rate, by showing any heat absorbed or liberated by the sample due to a phase change or to a chemical change (DTA), and by showing the rate and extent of weight loss (TGA). In some cases, studies have been made in vacuum, an inert atmosphere such as helium or nitrogen, or in air. Those in air may be the most reliable as far as correlation with combustion conditions is concerned. The time intervals of these tests are usually of the order of 0.5 hr to several hours, thus they are realistic in terms of exposure to extreme heat.

In the research on urethane foams and intermediates for foams, many intermediates were used with good results. Because of the obvious importance of added antioxidants and other trace components, it was considered necessary to identify each polymeric intermediate used in specific experiments. No indication of preference is intended.

THE THERMAL DECOMPOSITION OF POLYURETHANES

Since the key to flammability behavior is the thermal decomposition of the polymer, attention may now be turned to the behavior of polyurethanes in this respect. The reactions of each of the typical components of the polyurethanes will be considered first, followed by some recent studies of rigid foams as complete systems.

Reactions Associated With Urethane Groups

The stability of urethanes varies greatly, depending on the structure of the urethane. Urethanes from tertiary alcohols may decompose readily at temperatures as low as 50°C, whereas urethanes from many primary and secondary alcohols may undergo changes only slowly at 150–200°C. The environment, i.e., presence of other reactants and catalysts, also greatly influences the stability of the urethanes.

Studies of the thermal decomposition of substituted urethanes have shown that three general types of reactions may take place.[19-23]

1. Dissociation to isocyanate and alcohol

$$\mathrm{RNHCOOR'} \rightleftharpoons \mathrm{RNCO} + \mathrm{R'OH}$$

2. Formation of primary amine and olefin

$$\mathrm{RNHCOOCH_2CHR'} \rightarrow \mathrm{RNH_2} + \mathrm{CO_2} + \mathrm{R'CH{=}CH_2}$$

3. Formation of secondary amine

$$\mathrm{RNHCOOR'} \rightarrow \mathrm{R}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{R'} + \mathrm{CO_2}$$

Under the proper conditions, the dissociation of a urethane has been used to prepare isocyanates in good yield. In the special case where the urethane of a phenol is used, the dissociation may occur at temperatures as low as 150°C. Reaction 2 illustrates a typical dissociation.[20] This type dissociation will be expected to regenerate the starting materials, provide volatile gases if any of the starting materials are volatile, and cause a loss in melt viscosity.

$$\mathrm{C_6H_5NHCOOC_2H_5} \xrightarrow[2\ \mathrm{hr}]{200°\mathrm{C}} \underset{71\text{–}74\%}{\mathrm{C_6H_5NCO}} + \underset{90\text{–}92\%}{\mathrm{C_2H_5OH}} \qquad \text{(Reaction 2)}$$

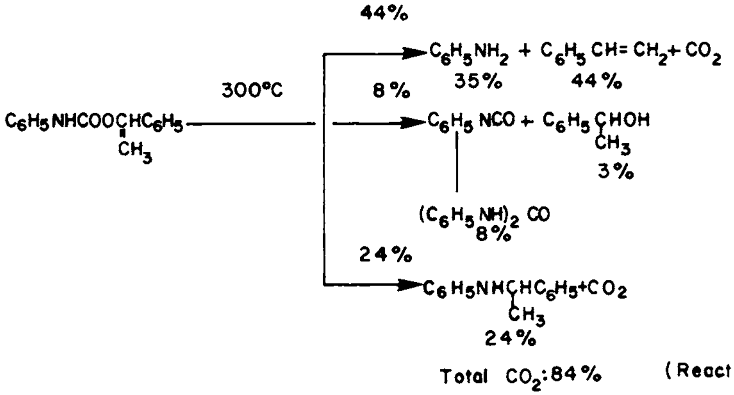
Ingham and Rapp have presented evidence that polyether glycol–TDI (tolylene diisocyanate) polymers decompose at about 200°C in a vacuum or in helium, primarily by dissociation of the urethane groups.[24] At 250–320°C, however, decomposition became more random, with typical decomposition of the polyether segment apparent. Treatment of poly(oxypropylene) glycol with ethylene oxide and subsequent reaction with TDI gave a more stable polymer than that from the original poly(oxypropylene) glycol. Degradation under these conditions (200°) gave TDI, which was volatilized from the hot zone, and no evidence of carbodiimide. This mode of degradation may have been influenced by the ferric catalyst used in preparing the polyurethane. Further studies of the same system are under way, using ^{14}C-labeled urethane groups.[25]

Engel and co-workers[26] studied the thermal decomposition of a variety of crosslinked polyurethanes prepared from polyesters and MDI (4,4′-diphenylmethane diisocyanate). They found that decompositions in air and in an inert medium were essentially the same, indicating that oxidation did not play a role in the initial decomposition. In addition, changes in crosslinking had no effect on the rate as long as the ester–urethane group ratio remained constant; otherwise, increases in crosslinking improved the thermal stability. An increase in the ester–urethane ratio also increased the stability. These results all support the belief that urethane dissociation is the primary reaction involved in initial decomposition of such polymers.

Since urethanes containing no hydrogen on the nitrogen cannot dissociate to the isocyanate and hydroxyl precursors, removal of this hydrogen should improve the thermal stability of the polymer. Dyer and Hammond have found this to be true.[27] Studies in the range of 230–285°C showed that polymers from aliphatic di-secondary amines and aliphatic bis-chloroformates were more stable than those from 4,4′-diaminodiphenylmethane derivatives. Beachell and Ngoc Son also found greatly improved color stability at 150°C when the urethane nitrogen atoms in a polyurethane were fully alkylated.[28]

The decomposition of a urethane to the primary amine and olefin is favored in cases where the corresponding alcohol is readily dehydrated. Urethane formation and subsequent decomposition have been used to dehydrate certain alcohols, e.g., tertiary alcohols in good yields. This type of reaction may also cocur to some extent with urethanes of primary and secondary alcohols at 200–250°C. In polyurethane decompositions this reaction would cause rupture of the polymer chains and provide a mixture of combustible and noncombustible gases.

An example of urethane decomposition with olefin and secondary amine formation (Reaction 3) was reported by Dyer *et al.*[20] Ester interchange reactions between urethanes and hydroxyl or amino end groups are also possible, but they seem relatively unlikely under conditions associated with combustion.



(Reaction 3)

Reactions Associated With Urea Groups

Substituted ureas are known to dissociate to the corresponding isocyanate and amine at elevated temperatures:

$$RNHCONHR' \rightleftharpoons RNCO + R'NH_2$$

Vapor density measurements have shown diphenylurea to be 99 percent dissociated at 370°C. Also when HCl was added to prevent recombination of the isocyanate and amine, yields of isocyanate up to 71 percent have been obtained, with nearly quantitative recovery of the amine salt.[29] Less extensive dissociation may be expected at lower temperatures.

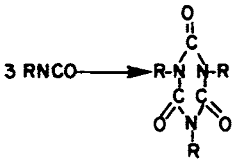
Thus urea structures in amine- and water-cured polyurea–urethanes may be weak links at high temperatures. This dissociation would break polymer chains, favoring regeneration of some starting materials, volatilization of combustible gas and loss of melt viscosity.

Reactions of the Isocyanate Component

It has been seen that dissociation of urethane and urea groups may liberate the isocyanate, either as an end group on a broken chain, or in the extreme case, as free monomeric isocyanate. Ingham and Rapp,[24] for example, apparently obtained free TDI from pyrolysis of a TDI–polyether polymer. The reactions to be expected from the monomeric isocyanate are then of importance.

The two reactions most likely to occur with isocyanates at high temperatures are carbodiimide formation and trimerization (isocyanurate formation). The resulting structures are relatively stable derivatives of isocyanates and at 200–350°C may be formed from the isocyanates obtained by dissociation of urethanes and ureas. In addition, it is possible that these products may be formed without requiring initial dissociation to isocyanates. The formation of both of these derivatives will act to preserve a polymeric state, thus favoring high melt viscosity, and will not provide combustible gases (see Reactions 4 and 5). Carbodiimide formation normally requires a high temperature, usually about 180–300°C in the absence of catalysts. Polymeric carbodiimides have been obtained by heating the bis-neopentyl urethane of diphenylmethane diisocyanate[20] (see Reaction 6).

$$2\ RNCO \longrightarrow \underset{\text{(carbodiimide)}}{RN{=}C{-}NR} + CO_2 \qquad \text{(Reaction 4)}$$

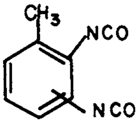


(isocyanurate) (Reaction 5)

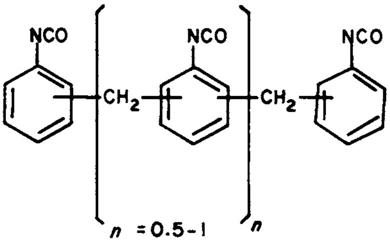
$$CH_2\left[C_6H_4NHCOOCH_2C(CH_3)_3\right]_2 \xrightarrow{300°C} \begin{array}{ll} CO_2 & 45\% \\ ROH & 91\% \\ \text{polymer} & 98\% \end{array} \qquad \text{(Reaction 6)}$$

The polymer thus obtained showed an infrared absorption at 4.7–4.8 μ, indicating the carbodiimide structure, $—N{=}C{=}N—$. Similarly, heating the isocyanate itself at 300°C gave a polymeric carbodiimide[20] (see Reaction 7). Under many conditions the isocyanate may not have an opportunity to react in the melt, but may be volatilized. This will be especially true of TDI, compared with the polymeric polyaryl isocyanates. A comparison of their structures readily explains the much higher boiling points of the polymeric types I and II. Further, Backus and co-workers[30] found this

$$CH_2(C_6H_4NCO)_2 \xrightarrow[45\ \text{min}]{300°C} \underset{92\%}{\left[N{=}C{=}N{-}C_6H_4CH_2C_6H_4\right]_n} + CO_2 \qquad \text{(Reaction 7)}$$



TDI
I



Polymeric Isocyanate
II

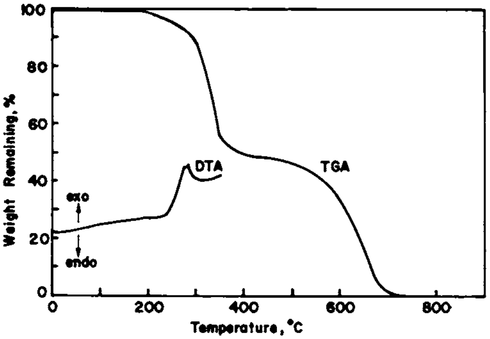


FIGURE 1
TGA and DTA curves of a polymeric isocyanate (Mondur MR). Heating rate: 10°C/min. Air flow: TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

polymeric isocyanate to be an excellent char former, undergoing some decomposition beginning at about 200°C, but retaining over 40 percent of its original weight at 550°C. The TGA and DTA curves for this product are shown in Figure 1.

The favorable decomposition behavior of this type of polyisocyanate is similar to the excellent behavior of phenol–formaldehyde polymers and poly(benzyls), as summarized by Madorsky.[10] The structural similarity between these types is quite marked.

DECOMPOSITION OF THE POLYETHER SEGMENT

Polyethers used as intermediates for urethane polymers have usually been poly(oxyethylene) polyols, poly(oxypropylene) polyols, or less frequently, poly(1,4-oxybutylene) glycols. The thermal decomposition of high-molecular-weight polymers of each type has been studied in some detail and should be an excellent guide to the decomposition of the polyether segments in polyurethanes.

Madorsky and Straus[31] pyrolysed poly(ethylene oxide) (mole weight 9,000–10,000), atactic poly(propylene oxide) (mole weight 16,000) and isotactic poly(propylene oxide) (mole weight 215,000). Samples were heated under vacuum for 30 min at the indicated temperatures. Volatile products were analyzed by a mass spectrograph. The percent volatilization versus temperature for each is shown in Figure 2.

Analyses of the fractions volatile at −80° (V_{-80}) and at 25° (V_{25}) from the poly(oxypropylene) glycol runs are shown in Table 1.

Davis and Golden studied the decomposition of poly(1,4-oxybutylene) glycol.[32] They polymerized tetrahydrofuran with PF_5 in air and under vacuum, obtaining products of molecular weight (light scattering) about 570,000. Without antioxidant the molecular weight fell considerably on storage at 111°C, presumably due to weak peroxide links in the polymer

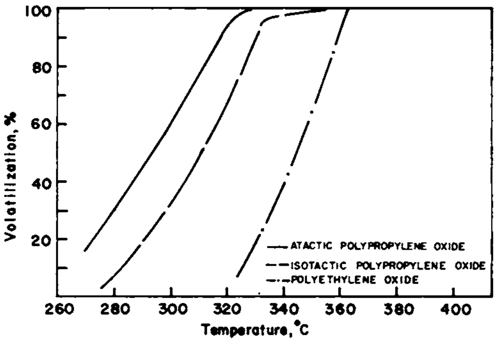


FIGURE 2

Relative stability of poly(alkylene oxides).

chain. Pyrolysis in a vacuum gave more than twenty volatile products, with no one dominating, and no monomer. The dry volatiles gave weak infrared absorption characteristic of hydroxyl groups and strong aldehyde absorption.

For comparison with the results of Madorsky and Straus on high-molecular-weight polyethers, the TGA and DTA curves (in air) for a polyoxypropylene adduct of sucrose are shown in Figure 3.[30] The exotherm

TABLE 1

Mass-Spectrometer Analysis of Combined Fraction $V_{25} + V_{-80}$ from Pyrolysis of Poly(propylene oxides)

	Isotactic[a]		Atactic[a]	
Component	Mole % of Fraction	Wt % of Total Volatiles	Mole % of Fraction	Wt % of Total Volatiles
Ethylene, C_2H_4	3.0	0.31	0.4	0.03
Ethane, C_2H_6	0.9	0.09	1.4	0.09
Acetaldehyde, C_2H_4O	39.6	6.34	40.3	4.00
Propene, C_3H_6	14.5	2.22	8.0	0.75
Propylene oxide, C_3H_6O	5.2	1.16	4.7	0.61
Acetone, C_3H_6O	11.3	2.39	17.0	2.22
1-Hydroxypropylene oxide-1,2, $C_3H_6O_2$	1.3	0.35	0	0
Isopropanol, C_4H_8O	2.4	0.53	4.4	0.65
Methyl ethyl ketone, C_4H_8O	2.1	0.55	3.1	0.50
Methyl isopropyl ether, $C_4H_{10}O$	1.3	0.35	2.1	0.35
Ethyl isopropyl ether, $C_5H_{12}O$	2.5	0.80	2.4	0.47
Dipropyl ether, $C_6H_{14}O$	5.9	2.19	6.2	1.43
Unidentified compounds with mass peaks up to 101	10.0	2.72	10.0	1.70
TOTAL	100.0	20.00	100.0	12.80

[a] Average of experiments at 275–335°C.

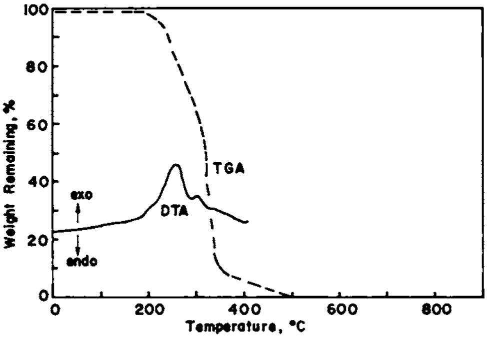


FIGURE 3
TGA and DTA curves of a polyoxypropylene adduct of sucrose (Dow Chemical Company's Voranol RS-410). Heating rate: 10°C/min. Air flow; TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

at about 200°C may be due to oxidation. Volatilization was essentially complete at 350°C, similar to the results with the simple linear oxypropylene polymer. Ingham and Rapp[24] also found that a poly(oxypropylene) glycol–TDI polymer gave degradation at 250°C and above, similar to that expected of the polyether alone.

DECOMPOSITION OF A POLYESTER SEGMENT

While detailed pyrolysis studies of the polyesters used in polyurethanes apparently are not yet available, poly(ethylene terephthalate) has been studied extensively. Results with this polymer may be a preliminary guide, at least for phthalic types of polyesters. Pyrolysis at 288°C, in nitrogen, gave acetaldehyde as the major gaseous product, along with significant amounts of CO and CO_2. Only traces of other gases were found. Nonvolatile products included low-molecular-weight esters of various types.[33]

The DTA and TGA curves of a chlorine-containing polyester (Hooker Chemical Company's Hetrofoam 250), useful in rigid foam systems are shown in Figure 4.[30] These show a weight-loss behavior similar to that of the sucrose-based polyether described previously, though with somewhat greater stability.

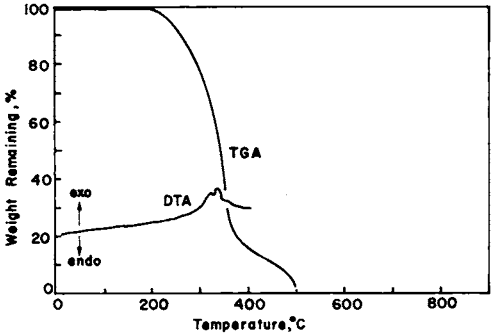


FIGURE 4
TGA and DTA curves of a chlorinate polyester (Hooker Chemical Company's Hetrofoam 250). Heating rate: 10°C/min. Air flow: TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

GENERAL CONSIDERATIONS OF POLYURETHANE COMPONENT BEHAVIOR

The polyurethanes, being very versatile in the structures that can be synthesized, are ideally suited to the design of flame-resistant systems. Since dissociation of the urethane group is one of the first reactions to be expected above 200°C, the components used initially in the preparation of the polymer may be regenerated, with decomposition and combustion approximately characteristic of the individual components.

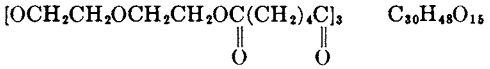
Selection of components may be made to favor a minimum of combustible gases and a low heat of combustion, for example. In general, a low heat of combustion is favored by a low hydrogen-to-carbon ratio, and by a low ratio of (carbon plus hydrogen)-to-oxygen. This may be illustrated by the following heats of combustion of simple compounds,[34] as shown in Table 2.

TABLE 2
Heat of Combustion of Model Compounds

Compound	Formula	ΔH Combustion kcal/mole at 18°C
Ethane[a]	C_2H_6	−372.87
Acetylene[a]	C_2H_2	−310.5
Ethyl alcohol[b]	C_2H_6O	−326.66
Acetic acid[b]	$C_2H_4O_2$	−206.7

[a] Gas.
[b] Liquid.

It is generally recognized that conventional polyester–urethane foams are more readily made self-extinguishing than are the conventional polyether–urethane foams. A comparison of a diethylene glycol–adipic acid with a poly(oxypropylene) segment of the same number of carbon atoms may explain this relation in terms of the C:H:O ratios:



$$[OCH_2CH_2OCH_2CH_2O\underset{\displaystyle O}{\underset{\|}{C}}(CH_2)_4\underset{\displaystyle O}{\underset{\|}{C}}]_3 \qquad C_{30}H_{48}O_{15}$$

polyester segment

$$[OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}]_{10} \qquad C_{30}H_{60}O_{10}$$

polyether segment

The lower hydrogen and higher oxygen contents of this ester segment, typical of polyesters used in flexible foams, should mean that this segment has a lower heat of combustion than the polyether segment. Related to this, the decomposition of the ester segment will give some noncombustible gas (CO_2), whereas none is to be expected from the polyether segment. Those polyesters derived from phthalic anhydride, sometimes used in rigid foams, should be even more favorable in this respect.

Foams prepared with a high content of aromatic isocyanate, as required by a resin with a high hydroxyl number, will have a favorable structure due to the excellent C:H:O proportion of the aromatic isocyanate. Data which are in agreement with this conclusion were presented by Dickert and Toone.[11]

For practical control of polymer behavior in or near a flame, a high melt viscosity is usually if not always desired. As was noted by Dickert and Toone,[11] increases in crosslink density, at least in a narrow family of polymers, favor flame resistance. This control of crosslinking is readily achieved in polyurethanes, where the degree of branching of both isocyanate and resin may be controlled.

The importance of trace quantities of a catalyst in the polymer should not be neglected. Traces of metals, acids, and bases are all known to be important catalysts for isocyanate reactions, and must be assumed to be potentially important for dissociation of urethanes and other reactions occurring during decomposition.

POLYURETHANE DECOMPOSITION RELATED TO ITS COMPONENT STRUCTURE

If the polyurethanes behave in thermal decomposition in direct relation to their component structure, the foregoing discussions should provide reliable guides to polymer behavior. That this relation does obtain to a large extent will be seen from the following data.

A series of solid polyurethanes was prepared in our laboratory using each of several isocyanates and one polyether, the propylene oxide adduct of trimethylolpropane, TP440 (Wyandotte Chemicals Corporation), prepared at 1.05 NCO/OH ratio, without catalyst. A comparison of the TGA curves of these materials is shown in Figure 5.[12]

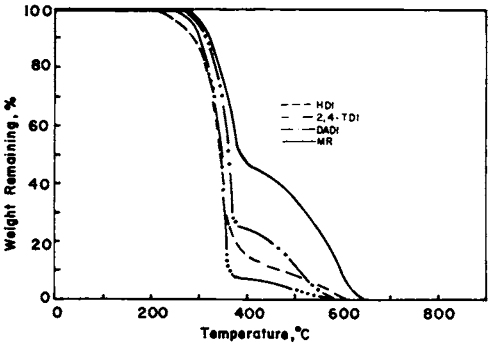


FIGURE 5

TGA curves for polymers from a polyoxypropylene triol, TP440, and four different isocyanates. Heating rate: 10°C/min. Air flow: 0.35 standard cu ft/hr.

While all the polymers showed an initial weight loss beginning at about the same temperature, the polymer from MR, a polymeric isocyanate, was distinctly better on retention of weight above about 400°C. It is interesting that the aliphatic diisocyanate gave essentially the same rate and degree of weight loss as did TDI. The use of dianisidine diisocyanate, containing two benzene rings, was only slightly more favorable than was TDI.

The thermal decomposition of three typical rigid urethane foams was studied in some detail by Backus and co-workers.[30] All were based on the polymeric isocyanate, using as resins a polyoxypropylene adduct of sucrose, the same with *O*,*O*-diethyl-*N*,*N*-bis(2-hydroxyethyl)aminomethyl phosphonate (Stauffer Chemical Company's Fyrol 6) as added flame retardant, and a chlorinated polyester (Hetrofoam 250). The TGA and DTA curves (in air) of the polyether foam are shown in Figure 6, and of the chlorinated polyester foam in Figure 7. The flame-retarded polyether foam was analyzed in air (Figure 8), and, for comparison, in helium (Figure 9).

In each case char formation in air is readily apparent, with considerable weight remaining at 300–400°C or 450°C. In helium, little char was formed and the weight loss was nearly complete at 400°C. It is noteworthy that a conventional flame retardant was not necessary for char formation when the polymeric isocyanate was used. It is also significant that the foam

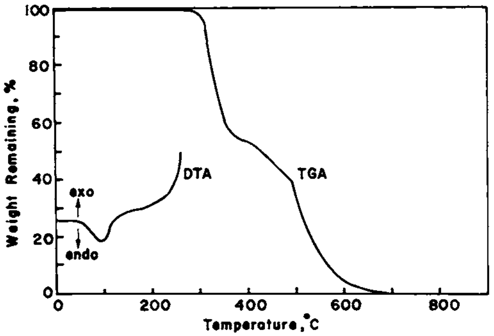


FIGURE 6

TGA and DTA curves for rigid foam from polymeric isocyanate (Mondur MR) and adduct of sucrose (RS-410). Heating rate: 10°C/min. Air flow: TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

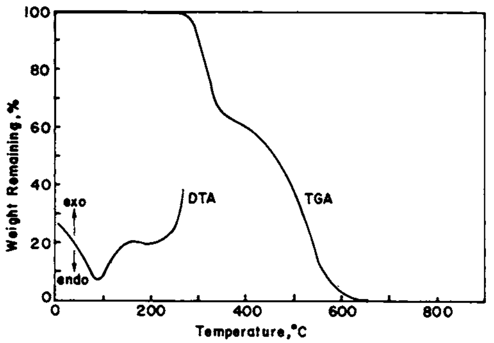


FIGURE 7

TGA and DTA curves for rigid foam from polymeric isocyanate (Mondur MR) and chlorinated polyester (Hetrofoam 250). Heating rate: 10°C/min. Air flow: TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

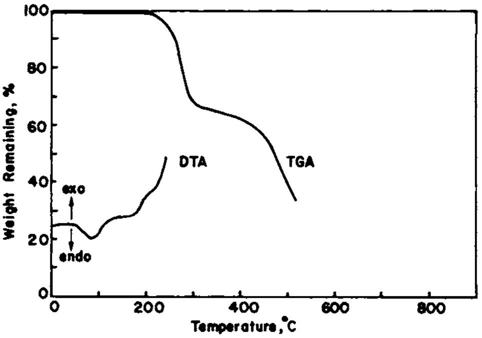


FIGURE 8
TGA and DTA curves for flame-retarded polyether rigid foam in air. Heating rate: 10°C/min. Air flow: TGA, 0.35 standard cu ft/hr; DTA, 10 ml/min.

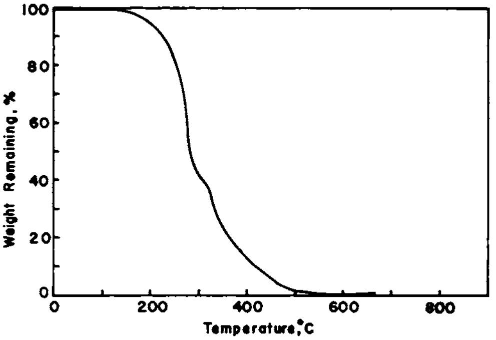


FIGURE 9
TGA curve for flame-retarded polyether foam in helium. Heating rate: 2.9°C/min. Helium flow: 0.20 cc/min.

containing the phosphorus-type flame retarder began to lose weight at a temperature nearly 100°C lower than the corresponding foam without this flame retarder. Endotherms at about 50–80°C in the DTA curves are believed to represent volatilization of the fluorocarbon blowing agent.

These foams were also decomposed in larger quantities, heating at a rate of 100°C/hr temperature increase, in a current of air. Volatile products were collected and analyzed as shown in Table 3.

The formation of volatile decomposition products similar to those expected from polyethers and polyesters is readily apparent. Both combustible and noncombustible types were present.

It is especially noteworthy that the loss of weight of these foams in the TGA experiments was nearly the same as the arithmetic sums of the TGA losses of the individual components,[30] as would be expected if dissociation of the polymer were the controlling decomposition reaction. The foams were slightly less stable than predicted from the weight losses of the individual components, perhaps due to interreactions of decomposition products.

Char residues were obtained by heating the flame retarded polyether foam for 30–120 min in air at temperatures of 200, 300, 400, 500, and 600°C. The weight losses correlated well with the TGA curves previously

TABLE 3

Volatile Degradation Products of Rigid Urethane Foam

	Products Detected		
Temperature	Polyether Foam	Flame-Retarded Polyether Foam	Chlorinated Polyester Foam
80–100°C		CO_2 Unsaturated gas (small amount)	
150–180°C		$CFCl_3$ CO_2	
Below 200°C	CO_2 $CFCl_3$ Volatile alkene		
Below 240°C		$CFCl_3$ CO_2 CO (small amount) Mixture characterized by —NH, —CH, COH, COC, and H_2O IR bands	
Below 300°C	H_2O CO_2 CO Alkene Mixture characterized by —NH, OH, COC, monosubstituted phenyl IR bands; ester, aldehyde and/or COOH carbonyl IR bands	CO_2 CO (small amount) Alkene H_2O Mixture characterized by —NH, OH, COC, and monosubstituted phenyl IR bands. Possible phosphorus-containing product; tar characterized by urethane structure in addition to above	H_2O CO_2 CO Alkene Product containing C—Cl bonds

obtained. Infrared analysis of the chars showed relatively little change due to heating at 200°C, but as the charring temperature was increased, the products gave spectra characteristic of increased degradation. The spectra of the chars obtained at 500°C and above were largely "washed out," showing only absorption due to aromatic unsaturation, P=O and P—O—P bonds.[30]

These degradation results compare with flammability behavior,[12] as shown in Table 4.

TABLE 4
Flammability of Rigid Urethane Foams Prepared from Polymeric Diphenyl Methane Type Polyisocyanate

		Flammability	
Polyol	ASTM D 1692	U.S. Bureau of Mines Torch Test, Horizontal Sample (min)	Initial Surface Flash
RS-410	Burns 8–10 in./min	<1	Rapid, flame continues
50/50 RS-410/Fyrol 6	Nonburning	10–12	Moderate; self-extinguishing when ignition source is removed
Hetrofoam 250	Nonburning	13–18	Moderate; self-extinguishing when ignition source is removed

SUMMARY

The thermal decomposition of polyurethanes derived from isocyanates may be assumed to proceed by dissociation of urethane groups to regenerate the initial reactants and also by more random decomposition of segments in the polymer chains and regenerated starting components. The ease of combustion depends upon the rate of decomposition, the volatility of the products, of decomposition, and their combustion behavior.

A reduced rate of burning may be expected if the dissociation products are high in molecular weight and do not readily decompose further to give highly flammable gases. Thus polymeric aromatic isocyanates are preferred to the lower-molecular-weight more volatile diisocyanates. Similarly, resin components that do not readily decompose to low-molecular-weight hydrocarbons and partially oxygenated hydrocarbons are preferred.

Further improvements may be obtained by adding Lewis acid-type flame retardants such as phosphorus compounds to promote char formation and by adding retardants that will interrupt free radical-catalyzed decompositions, such as halogenated compounds.

The ultimate flame resistance will doubtless be achieved by combining these design features into the polymer, along with the addition of noncombustible inorganic materials in large amounts.

REFERENCES

1. J. J. Anderson, *Ind. Eng. Chem. Res. Development*, *2*, 260 (1963).
2. N. E. Boyer and A. E. Vajda, *SPE Trans.*, *4*, 45 (1964).
3. C. Nametz, R. D. Deanin, and P. M. Lambert, *Mod. Plastics*, *41* (No. 1), 166 (1963).
4. L. I. Naturman, *SPE J.*, *17*, 965 (1961).
5. H. Piechota, *J. Cellular Plastics*, *1*, 186 (1965).
6. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology. II. Technology*, Interscience, New York (1964), Chapters 7 and 8.
7. E. N. Walsh, E. N. Uhig, and T. M. Beck, paper presented at the American Chemical Society Meeting, Division of Organic Coatings and Plastics, April 1963.
8. J. H. Saunders, *Rubber Chem. Technol.*, *32*, 337 (1959).
9. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology. I. Chemistry*, Interscience, New York (1962), Chapter 3.
10. S. L. Madorsky, "Thermal Degradation of Organic Polymers," in *Polymer Reviews*, Interscience, New York (1964), Vol. 7.
11. E. A. Dickert and G. C. Toone, paper presented at the Society of Plastics Engineers Meeting, Buffalo, N.Y., May 7, 1964.
12. J. H. Saunders and J. K. Backus, *Rubber Chem. Technol.*, in press.
13. G. S. Buck, Jr., "Fire-Resistant Textiles," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York (1951), Vol. 6, p. 543.
14. W. K. Tang and W. K. Neill, *J. Polymer Sci.*, *C6*, 65 (1964).
15. *Fire Retardant Paints*, American Chemical Society Advances in Chemistry Series, No. 9, ACS, Washington, D.C. (June 1954).
16. I. J. Gruntfest, "Ablation," in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Wiley, New York (1963), Vol. 1, p. 11.
17. H. D. Jones and J. E. Perham, "Bibliography of Ablative Materials," ASTIA Report AD 276,028 (April 20, 1962).
18. Anon., "Astonishing Behavior of Plastic Foam During a Fire on a Ship," *Resin News* (*London*) *3*, (No. 10), 5 (1963).
19. H. W. Blohm and E. I. Becker, *Chem. Rev.*, *51*, 471 (1952).
20. E. Dyer, G. E. Newborn, and G. C. Wright, "Thermal Degradation of Carbamates," paper presented at Delaware Chemical Symposium, Feb. 1958.
21. H. Lakra and F. B. Dains, *J. Am. Chem. Soc.*, *51*, 2220 (1929).
22. C. B. Reilly and M. Orchin, "The Dissociation of Ureas, Urethanes and Biurets," Paper 41, Symposium on Isocyanate Polymers, Division of Paint, Plastics and Printing Ink Chemistry, ACS Meeting, Sept. 1956.
23. J. Swerdloff and S. B. McFarlane, "Thermal Degradation of Polyurethanes," presented at ACS Meeting, Sept. 1954.
24. J. D. Ingham and N. S. Rapp, *J. Polymer Sci.*, *A 2*, 689, 4941 (1964).
25. R. Simha, J. D. Ingham, N. S. Rapp, and J. Hardy, *Polymer Letters*, *2*, 675 (1964).
26. J. H. Engel, Jr., S. L. Reegen, and P. Weiss, *J. Appl. Polymer Sci.*, *7*, 1679 (1963).
27. E. Dyer and R. J. Hammond, *J. Polymer Sci.*, *Pt. A 2* (1), 1 (1964).
28. H. C. Beachell and C. P. Ngoc Son, *J. Appl. Polymer Sci.*, *8*, 1089 (1964).
29. W. B. Bennet, J. H. Saunders, and E. E. Hardy, *J. Am. Chem. Soc.*, *75*, 2101 (1953).
30. J. K. Backus, W. C. Darr, P. G. Gemeinhardt, and J. H. Saunders, *J. Cellular Plastics*, *1*, 178 (1965).
31. S. L. Madorsky and S. Straus, *J. Polymer Sci.*, *36*, 183 (1959).
32. A. Davis and J. H. Golden, *ACS Polymer Preprints*, *5* (No. 2), 461 (Sept. 1964).
33. E. P. Goodings, *Thermal Degradation of Polyethylene Terephthalate*, Soc. Chem. Ind. Monograph No. 13 (1961), p. 211.
34. E. B. Millard, *Physical Chemistry for Colleges*, McGraw-Hill, New York (1941), p. 286.

SESSION 4

Chemistry and Physics of Cellular Materials (continued)

Chairman, ROBERT J. F. PALCHAK
Atlantic Research Corporation

Cell Structure: Physical Property Relationships in Elastomeric Foams

E. ALLEN BLAIR
Foam Division
Scott Paper Company

FOAM GEOMETRY

A foam is a mass of bubbles. If the bubbles occupy less than 76 percent of the foam volume, they may be spherical. If they occupy a volume larger than 76 percent, they must be distorted into polyhedra. Figure 1 shows a typical foam in which the bubbles occupy 97 percent of the volume. The polyhedral structure is clearly visible, and the polyhedra must be pentagonal dodecahedra on the average. The polymer is distributed between the walls of the bubbles and the lines where bubbles intersect, with most of the polymer at the intersections. In this work, the bubbles are called cells, the lines of intersection are called strands, and the walls are called windows. In an open-cell flexible foam, at least two windows in each cell must be ruptured for gases to pass freely through the foam. It is necessary for each window to be shared by two cells, and each strand to be shared by three cells.

CELL STRUCTURE

A single cell from an open cell foam is shown in Figure 2. The foam in this case is a 2-lb/ft^3 polyester urethane with a cell size of 0.1 in. All the windows are present, although a break can be seen in some of them. The polyhedral structure can be seen even more clearly. Adjacent to it is the same cell which has had the windows removed by leaching with caustic. About 5 to 10 percent of the polymer was removed in the leaching operation. The

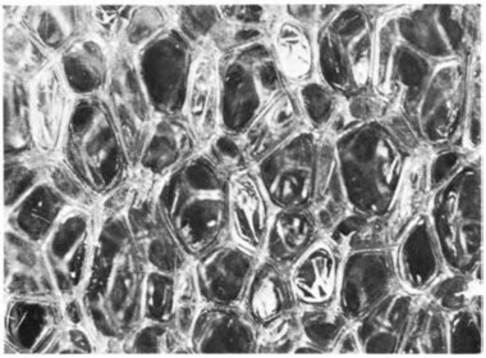


FIGURE 1
Typical polyurethane foam, 97 percent voids.

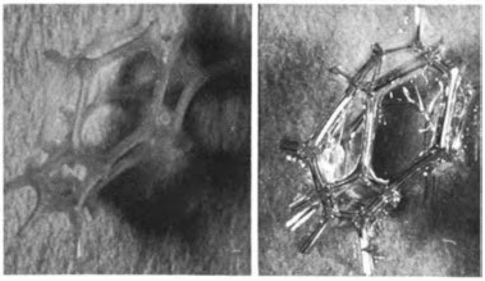


FIGURE 2
Single cells, nonreticulated (left) and reticulated (right).

amount of polymer in the windows seems to be constant for any given foam density over a wide range of cell sizes.

In this paper, structure refers to the presence or absence of windows in the cells, or to the number of windows per cell.

Figure 3 shows the foams corresponding to the cells in Figure 2. The structure made up of the windowless cells is called a reticulated foam. These two foams represent the extremes of structure considered here, and the difference in appearance is readily seen.

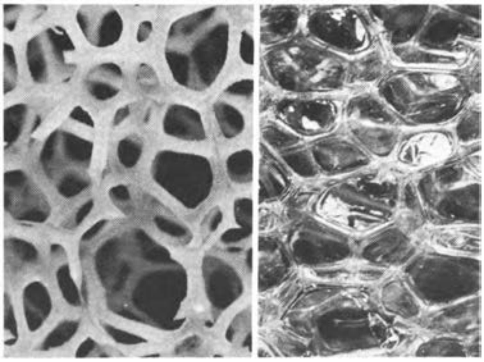


FIGURE 3
Foams corresponding to Figure 2.

CELL GEOMETRY

Figure 4 shows a series of polyester foams of varying cell size, all having the same density. The length of the strands and their size vary to allow all the foams to have the same amount of plastic per unit volume. The length of the strands is governed by Equation (1).

$$L = 6.45\,P^2, \tag{1}$$

where P is the number of cells per linear inch.

Since each strand is shared by three cells, it will have a triangular cross section, and the length of the side will be governed by Equation (2).

$$S = 0.0716\,(\sqrt{d}/P), \tag{2}$$

where P is the number of cells per linear inch and d is the density of the foam.

The surface area of a foam depends on cell size and structure. The relationships are shown in Equations (3) and (4), where A is surface area in $\text{in.}^2/\text{in.}^3$ and P is cells per linear inch.
For nonreticulated foam:

$$A = 4.2P. \tag{3}$$

For reticulated foam:

$$A = 1.39\sqrt{d}P. \tag{4}$$

Figures 5 and 6 show the area versus cell size curves on linear and log scales.

POROSITY

The property most obviously affected by cell structure is porosity, which is also governed by cell sizes. The more windows present, the greater the resistance to air flow for any given cell size. For any given cell structure, the finer the cells, the greater the resistance. Figure 7 shows the porosity of various types of foams versus cell size on a semilog plot. The porosity of reticulated foams in feet per minute of air flow at a pressure drop of 0.1 in. of water across a 1-in. sample versus the pores per inch is a straight-line relationship on a semilog plot. This agrees well with hydrodynamic theory. There is no clear trend in the porosity of the nonreticulated polyester foams. The porosity of the polyether foams shows a definite increase as pores per inch increases. This shows that as the cells become smaller their structure becomes more nearly reticulated. Figure 8 shows the same data on a linear plot, showing the great difference in porosity

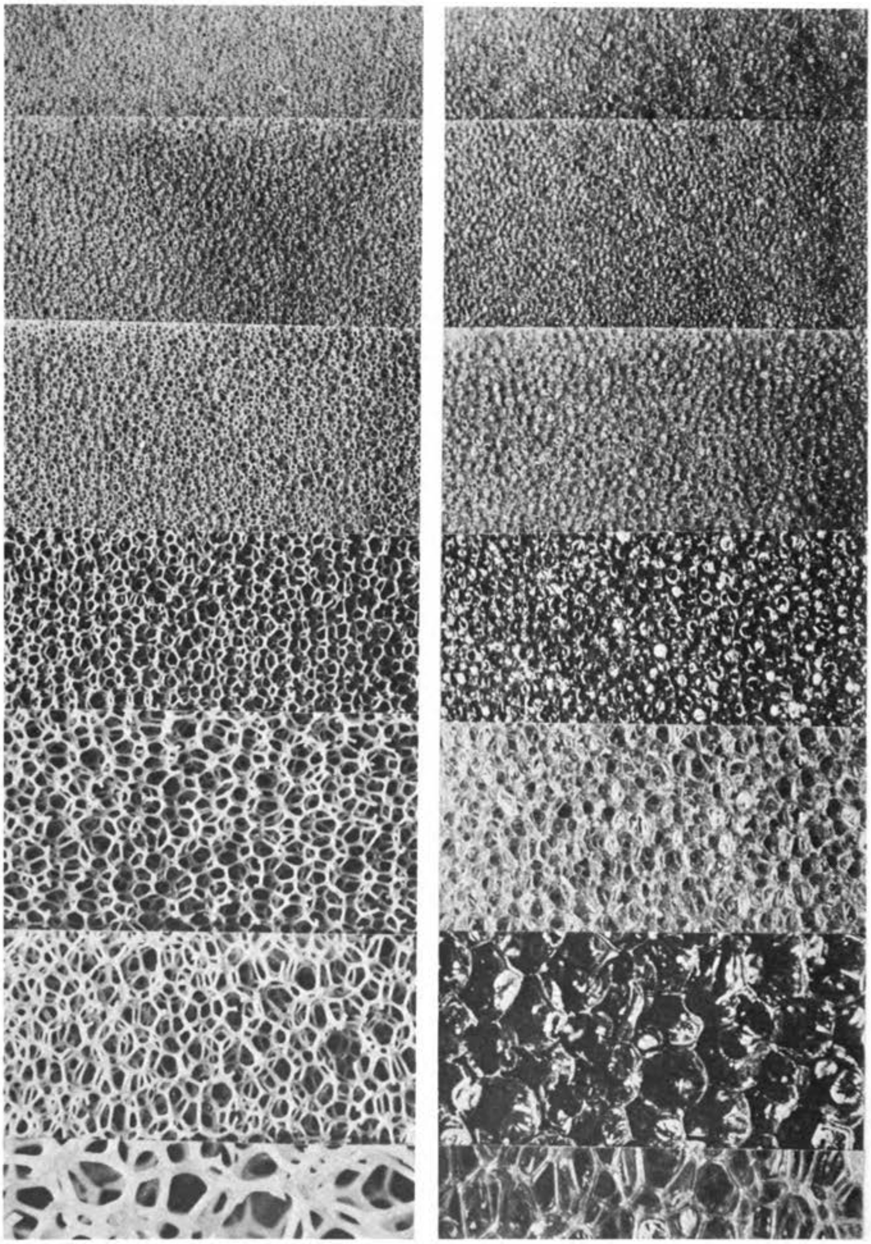


FIGURE 4
Cell size series, nonreticulated (left) and reticulated (right).

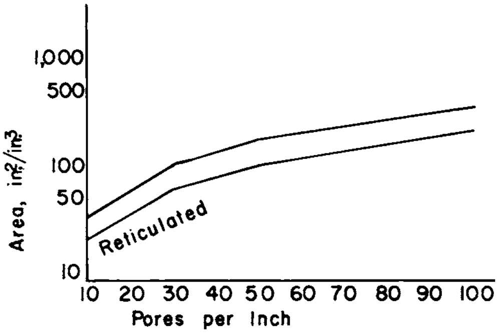


FIGURE 5
Surface area versus cell size, semilog scale.

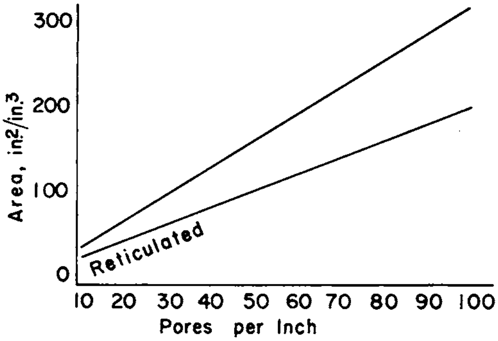


FIGURE 6
Surface area versus cell size, linear scale.

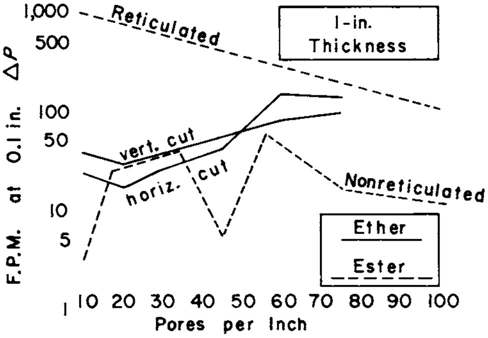


FIGURE 7
Porosity versus cell size, semilog scale.

between reticulated and nonreticulated foams. This also shows that the cell structure can be determined by porosity measurements.

TENSILE STRENGTH

Figure 9 shows the tensile strength of polyester foams—both reticulated and nonreticulated versus pores per inch. As the cells get smaller, the tensile strength increases. Reticulation increases the tensile strength also,

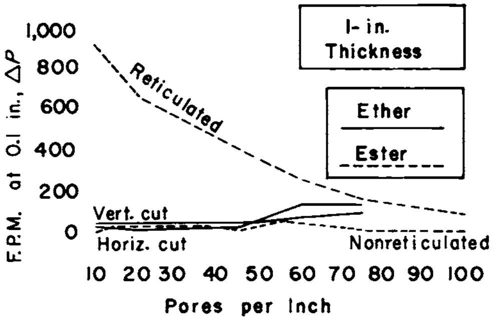


FIGURE 8
Porosity versus cell size, linear scale.

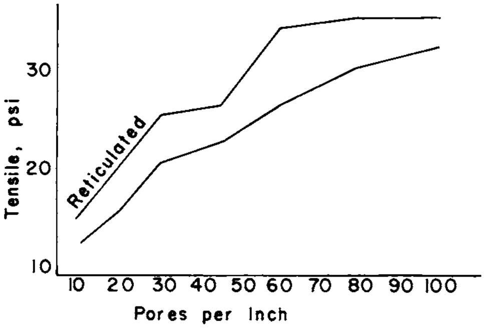


FIGURE 9
Tensile strength versus cell size.

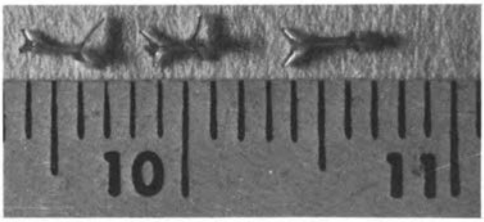


FIGURE 10
Single-strand tensile specimens (shown with centimeter ruler).

although as much as 10 percent of the polymer is removed in the reticulation process.

The reason for the effect of cell size on tensile strength is found in the strength of individual strands. Figure 10 shows single strands from a reticulated polyester urethane foam with 10 cells per inch. Tensile strengths were measured on these samples, as well as on strands from 20 and 45 ppi foams. The data are shown in Table 1.

The cross-sectional areas were calculated by Equations (5), (6), and (7).

$$A_c = V/L, \tag{5}$$

where A_c = cross-sectional area of strands, V = volume of strands, and L = length of strands.

$$V = \frac{\text{foam density}}{\text{polymer density}} = \frac{2\ \text{lb}}{\text{ft}^3} \times \frac{1\ \text{ft}^3}{70\ \text{lb}}, \tag{6}$$

TABLE 1
Tensile Strength of Reticulated Polyester Urethane Foam

Pore Size	Strength (gm)	Calculated Area (in.^{2})	Measured Area	Strand Tensile (psi)	Strands per Inch	Foam Tensile
12	52	4.45×10^{-5}	4.8×10^{-5}	2,600	333	38
20	20	1.16×10^{-5}	1.6×10^{-5}	3,950	1,350	52
45	14	2.13×10^{-5}	4×10^{-6}	14,500	20,000	210

where V = polymer volume in in.^{3}/in.^{3} foam.

$$L = 6.45P^2, \tag{7}$$

where L = length of strand in in./in.^{3} foam and P = pores per linear inch.

The cross-sectional areas were measured by measuring the areas of the broken ends of strands on photomicrographs such as Figure 11.

The agreement between calculated and measured cross-sectional areas of strands is quite good for the large cell foams, and the tensile strengths are quite reasonable for polyurethane elastomers. The poor values for the fine cell foam are due to the difficulty in manipulating samples 0.02 in. in length.

The foam tensile strengths are calculated from the strength of a single strand and the number of strands per square inch as given in Equation (8).

$$\text{Tensile} = \frac{\text{force}}{\text{area}} = \frac{\text{force}}{\text{strand}} \times \frac{\text{strands}}{\text{inch}^2}. \tag{8}$$

The number of strands per square inch is calculated according to Equation (9).

$$\begin{aligned} \frac{\text{strands}}{\text{inch}^2} &= \frac{\text{cells}}{\text{inch}^2} \times \frac{\text{strands}}{\text{cell}} \times \text{fractions of strands on axis} \\ &= \frac{\text{cells}^2}{\text{inch}} \times 10 \times 1/3. \end{aligned} \tag{9}$$

The cells per square inch equals the square of the cells per linear inch. Each cell has 30 strands, but each strand is shared by three cells. Therefore, each cell contributes 10 strands. One third of the strands may be considered to contribute strength in each axis. The foam tensile strengths calculated from the single strand tensiles are about 2.5 higher than the measured values. The low values for the foam tensiles must be caused by the unequal distribution of forces among the strands, causing some of the strands to break before maximum load is applied to the rest.

The variation of strength of the foams with cell size is caused by the variation of the strength of individual strands with cell size. This variation is also seen in textile fibers, and is generally explained by a decrease in the number of defects in a fiber as the size decreases.

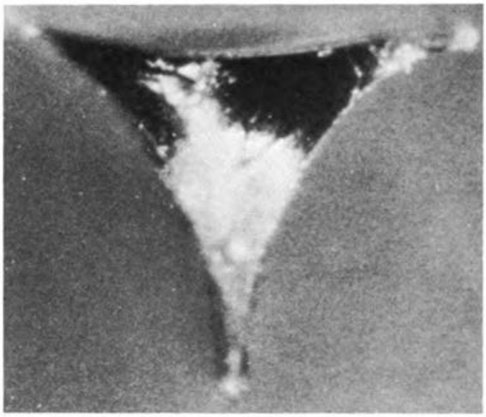


FIGURE 11
Cross section of single strand.

Reticulation of a foam increases its tensile strength by a factor of about 2, although as much as 10 percent of the polymer may be removed in the reticulation process. The explanation for this phenomenon is found in Figure 12. When nonreticulated foam is stretched, the windows are being stretched while the strands are only being flexed. Since the windows have very little cross-sectional area, their breaking elongations are exceeded at very low forces.

When the breaking elongation is exceeded, the windows break, and the breaks are propagated to the strands where they serve as notches. The notched tensile of urethane elastomers has been found to be about half that of unnotched samples. Reticulated foams, on the other hand, do not have the windows necessary to create weakening notches in the strands as they are stretched.

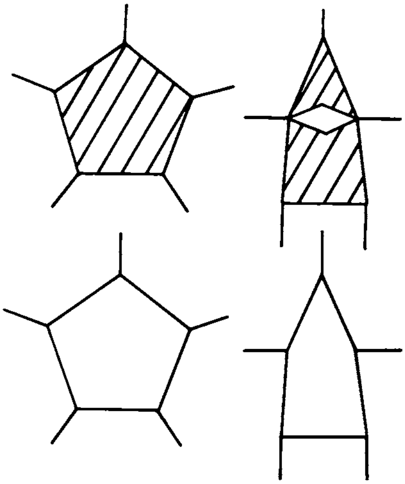


FIGURE 12
Role of windows in breaking.

ELONGATION

A further consequence of Figure 12 is the effect of windows on elongation. At low elongations, the windows break, propagating breaks through the strands. The absence of windows eliminates this source of breaks. This is shown in Figure 13 where the elongation is shown to be twice as great in a reticulated foam as in a nonreticulated foam. The reason for the effect of cell size is less clear, but also less pronounced.

TEAR STRENGTH

Figure 14 shows the relationship of tear strength to pore size in reticulated and nonreticulated foams. Since tear strength depends on tensile strength and elongation, the reticulated foam, with its higher tensile and elongation, has higher tear strength. The cell size also affects tear strength, since both tensile strength and elongation depend on cell size. In a reticulated foam, however, the cell size has little or no effect. The reason for this is not immediately apparent.

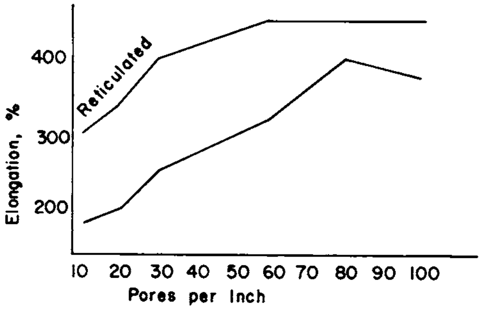


FIGURE 13
Elongation versus cell size.

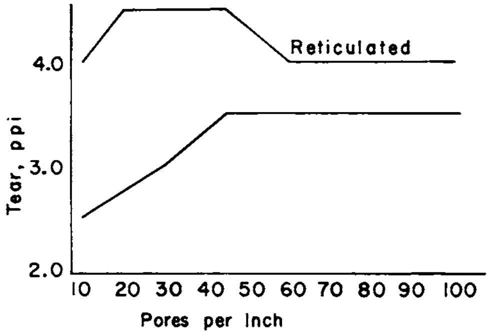


FIGURE 14
Tear strength versus cell size.

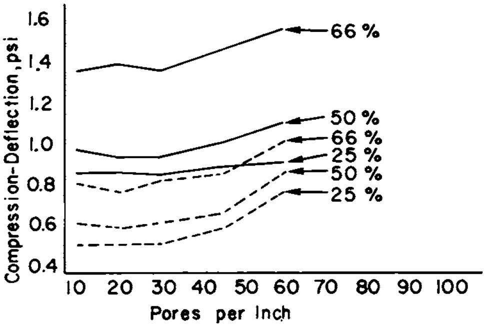


FIGURE 15

Compression deflection versus cell size. Broken line, reticulated; solid line, nonreticulated.

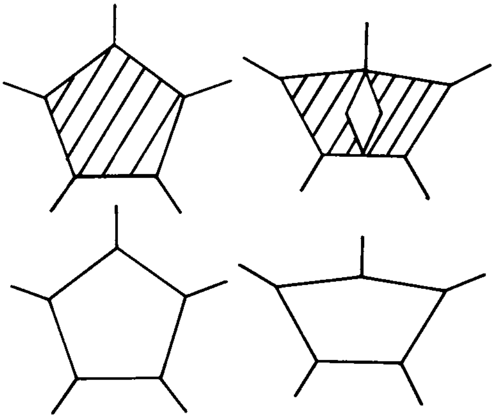


FIGURE 16

Role of windows in compression.

COMPRESSION-DEFLECTION

Figure 15 shows that the force for any given deflection is greatly decreased by reticulation. The explanation for this is shown in Figure 16, where the affect of compression along the plane of the side of a cell is shown.

When a cell having a window is compressed, the membrane, as well as the strands being bent, must be stretched. If the elongation of the resin in the window is exceeded, the window tears, but the break is not propagated through the strand. If there is no window present, the only distortion is the bending of strands, so less force is needed for a given deflection.

SUMMARY

The cell size and presence of cell walls have a major affect on the physical properties of foam. Removal of the cell walls greatly changes the properties of the foam. The observed effects are explained by simple mechanical models, and some of the properties are correlated with bulk polymer properties.

A Novel Process for the Preparation of Inorganic Foams

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The behavior of different polymers at elevated temperatures has been investigated in our advanced research laboratory. The strength of polymeric materials in their carbonized form has been of particular interest. It can readily be seen that this relates to the interesting relationship of flame retardancy and char formation during the exposure of a polymer to heat. During this investigation the possibility of improving the fire retardancy of organic foams by the incorporation of inorganic materials was also explored. This work led into the field of inorganic foams.

It is known that the insulating properties of a refractory material in a temperature range of 1,500–1,900°C (2,800–3,400°F) are improved at lower densities. Many different approaches for the production of low-density high-heat-resistant refractories have been explored. However, refractories in a density range of 20 to 25 lb/ft^3 have not been easily obtained. One of the methods for the preparation of such low-density refractories is the use of a mixture of organic and inorganic materials to form the refractory material. A gradual application of heat up to temperatures of 1,900°C (3,400°F) will convert this mixture into an inorganic refractory.

The idea of preparing inorganic refractories starting with organic foams containing inorganic fillers is not entirely new. Patent literature and government reports describe processes that claim to produce inorganic refractories from organic foams that contain large amounts of inorganic filler. Two basically different methods have been used. The firing of the inorganic refractory material was conducted either in an inert atmosphere or in the presence of oxygen. A complex mixture of phenol–formaldehyde resin, epoxy resin, and polyaryl isocyanate has been used to prepare a titanium carbide foam.[1] Another approach has been the use of resole resins as organic binders.[2] The manufacture of low-density ceramic products using combustible organic materials such as cork, sawdust, peat, and charcoal dust has also been reported.[3]

We duplicated many of the published processes and found that none of the inorganic foams obtained by these methods showed any appreciable strength properties combined with a cellular structure which could classify them as suitable refractory foams of low density. Therefore, to find a suitable organic foaming resin, we prepared a series of organic foams containing inorganic filler.[4]

The preparation of inorganic foams from organic materials loaded with inorganic fillers places severe performance requirements on the organic material in the temperature ranges in which it is being oxidized, volatilized, and carbonized. Most of the organic foams that are heavily loaded with inorganic materials will burn and yield a powdered mixture of inorganic materials and carbon when subjected to temperatures in the range of 420–700°C (800–1,300°F). Therefore, our objective was to find organic materials that provided charred structures that maintained strength properties in a temperature range of 260–1,100°C (500–2,000°F). In addition, these char structures should have the property of shrinking without internal cracking and without changing the shape of the object.

The preparation of organic foams containing large amounts of inorganic metal oxides was a technique of its own. Many foaming systems do not develop enough gel strength to prevent collapse during rise when heavily loaded with inorganic fillers. Therefore, it was necessary to modify our foaming techniques, catalysts, and blowing agents to achieve foam stability and gel strength.

The following resins and foaming techniques were used:

Unsaturated Polyester Resins. An unsaturated polyester resin, prepared by the reaction of 9.4 moles of triethylene glycol, 6.0 moles of maleic anhydride, and 4.0 moles of isophthalic acid, was thinned with 16.5 percent styrene. Foaming was achieved by mixing three components. The base mixture consisted of the above polyester, emulsifier (Tween 40), cellulose acetate butyrate, additional styrene, aluminum oxide, and sodium bicarbonate. Cobalt octoate, maleic anhydride, and water were added to the base mixture and stirred for 2 min; then methyl ethyl ketone peroxide was added and the mixture was stirred for 1 min. The mixture was poured into a mold; foaming occurred within 4 min and gelling occurred within 22 min producing a foam with a density of about 35 lb/ft^3 (Table 1). Foaming results by the liberation of CO_2 from the reaction of maleic anhydride with water and sodium bicarbonate.

TABLE 1
Polyester Formulation Used to Prepare an Alumina Refractory

Materials	Weight, gm
BASE MIXTURE	
Polyester-monomer-mixture	125.0
Emulsifier (Tween 40)	0.6
Cellulose Acetate Butyrate	2.5
Styrene (to reduce viscosity)	52.0
Refractory Grade Al_2O_3	308.0
$NaHCO_3$	4.0
1. Blend well	
2. % Organics = 36.6	
3. % Inorganics = 63.4	
4. % Total styrene = 14.2	
FOAMABLE MIXTURE	
Base Mixture	400.0
Cobalt Octoate	0.8
Maleic Anhydride	4.9
Water	7.3
1. Stir 1½–2 min	
FINAL ADDITIVE	
Methyl Ethyl Ketone Peroxide	0.8
1. Stir 1 min	
2. Pour into a mold	

Epoxy Resins. Several methods of foaming epoxy resins were investigated. It was found that the most suitable catalyst is triethylene tetramine. The use of liquid blowing agents (Freon 11, toluene) and chemical blowing agents that decompose to evolve carbon dioxide and ammonia were satisfactory (Table 2).

Urethane Resins. One-shot and prepolymer type urethane foams using different polyisocyanates such as toluene diisocyanate (TDI), polymethylene polyphenylisocyanate (PAPI), and diphenyl methane diisocyanate (MDI) were investigated. Only the polyaryl isocyanates showed promise. The foam composition in Table 3 gave optimum results. Little difference in properties between polyester polyol and polyether polyol-based urethane foams was observed.

Resole Resins. Phosphoric acid proved to be the best of numerous catalyst systems tried. Freon 11 and methylene chloride are by far the best

TABLE 2

Epoxy Resin System Used to Prepare an Alumina Refractory

A	
Epon 828	484.0 gm
Toluene	16.0 gm
Refractory grade Al_2O_3	725.0 gm
B	
Hardener (Triethylenetetramine)	
C	
Foamed by liquid blowing agent (Freon) or evolution of NH_3 and CO_2	

TABLE 3

Polyurethane Resin System Used to Prepare an Alumina Refractory

A	
Polyol (sucrose/propylene oxide-based polyol)	500.0 gm
Refractory grade Al_2O_3	725.0 gm
B	
Catalyst system (DMEA/DAbco)	
C	
Polyisocyanate (PAPI)	555.0 gm
Refractory grade Al_2O_3	797.0 gm
D	
Foamed by liquid blowing agent (Freon)	

blowing agents for a foaming system containing refractory fillers (Table 4). Freon 11 proved to be the best blowing agent for urea–formaldehyde resins using an aqueous solution of phosphoric acid and *p*-toluene sulfonic acid as catalyst (Table 5).

Attempts were also made to prepare suitable foams by techniques described in Government Report WADD 60-124 using several resole resins in admixture with Epon 828 (Table 6).

Alumina was the oxide used in our study, but other inorganic materials such as silica and zirconia can be incorporated. All foams contained about 60 percent by weight alumina and were foamed at room temperature or, if necessary, at elevated temperature. The completely cured foams were then subjected to temperatures up to 1,650°C (3,000°F) in a conventional oven or kiln with no attempt to exclude air. When lower melting fillers such as silica were used, the maximum temperatures were around 985–

TABLE 4

Phenolic Resin System Used to Prepare an Alumina Refractory

A	
Resole resin	500.0 gm
Refractory grade Al_2O_3	725.0 gm
B	
Catalyst system (H_3PO_4)	
C	
Foamed by liquid blowing agent (Freon or CH_2Cl_2). Difficult to control density and cell structure	

TABLE 5

Urea–Formaldehyde Resin System Used to Prepare an Alumina Refractory

A	
Urea–formaldehyde resin modified with furfuryl alcohol	500.0 gm
Refractory grade Al_2O_3	725.0 gm
B	
Catalyst system (Aqueous solution of H_3PO_4–*p*-toluene sulfonic acid)	
C	
Foamed by liquid blowing agent (Freon). Difficult to control density and cell structure	

TABLE 6

Phenolic–Epoxy–Isocyanate Resin System[1] Used to Prepare an Alumina Refractory

A	
Resole resin	294.0 gm
Epon 828	136.0 gm
Dimethylformamide	70.0 gm
Refractory grade Al_2O_3	725.0 gm
B	
Polyisocyanate (PAPI)	158.0 gm
Refractory grade Al_2O_3	227.0 gm
C	
Heat required to foam and cure (300°F)	
D	
Foamed by evolution of water vapor and CO_2. Difficult to control density and cell structure	

1,100°C (1,800–2,000°F). In the temperature range 260–875°C (500–1,600°F), substantial sintering of the inorganic materials does not occur and the organic material has ceased to exist, leaving a carbon structure behind.

The performance of the foams in this temperature range were evaluated by subjecting them to temperatures up to 650°C (1,200°F) in presence of air for a period of 1 hr. A comparison of the strength properties of the resulting charred foam structures shows that the unsaturated polyester resins have about 3 to 20 times the compressive strengths of the epoxy–phenolic, epoxy, and polyurethane chars after they were subjected to 650°C (1,200°F) temperature (Figure 1). The toughness of the polyester-derived chars is also far superior to that of the other chars as measured by a char friability tumble test based on ASTM C-421-61 (Figure 2).

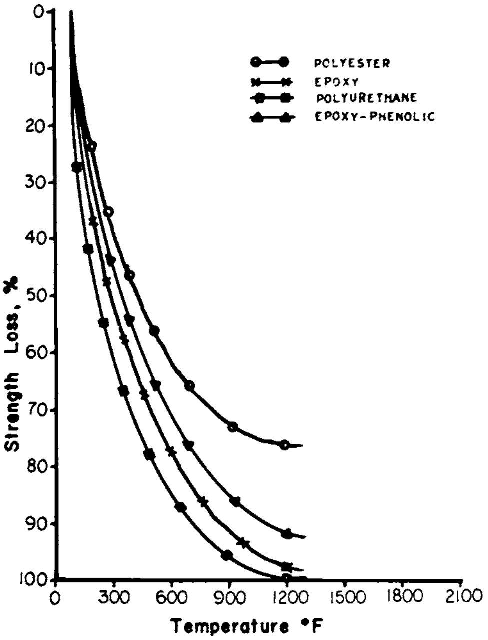


FIGURE 1

Compressive strength loss of the foamed objects during formation of the char structures.

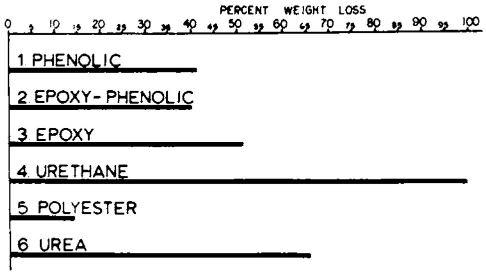


FIGURE 2

Percentage weight loss of the char structures of various polymer systems subjected to the ASTM Tumble Test (C-421-61). Char densities, 30 lb/ft³, charred at 1,200°F.

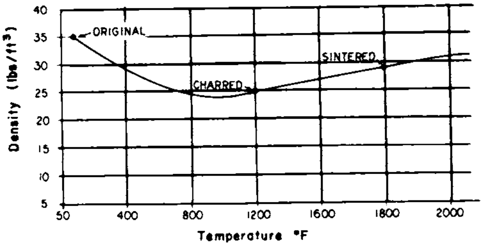


FIGURE 3
Density gradient of the polyester-derived foamed objects during the formation of the inorganic foams.

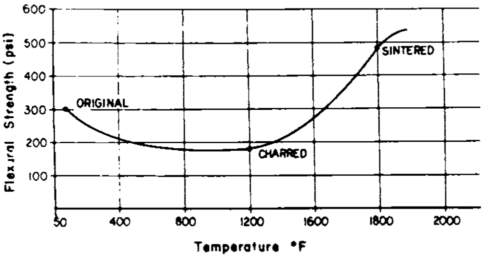


FIGURE 4
Change in flexural strength of the polyester-derived foamed objects during the formation of the inorganic foams.

The strength properties of the foam during the firing process, as well as the changes in density, were measured. Density and flexural strength decreased gradually to a minimum at a temperature range of 480–540°C (900–1,000°F) and then increased to a maximum near the sintering temperature of the particular refractory filler used (Figures 3 and 4).

The strength properties of the chars and of the refractory materials do not give the full picture since the uniformity of cell structure is obviously important for the manufacture of satisfactory refractory materials. After the exposure to 650°C (1,200°F), the most uniform cell structure was found in the polyester char; the epoxy char had less uniform cell structures. The cell structure of the urethane, epoxy–phenolic, and phenolic chars was very poor. All these foams had fairly uniform cell structure before the firing process.

After the superiority of the polyester system had been adequately demonstrated, we were curious to learn why polyesters exhibited such outstanding properties. The properties of solid cured castings of the resin systems used to produce the foams described earlier were compared. The heat distortion point of the polyester resin used is lower than the heat distortion points of three of the other resins. Obviously, this does not give the desired clue (Table 7).

One could speculate that the more aromatic groups or ring structures contained in the polymer, the stronger the resulting char. Here again, polyesters, with the exception of urea, have the lowest contents of aromatic groups. Therefore, this too, offers no explanation for the extraordinary behavior of the polyesters (Figure 5).

TABLE 7

Heat Distortion Points of the Cured Polymer Systems Used to Prepare the Foamed Objects

Polymer Systems	Heat Distortion, 10 mils at °C
Polyester	90
Epoxy	80
Polyurethane	128
Phenolic	149
Phenolic–epoxy	120

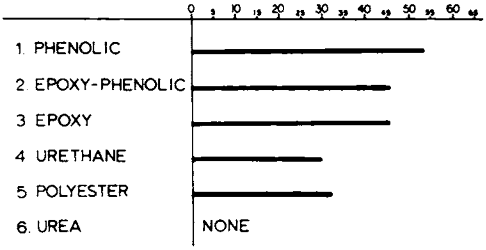


FIGURE 5

Percentage of aromaticity in the polymer systems used to prepare the foamed objects.

Another possible explanation for the stronger char formation and stronger final refractory could be that the internal temperature reached in the brick during the firing process differs. This in turn could be explained by the difference in the heat of combustion of the polymers used. The heat of combustion data obtained indicate, however, that the heat of combustion is not a significant factor in the differentiation of the polymers (Table 8). The fact that the firing of the refractories in our process occurs in an oxygen-starved atmosphere further diminishes the effect of heat of combustion.

The thermogravimetric analyses of the cured resins determined in the presence of air or helium showed the first major differences between the

TABLE 8

Heat of Combustion of the Cured Polymer Systems Used to Prepare the Foamed Objects

Polymer Systems	Heat of Combustion, cal/gm
Polyester	6,530
Epoxy	7,730
Phenolic–epoxy	7,420
Polyurethane	6,570

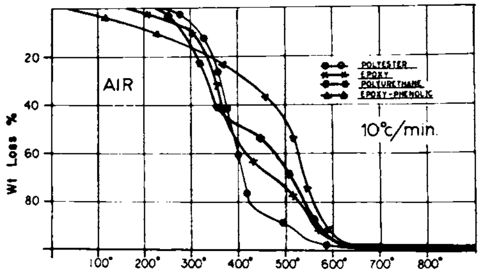


FIGURE 6
Programmed thermogravimetric curves (in air) of the polymer systems used to prepare the foamed objects.

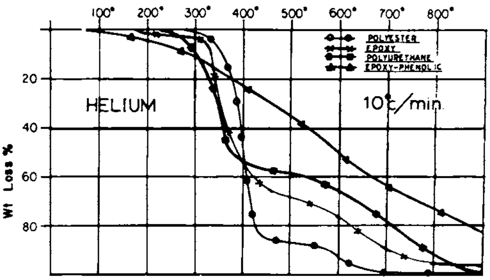
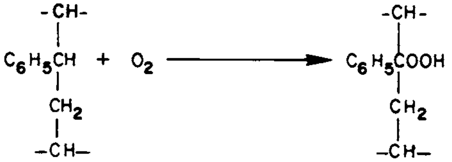


FIGURE 7
Programmed thermogravimetric curves (in helium) of the polymer systems used to prepare the foamed objects.

thermal degradation of cured unsaturated polyesters and the other resins (Figures 6 and 7). In the temperature range 300–420°C (570–790°F), the polyester resin loses about 80 percent of its weight. The other resins show a much more gradual loss of weight over a much broader temperature range.

Further evidence of the unique thermal degradation of cured unsaturated polyesters was obtained by differential thermal analysis. Only the polyester resin showed an endotherm in the temperature range 300–420°C (570–790°F), whereas all the other polymer systems showed an exotherm in the same temperature range. The endothermic reaction indicates distillation of low-molecular-weight polymer fractions, which results from bond rupture. It was suspected that these low-molecular-weight fractions could be low-molecular-weight polystyrene (Figure 8).

Anderson and Freeman suggested the following mechanism for the thermal degradation of polyesters in the presence of oxygen.[5] The reaction appears to involve hydroperoxidation at the alpha carbon of the styrenated branch of the polymer.



$$\begin{array}{c}-CH-\\ |\\ C_6H_5CH\\ |\\ CH_2\\ |\\ -CH-\end{array} + O_2 \longrightarrow \begin{array}{c}-CH-\\ |\\ C_6H_5COOH\\ |\\ CH_2\\ |\\ -CH-\end{array}$$

(Reaction I)

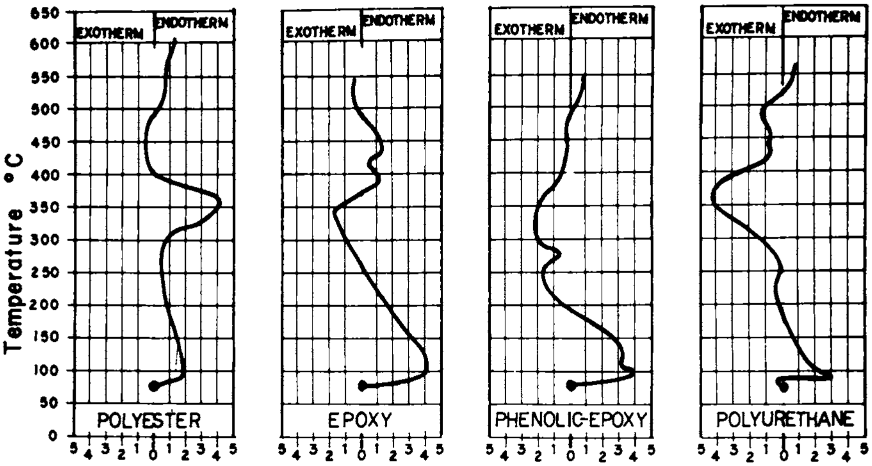
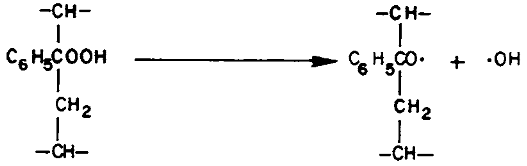


FIGURE 8

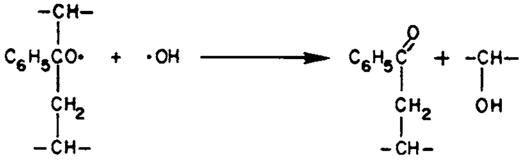
Programmed differential thermal analysis curves (in nitrogen) of the polymer systems used to prepare the foamed objects.

Rearrangement follows:



$$\begin{array}{c}-CH-\\ |\\ C_6H_5COOH\\ |\\ CH_2\\ |\\ -CH-\end{array} \longrightarrow \begin{array}{c}-CH-\\ |\\ C_6H_5CO\cdot\\ |\\ CH_2\\ |\\ -CH-\end{array} + \cdot OH$$

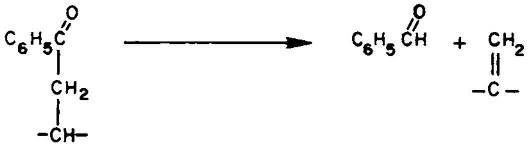
(Reaction 2)



$$\begin{array}{c}-CH-\\ |\\ C_6H_5CO\cdot\\ |\\ CH_2\\ |\\ -CH-\end{array} + \cdot OH \longrightarrow \begin{array}{c}O\\ /\!/\\ C_6H_5C\\ |\\ CH_2\\ |\\ -CH-\end{array} + \begin{array}{c}-CH-\\ |\\ OH\end{array}$$

(Reaction 3)

Cleavage may occur between carbonyl carbon and alpha carbon, followed by hydrogen transfer from the beta carbon to the benzoyl radical.



$$\begin{array}{c}O\\ /\!/\\ C_6H_5C\\ |\\ CH_2\\ |\\ -CH-\end{array} \longrightarrow \begin{array}{c}O\\ /\!/\\ C_6H_5CH\end{array} + \begin{array}{c}CH_2\\ \|\\ -C-\end{array}$$

(Reaction 4)

To elucidate further the mechanism of the thermal degradation of polyesters, we subjected the cured polyester to destructive distillation. The polyester that was coreacted originally with 32 percent monomeric styrene shows, when subjected to destructive distillation, a weight loss of 65 percent in the temperature range 280–390°C (535–735°F). The over-all weight loss was 81 percent, which corresponds to the thermogravimetric results. A large percentage of the fraction received between 280–390°C (535–735°F) was low-molecular-weight polystyrene as determined by infrared analysis. The pot residue solidifies to a *tough* solid char which becomes somewhat brittle upon cooling. None of the other resin systems investigated showed two distinct fractions of which one was of low molecular weight and the other of high molecular weight.

The rapid formation of a solid high-melting residue in the thermal degradation of unsaturated polyesters prevents distortion and excessive flow of the foam structure during the burning process.

Since large parts of the polyester molecule escaped the refractory structure before complete combustion occurred, it was expected that the charred foams obtained from polyesters would contain less carbon than the other foam systems. The polyester chars were found to contain 5 to 15 times less carbon (Table 9). This in turn may explain the higher strength of these chars since large amounts of carbon will insulate the surface of the refractory particles and prevent their sintering. The final inorganic content of the alumina refractory as determined by spectrochemical analysis was 99.9 percent.

TABLE 9
Percentage of Carbon Remaining in the Refractory Filled Foamed Objects Charred at 650°C (1,200°F)

Polymer Systems	Percent Carbon
Polyester	0.43
Epoxy	1.88
Epoxy-phenolic	2.02
Polyurethane	6.76

It was determined that the original foam contained about 50 percent open cells and the char contained 95 percent open cells. The essentially open cell structure allowed the rapid evolution and burning of low-molecular-weight substances without rupturing the foam structure during the firing process. Considerable volume shrinkage also occurred (Table 10) during the firing process, but the foam objects neither ruptured nor changed shape.

The *k* factor of an alumina refractory having a density of 28 lb/ft^3 was measured at 1,100°C (2,000°F) and was found to be 3.7 Btu/hr/sq ft/°F/in.

TABLE 10

Percent Shrinkage Undergone by Foamed Objects during the Formation of the Inorganic Foams

	Silica, 1,200°F	Silica, 1,800°F	Alumina, 2,900°F
Percent volume shrinkage	23.4	37.7	26.5
Percent linear shrinkage			
Length	5.0	14.0	8.55
Width	8.0	14.6	7.13

Lower-density materials and higher-purity alumina refractories produced even lower thermal conductivities (Figure 9).

The linear reheat shrinkage at 1,650°C (3,000°F) was 1 to 2 percent, whereas the linear reheat shrinkage at 1,750°C (3,140°F) was 2 to 4.7 percent (Table 11). These data were obtained through the courtesy of the Garber Research Laboratories of the Harbison-Walker Refractories Company, Pittsburgh, Pennsylvania.

The linear reheat shrinkage of a 40-lb/ft^3 alumina refractory aged 5 hr at 1,675°C (3,050°F) was found to be 2.0 at 1,850°C (3,200°F). Reheat properties at 1.65 percent shrinkage and 40-lb/ft^3 density after 24 hr at 1,620°C (2,950°F) are well within the ASTM C-155-57 specification which also requires that the density be less than 68 lb/ft^3. The room temperature flexural strength was 645 psi. These data were obtained through the courtesy of the Alcoa Research Laboratories, East St. Louis, Illinois.

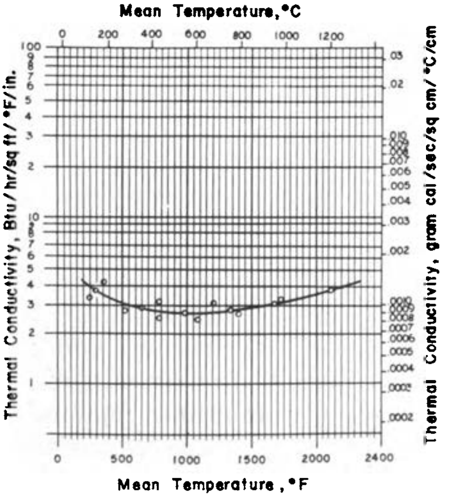


FIGURE 9

k-Factor of an alumina refractory (28-lb/ft^3 density) at various temperatures.

TABLE 11
Physical Properties of an Alumina Refractory at Two Different Densities

Tests	Physical Properties of Alumina Refractory	
Bulk density, lb/ft^3	35	28
Modulus of rupture, psi	520	140
Cold crushing strength, psi	560	270
Apparent porosity	85.9	85–90
Percent reheat shrinkage, 3,000°F (1,650°C) 5-hr hold (Sample size 1 in. × 1 in. × 6 in.)		
Linear change, width	1.2	1.1
Linear change, length	2.1	2.1
Volume change	5.5	4.8
Percent reheat shrinkage, 3,140°F (1,725°C) 5-hr hold		
Linear change, width	2.1	—
Linear change, length	4.7	—
k Factor		
2,000°F		3.7
2,400°F		4.6
Flexural strength, psi	345	

While we believe that, using our novel process, the unsaturated polyester foams are the most suitable organic carriers for the production of inorganic refractories, we do not exclude the possibility that such products can be produced using other foaming systems and other organic binders.

CONCLUSIONS

A polymer system has been found that can support inorganic fillers over a temperature range of 25–1,950°C (77–3,500°F). Although foamed shapes undergo considerable shrinkage in that temperature range, this system provides a method of producing low-density refractories without internal cracks and without the shape being changed substantially. This procedure permits the formation of foamed-in-place low-density refractories which previously had not been possible. The fact that unsaturated polyester foams perform best can be explained through the kinetics of the thermal degradation of these polymers.

REFERENCES

1. I. M. Logan, D. C. Wise, J. J. McGahan, and C. von Doenhoff, *Development of Non-Oxidic Refractory Foams,* WADD (Wright Air Development Division) Tech. Rept. 60-124 (April 1960). (Available from Clearinghouse for Federal and Technical Information, Springfield, Va.)
2. S. Kohn (to Office National d'Etudes, et de Recherches Aerospatiales), U.S. Pat. 3,124,542 (1964).
3. S. Fernhof, U.S. Pat. 2,996,389 (1961).
4. M. Wismer, L. D. Rood, and J. F. Bosso (to Pittsburgh Plate Glass Company), Can. Pat. 694,095 (1964); same as Brit. Pat. 1,012,478 (1965).
5. D. A. Anderson and E. S. Freeman, *J. Appl. Polymer Sci.*, *1*, 192 (1959).

The Development and Production of Urethane Foam for the Polaris Missile

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INTRODUCTION

A flexible, high load-bearing, shock-absorbing type of urethane foam was used in the construction of the launching tubes for the Polaris missiles. The foam was placed in airtight rubber bags and applied to the outside of the launcher, as shown in Figure 1. The flexible foam rested on curved slabs of rigid urethane foam, which served as spacers.

Figure 2 shows Dr. George F. Mechlin, Manager of Westinghouse's missile launching and handling department, by whom the launching tubes were built, holding samples of the flexible and rigid foam.

Originally, a liquid spring type of shock absorber was used, but space limitations prevented their use on the A-3 Polaris Missile. The foam system resulted in simplification of equipment, easier installation, weight reduction, improved reliability, and reduction in maintenance.

Figure 3 shows a horizontal drop test machine, which was used to evaluate the dynamic properties of the urethane foam.

The flexible foam used was not commercially available; a foam with unique physical properties and a very high degree of uniformity and reliability was desired.

This paper describes the development of a compound to Westinghouse's specifications, and a process to produce the flexible foam. It discusses the raw materials used, the processing of these materials, the quality and reproducibility of the resultant foam, and the effect of formulation and processing variables on the foam properties.

The first foam developed was designated WS-2722. Before we had the opportunity to produce any in quantity, new design and performance requirements of the launching tubes dictated that a different type of foam, designated WS-2730, be produced.

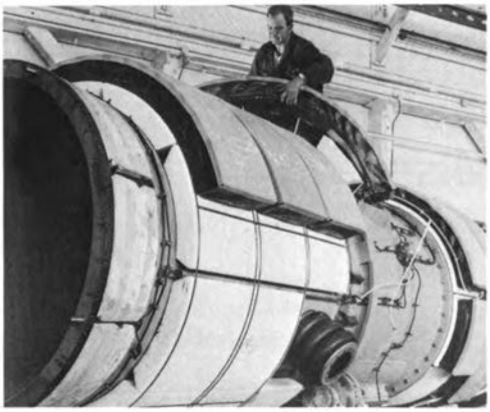

FIGURE 1
Launching tube for the Polaris Missile.

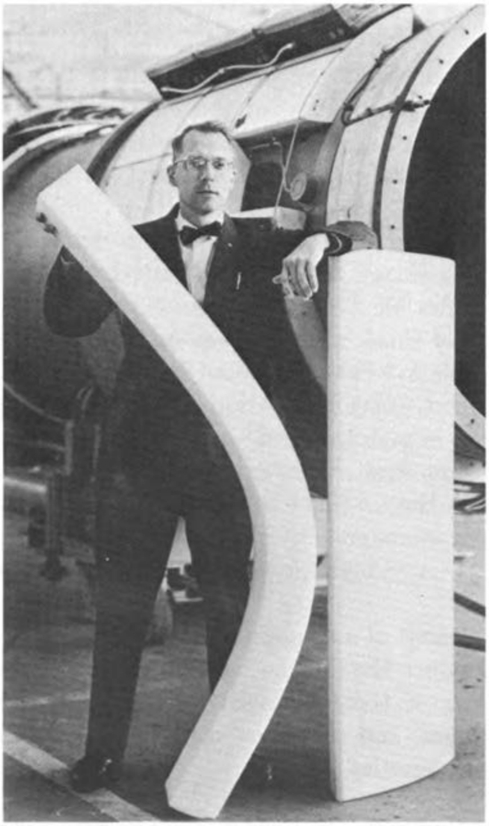

FIGURE 2
Urethane foam for the Polaris Missile.

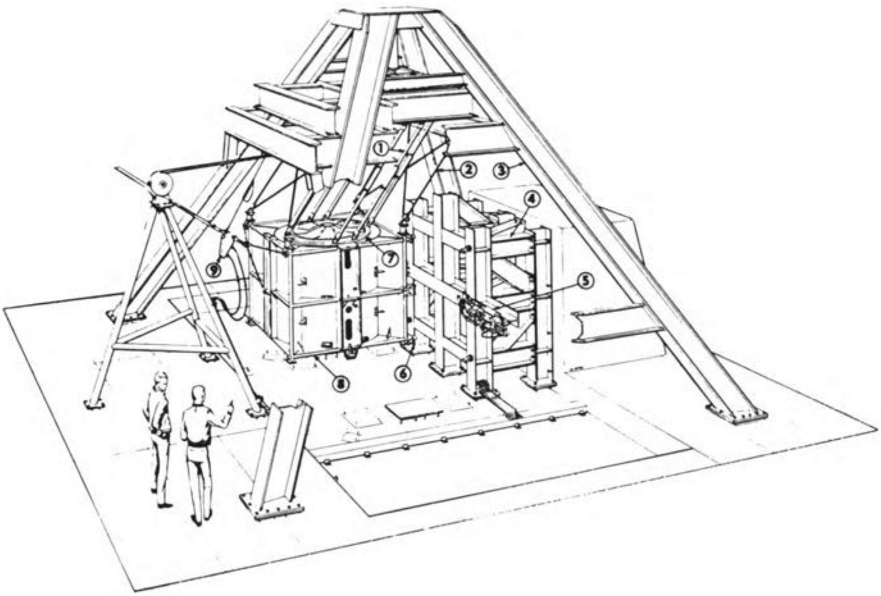

FIGURE 3
Horizontal drop test machine. 1, Slug swing rods; 2, box frame swing rods; 3, frame; 4, buttress; 5, antirecoil latch; 6, lead impact pad; 7, slug; 8, box frame; 9, release latch.

The basic development work on the WS-2730 foam was done by Westinghouse Research. Then foam producers were asked to supply it in quantity to Westinghouse's material and process specifications. This paper will also discuss the formulation and processing of this newer foam and present evidence of its uniformity.

The most interesting aspect of the whole development program was that it proved that flexible urethane foam could be formulated and produced to meet rigid requirements and be used as an engineering structural material. Normally, foam specifications are written around a material that is available. In this case, the specifications were written first, and the foams were designed to meet the requirements.

EXPERIMENTAL

WS-2722 Foam

Specifications

Table 1, WS-2722 Specifications—Bureau of Naval Weapons, gives the specifications for the WS-2722 flexible foam.

Specific test methods were developed by Westinghouse to obtain the values listed. For example, a 6 in. × 6 in. × 2 in. sample was used for

TABLE 1
WS-2722 Specifications—Bureau of Naval Weapons

Compression–Deflection

Deflection, %	Compression, psi	
	min	max
10	0.900	1.150
20	0.945	1.208
30	0.990	1.265
40	1.080	1.380
50	1.260	1.610
60	1.800	2.300
75	5.400	6.900

Unloading C–D Values

The values at 20, 30, 40, and 50 percent shall fall between 25 and 75 percent of the loading values.

Tensile

30 psi minimum.

Elongation

275 percent minimum.

Density

To be reported in pounds per cubic foot.

Cell Count

To be reported in cells per inch.

Compression–Set

5 percent maximum, based on original height.

Humidity Aging

(a) Loss in compression load deflection: the loss at 10 and 20 percent deflection shall not exceed 30 percent of the original values.
(b) Increase in compression set: the compression set shall not exceed twice the original value.

the compression–deflection test. It was deflected four times to 80 percent of the original height, and the load values for the fourth cycle were taken. The unloading values after the fourth cycle were recorded as a measurement of the hysteresis characteristic of the material. Westinghouse had developed a dynamic load–deflection curve, and related it to a static one, which then could be more easily checked, and hence used for quality control purposes.

Formulation

Table 2 shows the formulation developed to meet the requirements.

It was a polyester prepolymer system. We did our work with a polyester system because of the high strength requirements of the foam and because

TABLE 2
WS-2722 Formula, Compound 56320-46

	Parts by Weight	
Prepolymer		
Multron R-68[a]	100	
TDI[b]	25	
Catalyst		
N-Ethyl morpholine[c]		1.10
A-3[a]		0.70
Witco 77-86[d]		1.40
Water		1.35
TOTAL		4.55
Foam		
Prepolymer	100	
Catalyst		4.55

Sources of Raw Materials:

[a] Mobay Chemical Company.
[b] Du Pont, National Aniline, and Mobay.
[c] Union Carbide Corporation.
[d] Witco Chemical Company.

previous exploratory work had been done on such a formulation. Our first problem was to determine what was required to produce foam of consistent quality. We knew a polyester foam could do the job, if controlled, so we set out to prove it.

Raw Materials

Table 3 contains chemical and physical property data on the raw materials used to make the WS-2722 foam.

We did not have the opportunity to investigate the effect on foam quality of using ingredients with properties falling outside the ranges listed in the table, but we did determine that materials falling within these limits gave consistently good results.

Processing

Prepolymer Preparation. The polyester resin was added to a clean, dry, 5-gal tank. It was blanketed with dry air, the agitator was turned on to 200 rpm, and the temperature was adjusted to 80 ± 2°F.

All the toluene diisocyanate was added quickly, and the temperature was raised to 150 ± 2°F in approximately 30 min.

The batch was "cooked" for 1 hr at 150 ± 2°F. Then it was drained into a clean dry container, equipped with an air dryer, and allowed to cool to room temperature.

TABLE 3
Physical Properties of the Raw Materials Used in WS-2722 Foam

Multron R-68	
Hydroxyl number	47–52
Acid number	1.2 max
Water content	0.10 percent
Viscosity at 73°C	850–1,050 cps
TDI	
NCO content	47.3–48.3
2,6-Isomer content	19.0–22.0
Hydrolyzable chlorine content	0.008–0.012 percent
Acidity as HCl	0.012 percent max
N-*Ethyl morpholine*	
Assay	99.0 percent min
Witco 77-86	
pH of 3 percent aqueous solution	3.0–4.0
Acid number	12–16
Water content	0.5 percent max
Saponification number	86–92
A-3	
pH	7.5–9.8
Water content	0.5 percent max
Acid number	160–190
Viscosity at 25°C	80–120 cps

The properties of the prepolymer stabilized after about 3 days, and had the following properties:

NCO content:	6.35 ± 0.20 percent
Viscosity at 90°F:	30,000 ± 4,000 cps

Catalyst Preparation. A significant factor in the preparation of a consistent quality catalyst was the pretreatment of the emulsifier, Witco 77-86. The material contains several alkali-reactive functional groups, such as acids and esters, and it is very important that these constituents be uniformly distributed in the material to produce uniform foam. We found that it was necessary to preheat the material with agitation for approximately 8 hr at 140 to 175°F.

The catalyst was prepared as follows:

1. The *N*-ethyl morpholine was added to an agitated tank.
2. The A-3 was added and mixed in for 5 min.
3. The Witco 77-86 was added and mixed in for 5 min.
4. The distilled water was added and mixed in for 5 min.

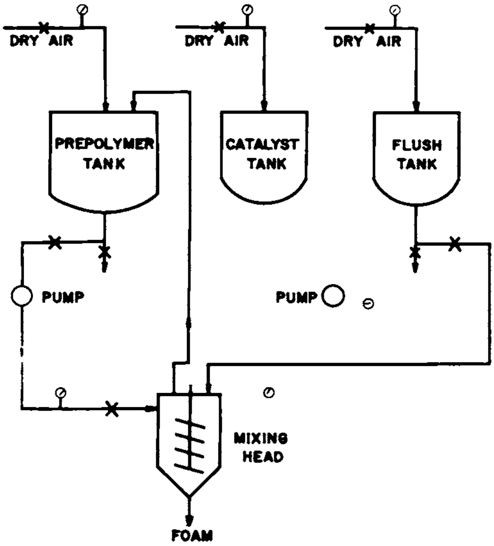

FIGURE 4
Flow diagram of foaming machine.

The catalyst was stored in a sealed container and used within 8 to 12 hr to ensure consistent results, by minimizing the evaporation of the NEM and the separation of the Witco 77-86.

Foaming. We obtained our best results with a high-pressure low-shear type of foamer.

Because of the high viscosity of the prepolymer, it was necessary to inject the catalyst as a spray into the mixing head.

We found that it was absolutely necessary to pressurize the mixing chamber by the use of an orifice on the outlet.

Also, due to heat build-up in the mixing head, we had to cool it to obtain any degree of consistency.

Figure 4 shows a very simple flow diagram of the foaming machine.

The mixing chamber used on the foamer is shown in Figure 5.

Figure 6 shows the pin-type mixer used on the foamer. It was a low-shear type.

After investigating many variables, we settled on the following list of operating conditions:

Prepolymer

Output	5,150 ± 20 gm/min
Temperature	100 ± 10°F
Pressure at head	75 ± 10 psi

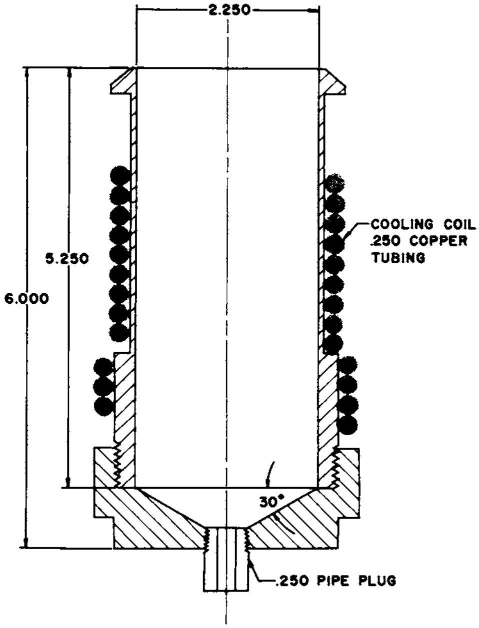

FIGURE 5
Mixing chamber used on foamer.

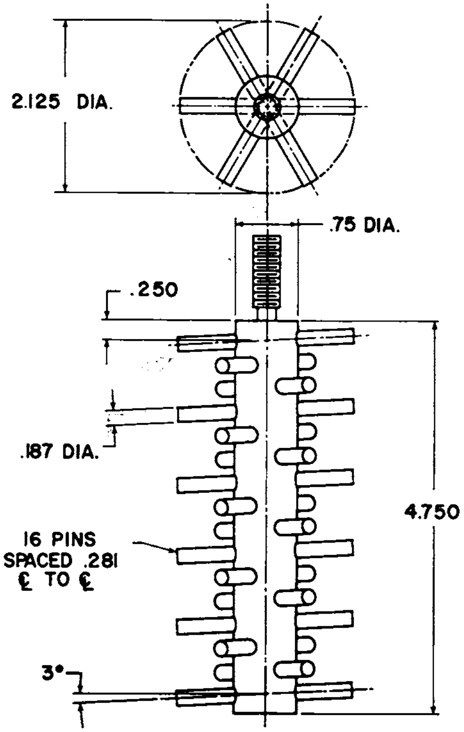

FIGURE 6
Pin-type mixer used on foamer.

Catalyst	
Output	234 ± 2 gm/min
Temperature	ambient
Pressure at head	1,500 ± 50 psi
Pressure recirculating	1,550 ± 50 psi
Mixing Head	
Mixer speed	5,000 rpm
Orifice size	7/32 in. i.d.
Cooling water	8–9 lb/min at 60°F
Mold	
Size	7 in. × 7 in. × 96 in.
Speed	5 ft/min
Angle	3° downward in direction of movement
Temperature	ambient
Cure	
Time	2.5 hr
Temperature	300°F

Results and Discussion

Figure 7 shows the average compression–deflection curve for 14 foamer runs, made at the end of the development period, using the above compounding and processing conditions.

Note that the average curve fell within the required limits up to 70 percent deflection.

We statistically analyzed all the physical property data on the foam made in the last 14 runs, and the results are shown in Table 4. The averages

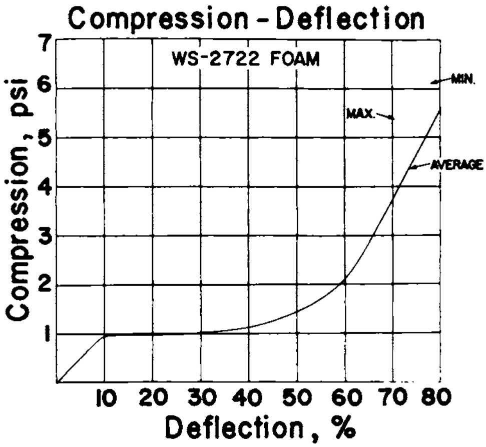

FIGURE 7

Average compression–deflection curve for 14 foamer runs (WS-2722 foam).

TABLE 4
Physical Properties of WS-2722 Foam

	Specification		Average of 14 Runs (95% Confidence)
Compression–Deflection, psi			
Deflection, %	min	max	
10	0.900	1.150	0.96 ± 0.10
20	0.945	1.208	0.98 ± 0.08
30	0.990	1.265	1.04 ± 0.08
40	1.080	1.380	1.16 ± 0.08
50	1.260	1.610	1.45 ± 0.10
60	1.800	2.300	2.06 ± 0.16
75	5.400	6.900	5.12 ± 0.76
Unloading C–D Values, psi			
Deflection, %	min	max	
20	25	75	68.7 ± 3.8
30	25	75	69.9 ± 5.4
40	25	75	68.6 ± 4.0
50	25	75	57.0 ± 2.4
Tensile, psi	30 min		48.0 ± 12.0
Elongation, %	275 min		469 ± 72
Density, lb/cu ft	None		5.00 ± 0.12
Cells per inch	None		40 ± 16
Compression Set, %	5 max		3.11 ± 0.90
Humidity Aging			
(a) *Loss in C–D Values*			
Deflection, %			
10	30 max		23.3 ± 6.2
20	30 max		22.2 ± 5.0
(b) *Compression Set, %*	100% increase over original values		4.79 ± 2.56 (actual value)

of all the properties are shown, with the tolerances within a 95 percent confidence level.

Study of Effect of Variables

In developing the best compound and optimizing the processing variables, we had the opportunity to study the effect of several factors on the quality of the foam. The results are presented in Table 5.

As can be seen, it is very important to control the amount of catalyst. Since it is used in a relatively small amount, and must be blended thor-

TABLE 5

Effect of Foam Variables

Test	Total Catalyst Used +10%	 −10%	*N*-Ethyl Morpholine Amt., −14%	Emulsifier Amt., −50%	Water Amount −5%	 −10%	NCO Content, −13%	Prepolymer Temp., 95 to 100°F	Age of Foam, 2 to 9 days
Compression Deflection, %									
10	−32%	+25%	+39%	+14%	−12%	−28%	+ 6%	− 7%	No effect
20	23	6	47	9	12	30	10	11	
30	19	14	41	6	17	33	5	16	
40	23	7	47	10	10	28	10	5	
50	21	17	42	8	11	27	16	1	
60	20	22	32	15	12	25	18	2	
75	17	36	23	11	8	17	33	—	
Unloading C–D Values	No effect	No effect	−25 to −6%	No effect	+8 to 14%	+1 to 4%	+6 to 14%	No effect	No effect
Tensile	+22%	−45%	+30%	No	—	—	—	—	—
Elongation	+17%	−47%	− 9%	No effect	—	—	—	—	—
Density	− 6%	+ 6%	+14%	+ 6%	− 8%	− 9%	+17%	+ 2%	—
Cell Count	No effect	No effect	No effect	No effect	−31%	−10%	No effect	No effect	—
Compression Set	+23%	—	−38%	—	—	—	—	—	—
Humidity Aging									
C–D	—	—	No effect	—	—	—	—	—	—
C–Set	—	—	No effect	—	—	—	—	—	—

oughly into a thick prepolymer, it is obvious that tight control of the formulation and mixing must be maintained.

WS-2730 Foam

Specifications

Table 6 presents the specifications for the WS-2730 flexible foam. It differed basically from the WS-2722 type in higher load deflection and in improved hydrolytic stability. The improved hydrolytic stability was the basic reason for changing foams, and it was accomplished by using a polyether instead of a polyester.

A 4 in. × 4 in. × 2 in. sample was used for the compression–deflection determination, and the values were read on the fourth cycle.

TABLE 6
WS-2730 Specification—Bureau of Naval Weapons

Compression–Deflection[a]

Deflection, %	Compression, psi	
	min	max
10	1.5	2.5
20	1.7	3.3
30	2.1	4.0
40	2.5	5.0
50	3.4	6.5
60	5.0	10.0
70	To be reported	

Unloading C–D Values

The values at 20, 30, 40, and 50 percent shall fall between 25 and 85 percent of the loading values.

Tensile

30 psi minimum.

Elongation

To be reported.

Density

To be reported.

Compression Set

8 percent maximum, based on original height.

Humidity Aging

Loss in compression–deflection shall not exceed 30 percent of the original values.

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[a] The average load values at 60 percent deflection of any one lot of material shall not exceed 9.0 lb/sq in.

Formulation

Table 7 gives the formulation we used. It is basically the one developed by Westinghouse Research. We increased the amount of Tall Oil slightly to raise the quantity of tin catalyst in order to improve the efficiency of the metering pump.

The formulation was basically a one-shot polyether system, modified with a trimer acid, and a polyisocyanate. Another interesting feature was the use of hydroquinone to control the exotherm in the large loaves which were poured.

Raw Materials

Table 8 contains the chemical and physical property data on the raw materials used to make the foam.

TABLE 7
WS-2730 Formula, Compound 56340-24

Component 1	Parts by Weight
CP–4000[a]	77.44
Empol 1040[b]	22.12
N-Ethyl morpholine[c]	0.44
	100.00
Component 2	
TDI[d]	25.40
Mondur MR[e]	41.60
	67.00
Component 3	
Stannous octoate[f]	0.149
Tall Oil[g]	0.896
	1.045
Component 4	
Ethylene glycol[c]	11.05
Hydroquinone[h]	1.77
Water	0.77
	13.59
Nitrogen	0.5 to 2.0 liters/min

Sources of Raw Materials:

[a] Dow Chemical Company.
[b] Emery Industries, Inc.
[c] Union Carbide Corporation.
[d] Du Pont, National Aniline, and Mobay.
[e] Mobay Chemical Company.
[f] M & T Chemicals, Inc.
[g] Arizona Chemical Company.
[h] Allied Chemical Corporation.

TABLE 8

Properties of the Raw Materials Used in WS-2730 Foam

CO-4000	
Hydroxyl number	41.1–45.5
Acid number	0.10 max
Water content	0.10 percent max
Unsaturates	0.06 mg Koh/gm max
Viscosity at 100°F	280–320 centistokes
pH	5.5–7.0
Empol 1040	
Trimer acid content	88 percent min
Acid value	183–191
Saponification value	190–200
Viscosity at 77°F	67,000 cps max
N-*Ethyl morpholine*	
Assay	99.0 percent min
TDI	
NCO content	47.3–48.3 percent
2.6-Isomer content	19.0–22.0 percent
Hydrolyzable chlorine content	0.008–0.012 percent
Acidity as HCl	0.012 percent max
Mondur MR	
Available NCO	29–30 percent
Hydrolyzable chlorine content	0.30 percent max
Total chloride content	0.70 percent max
Acidity as HCl	0.25 percent max
Viscosity at 77°F	100–300 cps
Stannous Octoate	
Total tin	28–29 percent
Stannous tin	96 percent min of total tin
Specific gravity	1.25–1.27 gm/cc
Viscosity at 77°F	300–400 cps
Tall Oil	
Total fatty acids	93 percent min
Rosin acids	5 percent max
Unsaponifiables	5 percent max
Acid value	185–205
Water content	0.10 percent max
Ethylene Glycol	
Specific gravity	1.1151–1.1156
Acidity	0.05 mg Koh/gm max
Water content	0.15 percent max
Hydroquinone	
Assay	98.5 percent min
Melting point	169°C min
Water content	1.0 percent max
Ash	0.07 percent max

Processing

The first operation was to prepare the four master batches. This was done by simple blending. These batches were then pumped through a low-pressure machine to produce foam, at a rate of approximately 60 lb/min.

The foamer was operated under the following conditions:

Component 1—Glycol Master Batch	
Output	14,280 ± 143 gm/min
Temperature	85 ± 1°F
Component 2—TDI Master Batch	
Output	9,568 ± 50 gm/min
Temperature	85 ± 1°F
Component 3—Tin Catalyst	
Output	150 ± 2 gm/min
Temperature	ambient
Component 4—Water Catalyst	
Output	1,979 ± 0–20 gm/min
Temperature	ambient
Mixing Head Speed	6,000 rpm
Conveyor	
Speed	71 in./min
Angle	1.26° downward in direction of movement
Cure	Room temperature

The foam was poured into 16 wooden molds, each approximately 6 in. × 18 in. × 77 in. in size, and allowed to rise freely. Each group of 16 buns constituted a run.

A unique quality control procedure was followed to ensure uniformity in product. The first, eighth, and sixteenth molds were actually 90 in. in length to provide material for testing. After the loaves were aged for a minimum of 72 hr, the sample buns were cut according to the plan shown in Figures 8 and 9 and crushed three times to 75 percent of the slab thickness.

The ends of the test slabs were cut off; half of each sample was sent to Westinghouse and we tested the other half. Note the care taken to ensure that the test specimens to be checked by the two laboratories were in close proximity to each other.

The foam was at least 10 days old before it was actually tested. Acceptable foam buns had to fall between acceptable foam samples. After we were notified about the results of the tests, we cut up the approved buns to the final shipping dimensions of 5.75 in. × 16.75 in. × 75 in. and

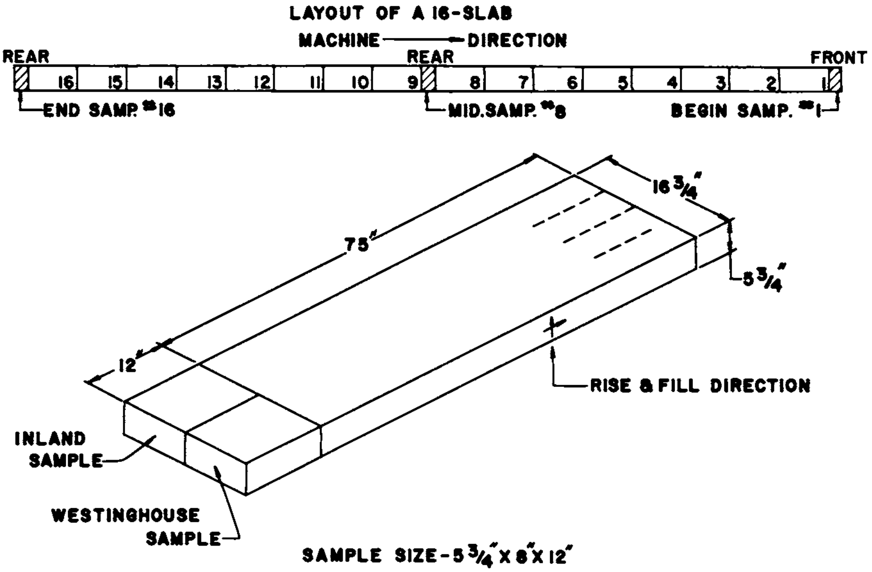

FIGURE 8
WS-2730 foam sampling procedure.

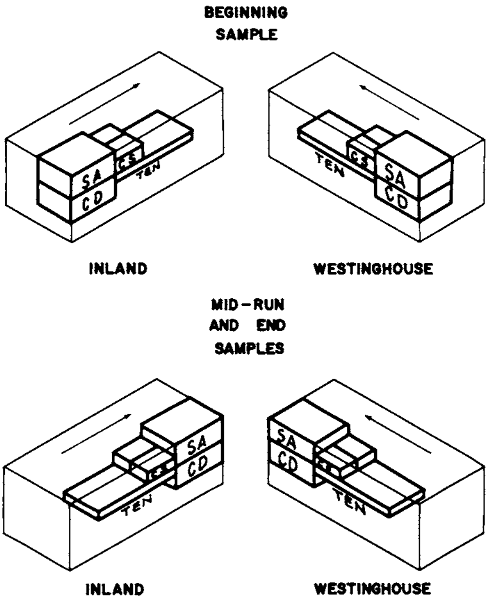

FIGURE 9
WS-2730 foam sampling procedure.

crushed them as above. Then a Westinghouse representative inspected the the cut slabs for visual defects before we shipped them.

Results and Discussion

We were first required to make several qualification runs, and then we produced approximately 1,400 buns, of which 96 percent met all the specifications.

The average compression–deflection curve for the last 40 runs, which were all acceptable, is shown in Figure 10. Note that the curve fell right in the middle of the required range. Not a single value fell outside.

Table 9 lists the average values of the physical properties determined by Westinghouse on the quality control samples from the last 40 runs. The values were analyzed statistically, and the table shows the tolerances within a 95 percent confidence level.

SUMMARY

The information presented in this paper shows that it is possible to produce flexible urethane foam to meet rigid requirements, with a high degree of

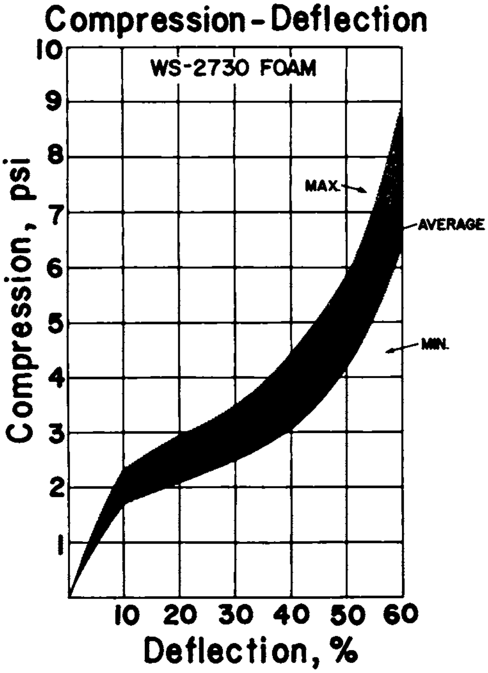

Figure 10
Average compression–deflection curve for 40 foamer runs (WS-2730 foam).

TABLE 9
Physical Properties of WS-2730 Foam

	Specification		Average of 40 Production Runs (95% Confidence)
Compression–Deflection, psi			
Deflection, %	min	max	
10	1.5	2.5	2.02 ± 0.34
20	1.7	3.3	2.51 ± 0.44
30	2.1	4.0	3.02 ± 0.52
40	2.5	5.0	3.77 ± 0.75
50	3.4	6.5	5.04 ± 0.87
60	5.0	10.0	7.70 ± 1.31
70	To be reported		15.28 ± 2.67
Unloading C–D Values, psi			
Deflection, %	min	max	
20	25	85	73.13 ± 3.49
30	25	85	72.58 ± 3.38
40	25	85	71.86 ± 3.62
50	25	85	71.05 ± 3.12
Tensile, psi	30 min		45.51 ± 3.54
Elongation, %	To be reported		67.98 ± 10.31
Density, lb/cu ft	To be reported		7.56 ± 0.27
Compression Set, %	8 max		3.40 ± 1.42
Humidity Aging			
Loss in C–D Values			
Deflection, %	max		
10	30		14.88 ± 6.36
20	30		14.73 ± 5.98
30	30		14.28 ± 6.00
40	30		13.70 ± 6.12
50	30		12.83 ± 6.14
60	30		12.02 ± 7.05
70	30		10.53 ± 9.20

confidence, if sufficient attention is paid to controlling the raw materials, the compounding, the processing, and the testing. Urethane foam technology has certainly outlived the "black art" stigma which is too often assigned to it.

The fact that urethane foam did such a good job on the Polaris launching tubes should lead to its acceptance as a reliable engineering material in other military and commercial applications.

ACKNOWLEDGMENT

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Rigid Urethane Slabstock by the One-Shot Technique

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INTRODUCTION

The plastics industry has observed during the past decade the phenomenal growth of a new family of polymers to serve mankind. Under the general heading of urethanes have emerged plastic materials for application as both resilient and rigid foams; elastomeric fibers, films, and coatings; and abrasion-resistant varnish coatings. Concurrent with this expanding market has been the development of processing and applications technology for urethane systems. By far the greatest advancements to date have been in the area of flexible and rigid urethane foams. Substantial information is currently available on flexible-foam technology.[1]

Rigid urethane foam technology for production-scale operations has progressed rapidly with the onset of one-shot foaming techniques. Prior to this, the quasi-prepolymer method was used, requiring prereaction of toluene diisocyanate (TDI) with 10–20 percent of the polyol before blending with the remainder of polyol. The one-shot method involves reacting all components at one time to produce the finished product. Thus, a significant saving is accomplished by reducing the manufacture of foam from a two-step (quasi-prepolymer preparation and foaming) to a one-step (foaming) operation.

Production of rigid foam slabstock by the one-shot method using TDI (80:20 blend of 2,4- and 2,6-isomers) consistently resulted in severe discoloration in the center of high-rise buns with subsequent deterioration of foam properties. The discoloration is referred to as "burnout" and is due to charring of the urethane polymer by the heat of reaction generated during foaming. Because rigid urethane foam possesses outstanding insulation properties, dissipation of exothermic heat is extremely slow. Since bun cores may remain at temperatures well in excess of 350°F for 6–10 hr, it is not surprising to observe severe burnout in one-shot systems based on TDI.

The introduction in 1959 of a lower-cost modified polyisocyanate (Allied Chemical Corporation's Nacconate 4040) made the one-shot method for slabstock foaming a reality and at the same time contributed additional cost savings. Possessing a higher equivalent weight than TDI, the modified polyisocyanate produced rigid foams with lower maximum exotherms and subsequent mitigation of burnout.

APPLICATIONS

Existing and potential military applications for rigid urethane foam are well known at the present.[2] These include radomes, prefabricated structural panels, temporary field shelters, packaging, flotation in rafts and personnel boats, buoys, unsinkable target ships, and ballast tank, engine room, and pipe insulation. Many of these applications are not conducive to on-site foaming because of serious technical limitations; rather, factory prefabrication under close quality control is required. Slabstock production of rigid urethane foam is presently produced under these controlled conditions.

As in many military applications, the primary market for rigid urethane foam is in insulation. The advantages of urethane insulation as compared with other familiar insulators, such as fiberglass, cork, rockwool, and expanded polystyrene, are well known. Low thermal conductivity (permitting the use of thinner insulation compared with other insulators which results in larger storage capacity) and inherent structural characteristics are perhaps the outstanding properties of urethane.

There are three methods of rigid foam production in current use:

1. Poured-in-place (both conventional and froth foaming)
2. Slabstock (the important factors of one-shot slabstock techniques will be discussed herein)
3. Sprayed

A previous publication[3] detailed techniques of molding one-shot rigid urethane foam where in-place foaming offers such advantages as improved structural strength (due to self-bonding characteristics of the foam to the panel skin) and ability to produce complicated shapes. There are, however, many applications where the pour-in-place method is not practical, such as insulation of outdoor storage tanks, refrigerated storage buildings, roofing, and pipes. Cutting uniform slabs of preformed and cured bun stock has proved most successful for this type of application.

The production of uniform high-rise good-quality slabstock by the one-shot method is dependent on control of chemical and mechanical variables. The contribution of each formulation ingredient to the properties of the finished foam is chemical in nature, whereas metering and mixing of ingredients, conveyor design, and automation of the foaming operation are distinctly mechanical.

Early one-shot formulations possessed inherent disadvantages that restricted attainment of maximum foam yield and uniformity of product. Improvements were desired to eliminate:

1. Burnout in continuous high-rise buns
2. Tendency toward external splitting
3. Nonuniform foam properties throughout buns
4. Rapid foam gelation which prevented the molding of buns with rectangular cross section.

TABLE 1
One-Shot Rigid Urethane Slabstock Foam Formulation and Process Conditions

Ingredients	Parts by Weight
Component A	
Polyether polyol[a] (460 hydroxyl No.)	100
N,*N*,*N'*,*N'*-Tetrakis(2-hydroxypropyl)ethylenediamine[b]	4
Phosphorous-containing polyol[c] (210 hydroxyl No.)	4
Triethylenediamine solution[d]	1.0
Silicone surfactant[e]	1.5
Trichlorofluoromethane[f]	32
Component B	
Stannous octoate	0.5–0.7
Component C	
Polyisocyanate[g] (107 amine equivalent)	101
TDI index (ratio of NCO/total active hydrogen), 1.03	
	Time, sec
Cream time	10
Gel time	45
Rise time	90

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[a] Actol 52-460 Polyol, National Aniline Division, Allied Chemical Corporation.

[b] Quadrol, Wyandotte Chemical Corporation.

[c] Vircol 82, Mobil Chemical Company.

[d] Dabco 33LV, Houdry Process Division.

[e] Dow Corning Corp., General Electric Co., Silicones Division, Union Carbide Silicones Company.

[f] Genetron-11, General Chemical Division, Allied Chemical Corporation.

[g] Nacconate 4040, National Aniline Division, Allied Chemical Corporation.

TABLE 2
One-Shot Rigid Urethane Slabstock Foam

Physical Properties	
Density, lb/ft^3	1.9
Closed cells, percent	95
Compression load, lb/sq in., parallel to rise	
at yield point	20
at 10 percent deflection	28
Flexural strength, lb/sq in.	45
Shear strength, lb/sq in.	30
Moisture vapor permeability, perm-in.	2
Water absorption, lb/sq ft of surface area	0.04
k-Factor, Btu/(sq ft) (hr) (°F/in.) (cut foam sample)	
Initial	0.115
After 10 days at 140°F	0.130
Dimensional stability, percent volume change	
24 hr at −22°F	<1
24 hr at 158°F	<1
24 hr at 230°F	2
24 hr at 158°F, 95–100 percent relative humidity	7
72 hr at 100°F, 95–100 percent relative humidity	2

A formulation for production of one-shot rigid slabstock without these disadvantages is shown in Table 1. Typical physical properties of the foam are given in Table 2.

The desired improvements in one-shot slabstock foaming were achieved using this formulation in a three-component foam system: the isocyanate constituted one stream; catalyst (stannous octoate), the second stream; and a premix of all other ingredients, the third stream. Close control on reactivity was maintained by separating the catalyst as an individual stream. Additional streams may be used to give greater formulation flexibility. However, more stringent control of ingredient calibration is needed as the number of streams is increased.

Close control on all established variables is essential for reproducibility of foaming operations. This includes both chemical and mechanical factors.

CHEMICAL FACTORS

Polyethers

Rigid-foam polyethers are usually propylene oxide adducts of sorbitol, sucrose, pentaerythritol, methyl glucoside, or similar polyols. In general, foam physical properties, especially dimensional stability, improve with increased polyether functionality and lower molecular weight. High functionality and low molecular weight are helpful in attaining the highly cross-linked rigid polymer that is necessary for good dimensional stability in the finished foam.

The hydroxyl number of the polyether (a measure of equivalent weight of the polyether) usually falls within the range of 300 to 550 units. In general, the dimensional stability of one-shot foam improves with increasing hydroxyl number; however, increased foam brittleness (i.e., friability) occurs. Since friability has a deleterious effect on compressive strength of the foam, a compromise must be made. Optimum over-all foam properties can best be attained by use of a polyether in the 430 to 530 hydroxyl number range.

Small amounts of water in the polyether generally result in slight increase in *k* factor and friability of the foam. Improvement in dimensional stability is normally observed.

The phosphorous-containing polyether in the formulation of Table 1 inhibits the development of burnout in continuous high-rise buns. Although the mechanism of burnout is not fully understood at this time, the addition of small amounts satisfactorily controls the polymer degradation process. Other materials, such as organic phosphates and phosphites, in small amounts, have exhibited a similar effect.

Polyisocyanate

The polyisocyanate used in the one-shot slabstock system described here is a modified toluene diisocyanate. A TDI index (ratio of NCO/total active H) of 1.03–1.05 produces excellent foam properties. Lower isocyanate index levels generally result in poorer dimensional stability. Higher levels lend some improvement to stability properties but increase friability.

Silicone Surfactant

The silicone surfactant serves a dual function. First, it serves to emulsify the hydrophilic polyether and the hydrophobic isocyanate and fluorocarbon into a homogeneous mixture, thus ensuring uniform reaction throughout the foam mass. Second, it controls cell size by stabilizing the rising foam and preventing coalescence of the tiny foam cells until gelation occurs.

Catalysts

Two classes of catalysts have found commercial acceptance in the production of rigid urethane foam: tin salts and tertiary amines. The tin salts are of two types; the organometallic type such as dibutyltin dilaurate and the organic acid salts of divalent tin such as stannous octoate. Some tertiary amines are triethylene diamine, *N*,*N*-dimethylethanolamine, and *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxypropyl)ethylenediamine tetramethylbutanediamine.

The various catalysts and their contributions to one-shot slabstock foaming are given below.

Stannous Octoate

This catalyst gives the rapid initial polymerization that is essential for fine uniform cell structure, yet final gelation or hardening of the foam is delayed until rise is almost complete. In combination with triethylenediamine, a synergistic behavior is noted which promotes reactivity faster than either catalyst alone.

Because of instability in the presence of the premix ingredients resulting in degradation of catalytic activity, stannous octoate is introduced as a separate stream. By this method, greater control on reactivity is achieved, permitting catalyst changes to be made during foaming. To obtain greater accuracy on delivery rate of stannous octoate, where generally small amounts are required and where slight changes will cause significant reactivity differences, it may be desirous to dilute the catalyst with dioctyl phthalate (DOP). A dilution rate of 2:1 DOP–stannous octoate may be used without deleterious effects on the resulting foam.

Because moisture contamination may degrade the catalytic activity of stannous octoate, the reservoir should be maintained under a blanket of dry nitrogen.

Triethylenediamine

This catalyst works in combination with stannous octoate first to promote initial polymerization and second to delay final gelation until rise is complete.

Molding characteristics are necessary in the formulation to allow forming of a flat-top bun to minimize foam scrap loss. The correct balance of catalysts is required to achieve a rectangular bun. Excess triethylenediamine may cause early foam hardening and, thus, interfere with complete and uniform molding. Therefore, the level of this catalyst should be maintained on the low side.

External splitting of long buns is a serious problem encountered in slabstock foaming. Generally, this may be attributed to an imbalance of catalysts which causes premature foam gelation (or to "undercutting" which is described later in this paper). Thus, extensive internal stresses develop that terminate in foam rupture. To prevent external splitting, proper catalyst levels should be selected that allow foam expansion to be complete before final gelation.

N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine

This catalyst improves moldability of the system and functions as a crosslinking agent to improve dimensional stability.

Fluorocarbon Blowing Agent

The fluorocarbon serves two important functions in rigid foams. First, it serves as a blowing agent for expansion of the urethane polymer. Second, the fluorocarbon gas, usually trichlorofluoromethane, trapped in the foam cells contributes to the low thermal conductivity of the foam because the thermal conductivity of the fluorocarbon itself is extremely low.

The thermal conductivity of cut urethane slabstock, expressed as the *k* factor, will exhibit a gradual increase with time until a maximum level is reached. Figure 1 illustrates this drift. It has been shown[3] that the increase is due to inward diffusion of atmospheric gases until equilibrium rates of diffusion exist. At this point, the maxiumm *k* factor value is reached.

Ingredient Temperatures

The temperature of ingredients can play an important part in obtaining proper foam reactivity. In general, reaction rate increases with increasing ingredient temperatures. To ensure constant reactivity from beginning to end of a slab run, proper temperature control is required.

Ingredient Stability

Component A (premix) in Table 1 is stable for several weeks if kept under a slight dry nitrogen pressure to prevent moisture contamination.

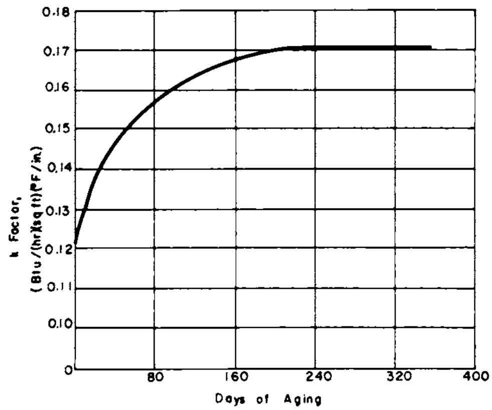


FIGURE 1
Effect of atmospheric aging on conductivity of one-shot rigid urethane foam at 110°F.

Components B and C (stannous octoate) are indefinitely stable at room temperature under dry nitrogen.

Deactivation of the premix is characterized by increased foaming time and foam having coarse irregular cell structure. Loss of fluorocarbon from the premix is evidenced by an increase in foam density.

MECHANICAL FACTORS

Three essential components of a rigid foam slabstock machine are:

1. Mixing and metering equipment
2. Mixing head and agitator
3. Conveyor and auxiliary equipment

Design features of each of these components are discussed in the following sections, along with operational technique for rigid urethane foam slabstock production.

Mixing and Metering Equipment

In one-shot rigid-foam slabstock production, the function of the mixing and metering equipment is to deliver three components (isocyanate, premix, and stannous octoate catalyst) to the mixing head in correct proportions and at controlled temperatures. This requires three separate reservoirs and pumping systems with service equipment. A typical schematic design is shown in Figure 2.

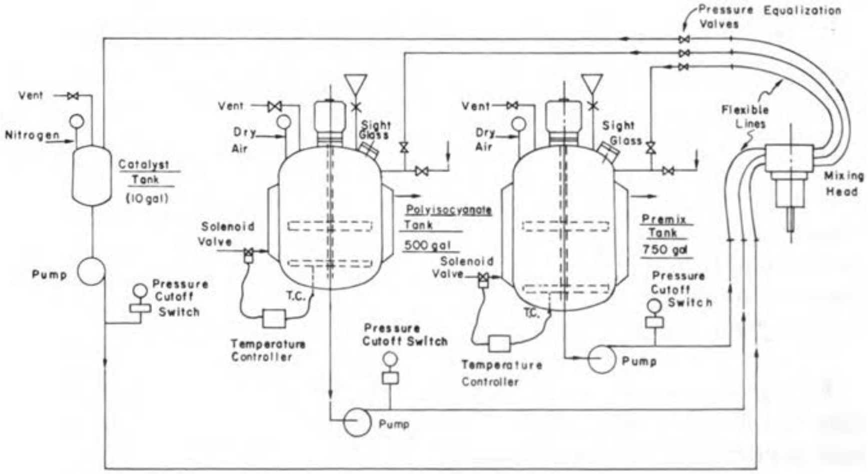


FIGURE 2

Rigid urethane slabstock manufacture, mixing, and metering equipment.

Capacity. This design specifies a 500-gal isocyanate tank that has a capacity of 5,250 lb (10.5 lb/gal). The stoichiometric equivalent amount of premix is 7,500 lb (premix: isocyanate::1.42:1) which requires a 750-gal tank (9.9 lb/gal). A 10-gal catalyst tank has excess stoichiometric capacity. This system has a total capacity of about 12,000 lb of foam, allowing for heel in the tanks and lines. At a machine throughput of 125 lb/min, 12,000 lb of continous slabstock would be foamed in 96 min.

Mixing. The premix is made by charging the ingredients to the premix tank (with agitator running) in the following order:

1. Polyether polyol
2. Phosphorous-containing polyol
3. *N*,*N*,*N'*,*N'*-tetrakis(2-hydroxypropyl)ethylenediamine
4. Silicone surfactant
5. Triethylenediamine solution
6. Trichlorofluoromethane

After the last ingredient is charged, the recirculation pump is started and mixing is continued for 30 min.

Temperature Control. Accurate temperature control of the two major components, premix and isocyanate, is maintained by cooling-water flow to the tank jackets. This is done automatically to maintain a preset temperature by a thermocouple, controller, and solenoid valve circuit.

Pressure Blankets and Venting. The isocyanate and premix tanks should be equipped for dry-air blanketing to prevent moisture from entering the system. The stannous octoate tank is equipped with a nitrogen blanket to prevent oxidation and degradation of the catalyst. All tanks are usually pressurized to 2–5 psi with the vents valved to release at 10 psi.

Pumps. Each system is equipped with a highly accurate positive displacement metering pump with variable-speed drive, permitting accurate calibration of flow rates. Packed seal pumps are normally employed; however, mechanical seal pumps have also been successfully used, particularly in the isocyanate system.

Pressure Cut-Out Switches. Each pumping system is fitted with a pressure switch which shuts off the pump drive when excessive pumping pressure is developed. This protects the system and prevents material loss.

Recirculation—Flexible Lines. Each stream is piped for flow to the mixing head and back to the tank. This permits continuous recirculation prior to foaming which aids mixing and provides correct ingredient mixing temperature at the head at all times. Connection to the mixing head is through flexible lines to permit traverse of the mixing head.

Pressure Equalization Valves. A valve located in each return line is used to equalize recirculating and forward-flow (foaming) pressure. This assures uniform flow rate in each stream from the first instant of forward flow. Thus, accurate calibration based on a small shot is possible, and yield losses are prevented during actual foaming.

Materials of Construction. The isocyanate and premix may be handled in carbon steel tanks, pumps, and lines. Bronze fitted pumps are also satisfactory for handling the premix. Butyl rubber or Teflon-lined reinforced flexible hoses are recommended. Stannous octoate catalyst should be handled in a completely stainless steel system.

Mixing Head and Agitator

The function of the mixing head is to blend thoroughly the three liquid streams to achieve a foam with fine uniform cell structure and optimum physical properties. Insufficient mixing will result in weak foam with coarse irregular cell structure.

Figure 3 shows a typical mixing head consisting of the agitator, housing, and outlet. The degree of mixing achieved in the head is largely dependent upon agitator design, clearance between the housing and agitator, agitator speed, and the diameter of the outlet. Each of these is discussed below.

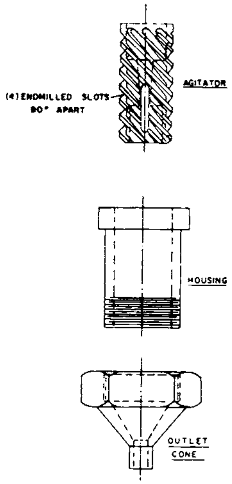


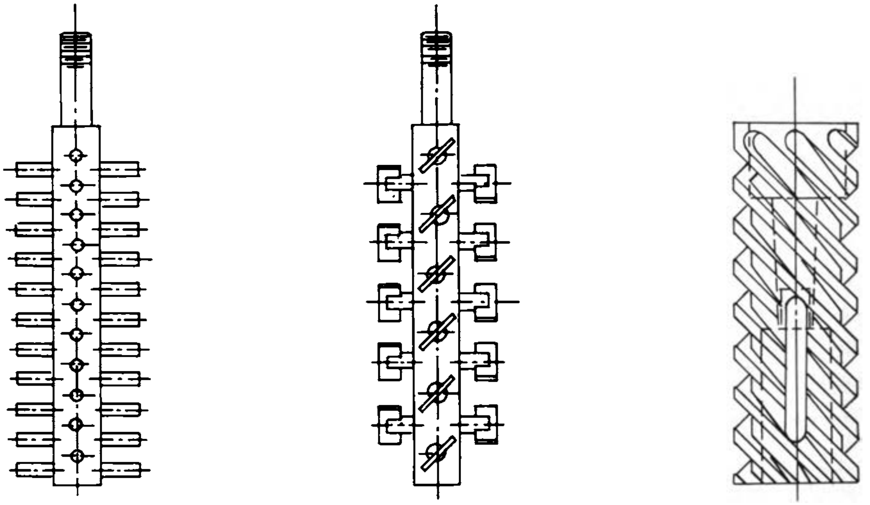
FIGURE 3
Typical mixing chamber.

Agitator Design. Typical agitator designs are shown in Figure 4. At equal operating speeds the pin type, pin–paddle type, and helical-gear type, respectively, will provide low, medium, and high rates of mixing shear. The helical-gear and pin–paddle type are preferred for slab production because they have consistently given fine cell structure foam and thorough mixing from the beginning to the end of a continuous slab run.

The clearance between the housing and the agitator is very important. A clearance of 0.010–0.030 in. between the housing and the helical agitator will provide a high degree of mixing shear. The specific clearance to be used for a particular system is dependent on ingredient viscosities. Generally, higher viscosities require increased clearance.

Outlet Diameter. Restriction at the outlet of the mixing head creates slight back pressure and "floods" the bottom section of the mixing chamber which results in smooth flow from the chamber and prevents air entrapment. Excessive restriction of the orifice, however, tends to result in foam of increased cell size, which is undesirable.

Agitator Speed. Agitator speed may be increased or decreased to bring about a corresponding change in the degree of mixing. Normal speeds for the helical-gear and pin–paddle type agitators are 4000–6000 rpm.



PIN TYPE

PIN-PADDLE TYPE

HELICAL TYPE

FIGURE 4
Typical agitator designs.

Nitrogen Injection. Injection of nitrogen or dry air into the mixing chamber is recommended. This will provide additional cell nucleation which generally improves cell structure. At 125–150 lb per minute throughput rate, nitrogen or dry air injection rates of 0.25–1.0 standard cu ft/hr provide optimum results.

Outlet to Conveyor Distance. Smooth laydown of the foaming mix with a minimum of splashing is achieved by positioning the outlet close (approximately 2 in.) to the conveyor surface. If the mix is not deposited smoothly, striations may be present in the foam. If splashing occurs with resultant air entrapment, bubbles or elongated holes may occur. Both conditions have deleterious effects on foam properties.

Traverse Speed. Smooth laydown of the foaming mix is also dependent on traverse speed. Traverse speed must be uniform and equal in both directions and sufficiently fast so that each succeeding deposit of mix immediately flows into the preceding deposit to form a continuous flow. Too fast a traverse speed may cause splashing or uneven distribution of mix on the conveyor. Traverse speeds in the range of 30–40 strokes/min have provided smoothest laydown for most rigid slabstock systems.

Foaming Conveyor and Auxiliary Handling Equipment

Conveyor Design. The function of the conveyor is to provide a cavity in which the rising foam can be continuously foamed into a bun with the desired shape and dimensions. A rectangular cross section is normally desired to achieve maximum yields in slabbing and fabrication. This cross section is obtained by utilizing a conveyor with four synchronized drive belts on the bottom, sides, and top. Steel slat-type conveyors or synthetic-fabric belt conveyors supported by steel plates are normally used.

Tilt. It is necessary that the conveyor be tilted downward away from the mixing head so that the mix flows away from the mixing head immediately after being deposited on the bottom conveyor. This prevents succeeding layers of mix being poured on top of previous layers as the head traverses. This latter condition would result in defects (splits and knit lines, for example) in the bun. A tilt range of 6 to 10° is satisfactory for rigid-slab operations.

Release Paper. It is necessary to feed continuous rolls of release paper onto the moving conveyors to prevent the foaming mass from contacting the conveyor surfaces. Although operation with two rolls of release paper, one folded across the bottom and up both sides and one across the top, has been accomplished, more wrinkle- and tear-free operation is attained with four separate paper rolls. The bottom release paper must be folded 6 in. up each side, overlapping side papers, to contain the liquid mix. Silicone-treated paper promotes easy release from the foam at the conveyor exit.

Cutting Saw. The production unit is equipped with a saw to cut the continuous bun in convenient lengths for subsequent processing such as weighing, curing, and fabrication. Since the foam bun is moving continuously, the saw is mounted on rails to allow movement at the same speed as the bun. At the completion of the cut, it returns to the starting position on the rails.

Scale. A scale capable of weighing each cut length of bun is an advisable component of the production unit. This provides a positive check upon yield.

Storage. The buns must be cured for at least 16–24 hr to allow development of optimum properties and release of exothermic heat of reaction prior to further processing. Sixteen hours is recommended for a bun of 24 in. or less and 24 hr for a larger size bun. Therefore, a curing room with capacity for at least 16 to 24 hr of foam production should be provided. The room should be adequately ventilated to remove heat. The buns should be stacked with sufficient separation for cooling.

Operation

The control of a few important variables is necessary in the production of rigid-foam slabstock to achieve the best foam quality at a high yield rate. These variables and their effect on operation, quality, and yields are discussed in detail below.

Conveyor Speed versus Throughput Rate. To achieve maximum yield, a perfectly rectangular bun cross section is required. To achieve this, the rising foam must fill the conveyor cavity and conform to its contour. Thus, for a given conveyor opening and foam density, the conveyor speed is directly proportional to the throughput rate and expressed by the following relationship:

$$\text{conveyor speed (ft/min)} = \frac{\text{throughput (lb/min)}}{\text{density (lb/cu ft)} \times \text{width (ft)} \times \text{height (ft)}}.$$

At a throughput rate of 125 lb min, foam density of 2.0 lb/cu ft, and conveyor cross section of 3 ft × 2 ft, the theoretical speed would be

$$\text{conveyor speed} = \frac{125}{2 \times 3 \times 2} = 10.4 \text{ ft/min}.$$

The actual speed generally closely conforms to the theoretical speed. A significant decrease below this speed will cause overfill and usually result in extrusion of partially gelled foam from the openings between the side and top conveyors.

A significant increase above theoretical speed will cause underfill and result in a crowned bun with undesirable yield loss in slabbing. In actual operation, the conveyor speed at startup is usually slightly above theoretical. This is decreased during the first 1–2 min of operation until a good flat-top bun is achieved with no overfill.

Cream Line. The primary indicator of satisfactory foam formation in slabstock manufacture is the nature of the cream line. The cream line is that area on the bottom conveyor where the liquid mix flowing down the conveyor shows cell formulation and start of rise. It is observed by a lightening (or creaming) of the liquid mix. Satisfactory operation is evidenced by a cream line which shows "fingers" or "streamers" from 3 to 12 in. in length. A uniform defect-free bun usually results from this. If the liquid mix "undercuts," or flows beneath the rising foam, the "fingers" are not apparent and the foam bun will usually show splitting. Splitting causes considerable yield losses in fabrication. Undercutting usually occurs when the initial reaction rate is too fast and creaming occurs too close to the mixing head.

The position and nature of the cream line can be controlled by varying the level of stannous octoate catalyst in the formulation, the conveyor tilt, and/or stream temperatures. As stannous octoate is increased, the reaction rate increases and the cream line tends to move back up the conveyor toward the mixing head and toward a condition of undercutting. As the catalyst is decreased, the cream line moves down the conveyor away from the mixing head to a satisfactory condition. However, this catalyst also affects the latter stage of the reaction and excessive reduction will result in a bun that has not hardened before leaving the conveyor. This causes loss of bun shape.

The cream line may also be moved up or down the conveyor by decreasing or increasing conveyor tilt, respectively. This occurs because the liquid mix flows down the conveyor at a rate governed by the tilt. If the conveyor is equipped with a motorized tilt adjustment, tilt can be varied while running.

The cream line may also be moved up or down the conveyor by increasing or decreasing stream temperature, respectively. Warmer streams react (and cream) faster, while cooler streams react slower. Stream temperature cannot normally be adjusted while running, however.

The one-shot slab formulation detailed in Table 1, has a catalyst balance which permits a relatively broad latitude in stannous octoate level so that the level of this catalyst may be used as the primary control upon cream line and, hence, satisfactory foam formation. This is the most easily controlled variable affecting the foaming operation.

Yields. The prevention of yield losses due to bun shape is of primary importance in slabstock production. Maximum yields are achieved by making a perfectly rectangular bun (especially a flat top) and by squaring off the bun at the start and finish of each run. The recommended formulation provides a sufficiently slow foam gelation rate to permit "molding" of the foam to fit the rectangular contour of the conveyor. If rounded corners occur at the top of the bun, a slight reduction in stannous octoate catalyst or a slight reduction in conveyor speed will usually produce the desired square corners. At startup, the bun can be squared off by pouring several seconds of mix against a flat "dam" slightly smaller than the conveyor cross section prior to starting the conveyor. At shutdown, the bun can be squared off by pushing a similar dam against the rear of the foaming mix.

Balanced Operating Conditions. The manufacture of high-quality one-shot rigid urethane foam is markedly simple if proper operating conditions are maintained. Table 3 details a complete combination of conditions that has repeatedly resulted in successful processing.

TABLE 3

Process Conditions for Slabstock Production of One-Shot Rigid Urethane Foam

Formulation: See Table 1	
Mixing Head Design (Martin Sweets Company VMD-600, Pin–Paddle Agitator):	
Throughput, lb/min	125–150
Conveyor tilt, degrees	8–10
Premix temperature, °F	60–70
Polyisocyanate temperature, °F	65–75
Conveyor cross section	36–48 in. wide × 24 in. high
Conveyor speed, ft/min	9–11
Agitator speed, rpm	5,000–5,500

SUMMARY

It has been shown that the successful production of rigid urethane slabstock by the one-shot technique is accomplished by careful control of chemical and mechanical variables. As a result, foam of consistent quality and properties can be produced. These techniques are presently being employed in commercial operations to provide rigid urethane slabstock for rapidly expanding military and civilian markets.

REFERENCES

1. G. Gmitter and E. Jaul, "One-Shot Urethane Foam Production," *Plastics Technol.*, 28 (July 1963); G. K. Dono and G. G. Shelton, "The Technology and Applications of Flexible One-Shot Polyether Foams," *Chem. Ind.*, 1158 (June 30, 1962); E. J. Dwyer, M. Kaplan, E. L. Piver, and H. Stone, "Technology of Super-Soft Flexible Urethane Foams," *7th Annual Conference Proceedings, Society of Plastics Industry*, April 24–25, 1963.
2. B. Fisher, "Army Interests in Foamed Plastics," in *Foamed Plastics, Proceedings of a Conference* (Govt. Res. Rept. *PB181576*), April 22–23, 1963, p. 161; B. A. Domning, "Urethane Foam Packaging at the Air Force Packaging Laboratory," in *Foamed Plastics, Proceedings of a Conference* (Govt. Res. Rept. PB181576), April 22–23, 1963, p. 182; R. J. Palchak, "Field Foaming Systems and Devices," in *Foamed Plastics, Proceedings of a Conference* (Govt. Res. Rept. PB181376), April 22–23, 1963, p. 189; W. S. Brown, "Navy Interests in Foamed Materials," in *Foamed Plastics, Proceedings of a Conference* (Govt. Res. Rept. PB181576), April 22–23, 1963, p. 215.
3. E. A. Dickert, W. A. Himmler, D. E. Hipchen, M. Kaplan, H. A. Silverwood, and R. Zettler, "Molding of One-Shot Rigid Urethane Foam," *Chem. Eng. Progr.*, *59* (No. 9), 33 (1963).
4. M. R. Hallinan, W. A. Himmler, and M. Kaplan, paper presented at Society of Plastics Engineers Annual Conference, Feb. 2, 1962.

Design Considerations in Sandwich Panel Construction

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INTRODUCTION

The following paper is an attempt to give an introduction to the major points of sandwich panel design. It cannot, obviously, be a complete guide to deal with every problem that may occur in practice. It rather will serve as a summary of well-established theoretical principles and for the interested reader, a few points of the theoretical economy and design efficiency in the selection of properties and/or materials will be pointed out.

There are two main design criteria that must be considered in the development of any structure or structural element, namely, (1) adequate strength to stand up without failure against forces acting upon it; and (2) adequate rigidity, so that any deformations, either temporary or remaining, will not lead to deterioration and loss of strength, or create uncomfortable feelings in the persons using the structure, or be detrimental to other elements or accessories attached to it (for example, inadequate stiffness of a floor panel may create a sense of insecurity when people walk on it, or large deformations in a wall panel may lead to breakage of glass in the windows).

Let us consider the criterion of adequate strength. Every material deforms when subjected to loads and by resisting that deformation builds up internal stresses. As long as these stresses are kept within certain limits, depending on the properties of the material, the structure will stand up. However, if at some point or points the stresses created by the loads exceed the capability of the material, there the structure will fail. The failure could be local (i.e., equilibrium could still be maintained in the structure as a whole through automatic reorganization of the internal stresses) or it could be over-all failure (i.e., total collapse). Thus, to satisfy the criterion of adequate strength (a) there must be a reasonably thorough knowledge of stress distribution within the structure; and (b) materials must have adequate size and strength so that they will be able to resist the stresses and still offer suitable safety factors.

The second structural design criterion, adequate rigidity, has other controlling factors to be considered. Deformations and their control depend upon important mechanical properties of the materials involved. These are the modulus of elasticity and modulus of shear as represented by the stress–strain behavior of the material.

ON THE SAFETY FACTORS

In the preceding paragraph we have mentioned "safety factor," which in my opinion is the most abused technical term, probably because it is one expression everybody seems, or pretends, to understand. If I would have to choose one from a long list of "design considerations" that I consider the most important one, I would select the safety factor. I am convinced that more money has been and is being wasted continuously because of improperly selected safety factors than for any other single reason.

The subject is broad enough to warrant an entire paper. However, since this is not possible here, I will try to list the most important governing thoughts.

The possibility of any structural failure that may bring total collapse and endanger life and property has to be prevented. Other failures, which will not bring about an immediate structural collapse and may require only minor repairs, can be treated with lower safety factors. In establishing proper safety factors, one should clearly distinguish between overload and understrength.

The investigation of overload involves the possibility and probability of larger service loads (live loads) than the ones the structure was originally designed for. This is rather easy.

To estimate possible understrength, however, is a much more complicated business. Understrength, as the name implies, means lower strength in the structure than expected. The problem involves a thorough study of the following questions: (1) What is the expected average strength of the material? (2) What are the standard deviations in strength due to formulations or production methods? (3) If flaws in the material cannot be avoided, what are the chances of their occurring and what is the likelihood that they will occur in highly stressed areas? (4) Where flaws are likely to occur because of the method of production, will they create unsurmountable problems in the use of the structure? (For example, a shear flaw in the core of a sandwich panel parallel with the facing could lower substantially the bending capacity of the panel. At the same time, the panel may lose much less in its capacity to carry compression in its plane.)

Here we do not want to go too deeply into all the ramifications. It must be stressed, however, that different factors of safety may be assigned to different modes of failures. For example, this writer would like to recommend that larger safety factors be assigned to prevent a shear failure in a foamed plastic core than to prevent a tension failure in an aluminum skin. Since there are larger variations in the strength of foamed plastics, there should be a larger factor of safety assigned to the average ultimate strength of these materials.

BRIEF REVIEW OF DESIGN OF SANDWICH PANELS

The design of sandwich panels, like that of any other type of structural element, begins with the consideration of (a) type of loadings and (b) type of supports.

Generally speaking, these will adequately describe the internal stress distribution and the deformations in the panel, or, in other words, the relationship between the loadings and the internal stresses produced by them can be established with sufficient accuracy. For the computation of internal shears and moments, the assumption of elastic behavior and the appropriate equations of equilibrium are used. The assumption of elastic behavior may be questionable in local highly stressed areas (for example, in the immediate neighborhood of concentrated loads), however, we may assume that these will have "local" effects only, without disturbing the general internal stress pattern. It is recommended therefore that these areas be subjected to additional investigation after the general design and proportioning have been completed.

Once the internal moments and shears have been computed, the actual stresses in the skins and the core can be easily evaluated. The theory of sandwich and the functions of its components (i.e., skins and core) could best be described by an analogy to an I beam. In an I beam we may say the flanges carry the bending and the web is being used to support the flanges, to hold them apart in their respective position, to force them to act as a unit. In a sandwich panel, the skins (usually high-density and, relative to the core, high-strength material) correspond to the flanges of an I beam and the core corresponds to the web. One important advantage of sandwich panels is that while the light weight core acts like the web of an I beam in holding the skins apart and carrying the shear stresses, it also provides a continuous supporting medium for the skins, allowing them to work up to very high stresses without buckling or wrinkling. The adhesive bond between the dissimilar materials must be capable of transmitting shear, thus making the lamination an integral unit.

This analogy to the I beam is more apparent if we apply the method of transformed sections to the sandwich laminate.

Figure 1 shows the section of a sandwich. If we apply the well-known assumptions of the theory of elasticity, namely, the Bernoulli-Navier hypothesis, that planes remain planes after deformation and that strains are in linear relationship with stresses (Hooke's law), then the strain and normal stress distribution will be as shown in Figure 1. This shows that since the modulus of elasticity of the skins is much larger than the modulus of elasticity of the core, the skins will carry larger stresses than the core, and that this relationship depends on the ratio of their moduli of elasticity. Thus, if we designate

$$n = E_s/E_c, \tag{1}$$

the core material can be transformed into an "equivalent" skin material by reducing its width to b/n as shown in Figure 2. This so-called transformed section truly resembles an I beam.

The moment of inertia and the stiffness factor of such a section can be then written in the following forms, respectively:

$$I = \frac{b}{12}\left[\frac{t_c^3}{n} + 6t_s(t_c + t_s)^2\right], \tag{2}$$

$$E_s I = \frac{b}{12}\left[E_c t_c^3 + 6E_s t_s(t_c + t_s)^2\right]. \tag{3}$$

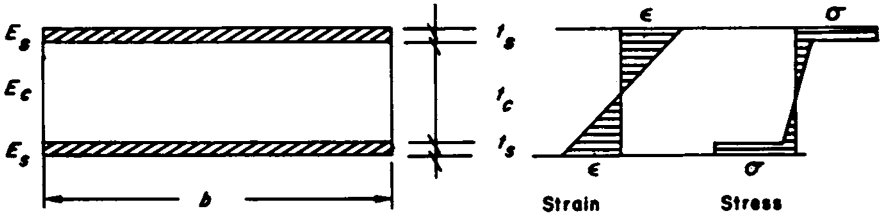
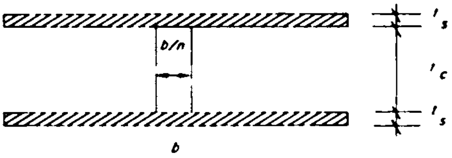


FIGURE 1
Sandwich section.

FIGURE 2
Equivalent skin material.



In "plate" problems, like the treatment of sandwich panels, the stiffness factor (flexural rigidity factor) is modified according to the theory of elasticity by a λ factor in the denominator which is defined as

$$\lambda = 1 - \nu^2, \tag{4}$$

where ν = Poisson's ratio of facing.

Hence:

$$N = \frac{b}{12\lambda}\left[E_c t_c^3 + 6E_s t_s (t_c + t_s)^2\right]. \tag{5}$$

This modification factor is usually close to 1 and, if it is omitted, it results in an error on the conservative side.

Once the bending moment acting on a b wide section is known, the stresses in the skins can be computed with good approximation as follows (see Figure 3).

The forces in the facings are created by the force couple representing the M moment.

$$\sigma_s = \frac{M}{b t_s (t_c + t_s)}. \tag{6}$$

This approximation is valid as long as $t_c \gg t_s$ and $E_c \ll E_s$.

Furthermore, once the shear force (see Figure 4) acting on a section is known, the shear stresses in the core can be computed with good approximation as follows:

$$\tau = \frac{V}{b(t_c + t_s)}. \tag{7}$$

This approximation is valid also as long as $t_c \gg t_s$ and $E_c \ll E_s$.

Besides the knowledge of stresses, as we mentioned before, the knowledge of the resulting deformations is equally important, for in many cases a certain maximum allowable deformation is the governing design criteria.

When a panel deforms, the forces acting upon it move along, therefore work is done by them. This work is stored in the panel in the form of elastic energy or strain energy. Since this strain energy can be readily evaluated, we are able to compute the deformations along which the loads

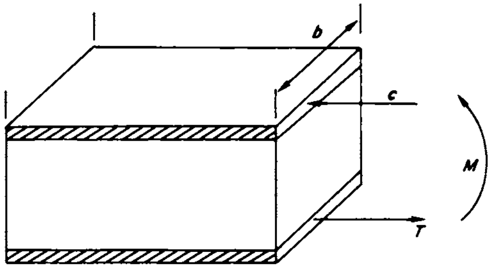


FIGURE 3
Role of stresses in the skin.

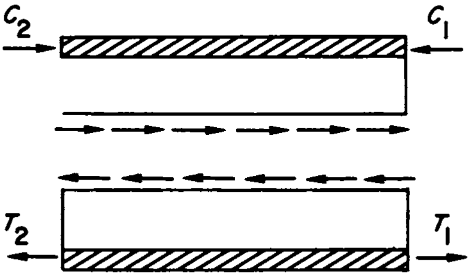


FIGURE 4
Role of the shear forces in the core.

have traveled. The strain energy on a panel in bending has two parts. One part is the energy stored in the deformations of the skins (or more properly in the deformations caused by the flexural stresses), the other part is the energy stored in the shear deformations of the core (or the work spent on deforming the core). A simple numerical check will convince that this latter part, which sometimes is negligible when we work with other structural materials, in the case of sandwiches, especially in those with low-density foamed plastic cores, the deflections caused by shear deformations constitute the major portion. For example, a 3 in. thick sandwich panel with 0.040-in. aluminum skins and a 2-lb/cu ft urethane foam core spanning over 100 in. deflects under 50-lb/cu ft loads approximately 0.6 in. About 60 percent of this deformation is contributed by the shear deformations of the core.

EXAMPLES OF A FEW LOADING CASES

Panel Supported along L_2, Uniformly Distributed Load

Looking at Figure 5:

$$M_{\max} = \frac{1}{8} wL_1^2 \text{ (lb-ft/ft width)},$$

$$V_{\max} = \frac{1}{2} wL_1 \text{ (lb/ft width)}.$$

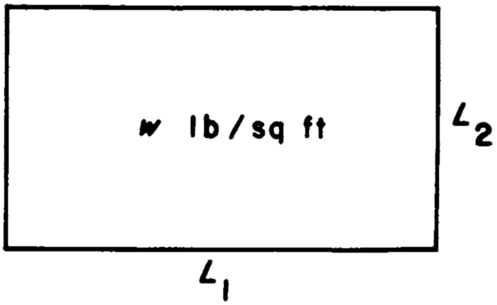


FIGURE 5
Uniformly distributed load, supported along L_2.

Maximum deflection:

$$\Delta_{\max} = \frac{5}{384N} wL_1^4 + \frac{1}{8G_c} \frac{wL_1^2}{t_c}.$$

Panel Supported on All Four Sides, Uniformly Distributed Load

$$L_1 > L_2,$$

$$M_{\max} = \beta wL_2^2,$$

$$V_{\max} = \gamma wL_2,$$

$$\Delta_{\max} = \frac{\alpha_1}{N} wL_2^4 + \frac{\pi^2 \alpha_1 \alpha_2 wL_2^2}{G_c}.$$

The constants α_1, α_2, β, and γ depend on the ratio of L_1 and L_2. Table 1 indicates the values for β and γ.

TABLE 1
Values for β and γ.

L_1/L_2	1.0	1.2	1.4	1.6	1.8	2.0	3.0	4.0	5.0	∞
β	0.048	0.063	0.075	0.086	0.095	0.102	0.119	0.1235	0.1246	0.1250
γ	0.420	0.455	0.478	0.491	0.499	0.503	0.505	0.502	0.501	0.500

It also can be seen from Table 1 that beyond the ratio of $L_1/L_2 = 3$ (elongated panel) very little "help" is received in carrying the loads two ways, and the computation can be simply made for the "one-way" case without undue error.

The values for α_1 and α_2 can be found in reference 2.

Sandwich Panel as Column Supported and Loaded along b

Looking at Figure 6:

Maximun skin stress

$$\sigma = w/2t_s.$$

Critical load

$$w_{\text{crit}} = \frac{\pi^2 N}{L^2 + (\pi^2 N/t_c G_c)}.$$

These formulas are good approximations as long as $E_s \gg E_c$. More accurate solutions may be found in references 1–3.

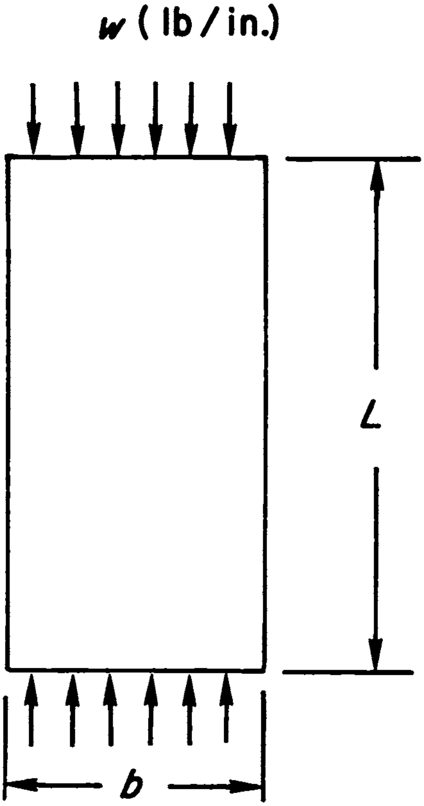


FIGURE 6
Panel supported and loaded along *b*.

PROPORTIONING SANDWICH PANELS

Selection of Skin Thickness to Produce Maximum Allowable Stresses Both in Skins and Core

By manipulating the well-known formulas of the previous section, very interesting relationships can be established. It is my belief that they have never been proposed in this form, therefore, I would like to describe them in some detail. The discussion shall, for easier understanding, be restricted to a symmetrical sandwich panel that has skins of the same material and the same thickness. This restriction does not limit the generality of the method proposed here, and, following the procedure outlined below, the reader should be able to work out the problem of nonuniform skins.

Suppose that the skin material has an allowable stress of σ_s, then the maximum allowable moment on a panel section of unit width can be written as follows:

$$M_{\mathrm{all}} = \sigma_s t_s (t_c + t_s). \tag{8}$$

If the core thickness is much larger than the skin thickness, that is if $t_c \gg t_s$, then

$$M_{\mathrm{all}} = \sigma_s t_s t_c. \tag{9}$$

The maximum moment in a panel with uniformly distributed loads can always be expressed in the following form:

$$M = C_1 w L^2, \tag{10}$$

where C_1 is a constant depending on the mode of support. (For example, in case of simple supports at two opposite sides $C_1 = 0.125$.) Thus, in case of "efficient" design

$$C_1 w L^2 = \sigma_s t_s t_c \tag{11}$$

and

$$w = \frac{\sigma_s t_s t_c}{C_1 L^2}. \tag{12}$$

Let us now assume that the kind of core material we intend to use has an allowable shear stress of τ_c, then the maximum allowable shear on a panel section of b width can be written as follows:

$$V_{\mathrm{all}} = \tau_c (t_c + t_s), \tag{13}$$

or if $t_c \gg t_s$, then with sufficient accuracy

$$V_{\mathrm{all}} = \tau_c t_c. \tag{14}$$

The maximum shear in a panel with uniformly distributed loads can be expressed as follows:

$$V = C_2 w L, \tag{15}$$

where C_2 is a constant depending on the mode of support. (For example, in case of simple supports on two opposite sides, $C_2 = 0.500$.)

Thus, in case of "efficient design," it is desirable that

$$C_2 w L = \tau_c t_c \tag{16}$$

and

$$w = \frac{\tau_c t_c}{C_2 L}. \tag{17}$$

If we now combine Equations (12) and (17), we obtain the following relationship:

$$\frac{\sigma_s t_s t_c}{C_1 L^2} = \frac{\tau_c t_c}{C_2 L} \tag{18}$$

or, after simplification,

$$\frac{\sigma_s}{\tau_c} = \left(\frac{C_1}{C_2}\right)\left(\frac{L}{t_s}\right). \tag{19}$$

It is of interest to examine Equation (19). It indicates that it is possible for a given size of panel (L) and given materials (skin and core) to select the thickness of the facing in such a way as to produce maximum allowable stresses in each material, because expressing t_s from Equation (12) we obtain

$$t_s = \left(\frac{C_1}{C_2}\right)\left(\frac{\tau_c}{\sigma_s}\right) L. \tag{20}$$

In Equation (20) the most interesting phenomenon is that if we want to utilize both the core and the skin material to their respective maximums, the selection of skin thickness will depend on the support conditions (C_1/C_2), the ratio of allowable stresses in the core and skins, and the span, but it is independent of the depth of the panel or the magnitude of the loads.

Example 1. Let us assume that we want to design a simply supported panel to span $L = 100$ in. The allowable stresses in the skins $\sigma = 10{,}000$ psi and in the core $\tau_c = 16$ psi shear.

In case of simple support $C_1 = 0.125$ and $C_2 = 0.500$.

Substituting these data in Equation (20), we get

$$t_s = \left(\frac{0.125}{0.500}\right)\left(\frac{16}{10{,}000}\right) 100 = 0.040 \text{ in.}$$

and this says that when this skin will be stressed to 10,000 psi by some uniformly distributed loading over a 100-in. span, then the core will have, regardless of its thickness, been stressed to 16 psi. It is obvious that the core thickness will enter into the design when the depth is chosen to satisfy one of the following equations:

$$\sigma_s = \frac{M}{t_s t_c}, \tag{9a}$$

$$t_s t_c = \frac{C_1 w L^2}{\sigma_s}. \tag{12a}$$

Selection of Core Density

By further manipulation of Equation (20), interesting guidance can be obtained for the selection of the core quality (density).

It is known that the mechanical properties of urethane foams can be expressed with exponential functions of the density as independent variables.[4] Although little information of that sort is available with respect to other foam plastics, presumably some similar relationships can be obtained for these. Thus,

$$\tau = A(D)^B, \tag{21}$$

where A and B are constants and D is the density of the core material.

Expressing τ_c from Equation (20) and combining it with Equation (21), we obtain

$$\left(\frac{C_2}{C_1}\right)\left(\frac{\sigma_s t_s}{L}\right) = \frac{A(D)^B}{S}, \tag{22}$$

where s is a properly selected safety factor for the core material. (The formulas in Stengard's work[6] are for ultimate strength.)

Solving Equation (22) for D we obtain

$$D = \left[\left(\frac{S}{A}\right)\left(\frac{C_2}{C_1}\right)\left(\frac{\sigma_s}{L}\right) t_s\right]^{1/B} \tag{23}$$

or solving for t_s we obtain

$$t_s = \left(\frac{A}{S}\right)\left(\frac{C_1}{C_2}\right)\left(\frac{L}{\sigma_s}\right)(D)^B. \tag{23a}$$

Example 2. Assume as before that $\sigma_s = 10{,}000$ psi and $L = 100$ in. in a simply supported panel with a urethane from core. Formula (21) for urethane foam is as follows:

$$\tau = 14.9(D)^{1.077}$$

or, according to our notation,

$$A = 14.9,$$

$$B = 1.077,$$

with a factor of safety of 2 against shear failure

$$D = \left[\left(\frac{2}{14.9}\right)\left(\frac{0.500}{0.125}\right)\left(\frac{10{,}000}{100}\right) t_s\right]^{1/1.077} = (0.53.6t_s)^{0.929}$$

For example, if $t_s = 0.040$,

$$D = (2.15)^{0.929} = 2.04 \text{ lb/cu ft}.$$

REFERENCES

1. H. W. March, *Sandwich Construction in the Elastic Range,* ASTM Spec. Tech. Publ. No. 118, Am. Soc. for Testing and Materials, Philadelphia, Pa. (1951), p. 32.
2. J. J. Zahn and S. Cheng, *Edgewise Compressive Buckling of Flat Sandwich Panels,* Forest Products Lab., Madison, Wis. (Feb. 1964).
3. W. R. Kimel, *Elastic Buckling of a Simply Supported Rectangular Sandwich Panel,* Forest Products Lab., Madison, Wis. (Sept. 1956).
4. R. A. Stengard, *Properties of Rigid Urethane Foams,* Du Pont Tech. Publ., Du Pont, Wilmington, Del. (June 1963).

BIBLIOGRAPHY

S. Timoshenko, *Strength of Materials,* 3rd ed., Van Nostrand, Princeton, N.J., Part 1 (1955), Part 2 (1956).

R. M. Darvas, "The Theoretical Economic Relationship between Core and Skins of Sandwich Panels," presented at SPE Reg. Meeting, Buffalo, N.Y., 1964; reprinted in *Mod. Plastics, 41* (10), 125 (June 1964).

SESSION 5

Application of Cellular Materials

Chairman, IRVING N. EINHORN
Wayne State University

Trends in Equipment, Application Techniques, and Use of Rigid Urethane Foam

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INTRODUCTION

The first foam plastics review was held for the U.S. Natick Laboratories in Boston in April 1963.[1] At that time several new equipment features, application techniques, and uses for foam plastics were presented. The 1963–1966 interval has seen the commercial demonstration of many of these advances. All indications are that the next 3-year interval will be as active as the last in the continued refinement and practical demonstration of the basic technology already developed. This discussion will be confined to rigid urethane foam. We believe this material, commercially available in quantity, will be of greatest interest since many of the developments can be applied, with little modification, by the military. This paper is based on available published information and will include a discussion of trends that can be expected in equipment, application techniques, and uses.

Rigid urethane foam is an established material, useful for many end-product applications in the refrigeration, transportation, and structural insulation fields.[2,3] The chemistry of urethane foam has been well documented and need not be reported here.[4] Urethane foam is adaptable to factory or field application since the foam is formed *in situ* by the reaction of easily transportable liquid feed streams. Additionally, rigid urethane foam is a durable, strong, low-cost, and effective insulating material. The structural, insulating, foam-in-place qualities of urethane foam have already placed this material in applications ranging from surf boards to ships[3] and have opened new design possibilities ranging from new structural concepts to space applications.[5-7]

URETHANE FOAM PROCESSING

Urethane foam can be poured or sprayed as a liquid or as a froth. Figure 1 differentiates between these two basic systems.[8]

The most distinguishing feature of frothing, relative to conventional foaming, is that the reactive urethane mixture has the appearance of an aerosol shaving cream as it discharges from the processing equipment. In conventional, i.e., nonfroth processing, the reactive urethane mixture discharges from mixing equipment as a liquid. In either process, the liquid reactive urethane mixture ultimately expands 30 to 45 times. In the conventional process, all the expansion takes place after the material has been deposited. The froth process is a two-stage expansion system. The material expands 10 to 12 times as it leaves the mixing equipment with only a three- to fourfold expansion after material deposition. These two basic foaming systems provide versatility since both can be used to meet specific needs in the factory or the field. The major equipment difference is that in frothing the mixer is operated under pressure (60 to 100 psig), while in conventional foaming the mixer is operated at atmospheric pressure.

Figure 2 lists the application techniques that utilize the basic foaming systems described.

The choice of the basic foaming system used with these application methods will be largely controlled by the end-product application.

Figure 3 illustrates the basic processing steps and their relation to the application techniques.

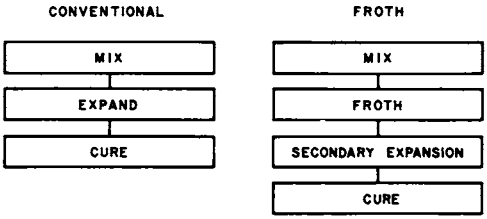

FIGURE 1
Comparison of foaming processes.

FACTORY

PREFORMING (MOLDING)

SLAB

LAMINATES

POSTFORMING

FIELD

POUR-IN-PLACE

SPRAY

RIGIDIZATION OF FLEXIBLE STRUCTURES

FIGURE 2
Foam application methods.

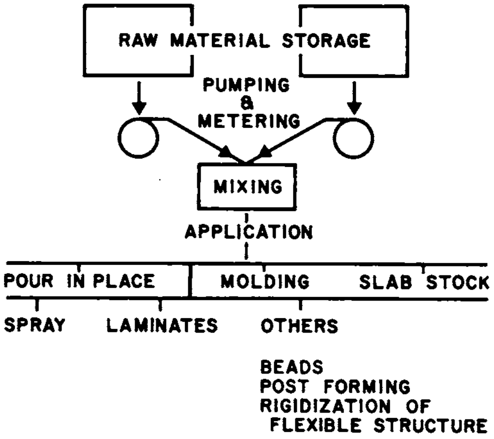

FIGURE 3
Urethane foam processing steps.

URETHANE FOAMING EQUIPMENT

The complexity of the equipment required for the production of urethane foam depends on whether it is frothed, sprayed, or poured. It will also depend on whether the material is being factory or field applied. The following brief review describes the equipment now used which is expected to find continued use in urethane foam production.

AUXILIARY EQUIPMENT

The auxiliary equipment, e.g., storage tanks, pumps, and heat exchangers, used are, in general, common to the foam application methods shown. We do not anticipate major changes in the auxiliary equipment used for foam production. However, refinements can be expected that will result in greater reliability and temperature and metering control under varying conditions. Some of the equipment now used in other chemical processes will continue to be adapted to urethane foam production.

Raw Material Storage

Steel is commonly used as the material of construction for raw material storage tanks. The main storage requirements are temperature maintenance and exclusion of moisture, sufficient to ensure that the raw materials will remain liquid and homogeneous. The raw materials are generally stored between 60 and 90°F with an allowable ±2°F temperature variation. To prevent raw materials loss, it is common practice to pressurize the masterbatch storage.

Heating

Process-stream temperature control is important since temperature variation can adversely affect processing reproducibility, primarily foam reaction time and foam density. Temperature control is obtained by installing heat exchangers in the feed stream and recycling to storage. A ±1°F temperature variation is usually specified.

Pumping–Metering Units

Pumps are used to transport the liquid feed streams to the mixer. The pumps in current use are reliable, accurate, and provide flexibility to the modern foaming operation. The pumping units serve a threefold function: (1) liquid recycling for temperature maintenance, (2) transportation of reactant feed streams to the mixing unit, and (3) metering of the feed streams. The pumps currently available are capable of outputs ranging from a few grams/minute up to 1,000 lb/min, pressure operation up to 3,000 lb/in.^{2} gauge, with a metering accuracy of ±1 percent. The pumping–metering units are usually supplied by equipment as a package. The package units include storage tanks, metering pumps, the heat transfer unit, and associated controls for regulating temperature, pressure, and flow. The pumps used are usually positive displacement and include pneumatic piston, vane, gear, and submerged types. The complexity of the metering units depends on the number of feed streams which can range from two to six.

MIXING

Mixing is critical to the production of high-quality urethane foam. The mixing units now available are capable of operating over a wide range of outputs and have minimum weight and bulk. They operate either intermittently or continuously and are designed to be portable or adaptable to factory or field use. The mixers are capable of efficiently blending the several feed streams of widely different viscosities and ratios.[1,2,9]

Most machine builders utilize a recirculating system in combination with the mixer since it assures constant temperature and uniform flow of the feed streams. The material leaves the metering unit, pumps through a three-way valve, and returns to storage. To produce foam, the three-way valve is automatically moved into the pour position; the feed streams, at the proper temperature and ratios, are introduced into the mixing chamber. Internal recirculatory mixer assemblies have pressure balancing devices to maintain accurate flow. The feed streams can be blended by the use of high-pressure feed streams,[1,10] air,[11] the use of helix mixers,[12] or power-driven mixers. Power-driven mixers have taken on many shapes: cylindrical agitators are straight in the outside diameter with flutes cut in their entire length; and three-section tapered agitators have a basket section, mixing section, and pumping section. Straight-pin agitators and "Christmas tree" pin agitators are also used. Specialized mixers have been developed for froth mixing. Figure 4, a—e, shows typical mixers now in use.

One of the more interesting developments in pumping–metering–mixing units is the use of prepackaged urethane foam reactants, hydraulic pressure with frothing, and a helix mixer.[13,14] This system, shown in Figure 5, is being used in the field for small pour or spray applications.

MOLDING—FACTORY APPLICATION

Urethane foam is widely used for molding. The change from liquid to foam provides a convenient means of distributing the foaming mass and allows the formation of intricately shaped articles. Foam formation, however, involves pressure generation. This imposes restraining problems and requires the design of suitable molds to contain the foaming mass.

Material distribution is important in molding to minimize foam breakdown, excessive pressure generation, and subsequent loss of foam quality. The foam ingredients discharging from the mixing head can be distributed by reciprocation of a single head, the use of multiple heads operating simultaneously (Figure 6), or by spraying. All of these techniques are used to minimize pressure and the associated problems of foam flow and subsequent foam breakdown.

Frothing has been instrumental in reducing the pressure generated during molding and in reducing shear and pressure generation. Frothing provides the following:

Lower mold pressures during foaming
Lower foam density
More uniform density throughout the finished foam
Simplified void filling, since froth can be deposited directly on expanding foam with less foam collapse and density variations
Self-nucleation
The use of froth minimizes the need for tight sealing of the mold to prevent material loss during filling
The molds or hi-rise forms can be bottom filled

Significant strides in frothing equipment and techniques have been made. Froth equipment is now available for factory use, gives reproducible products, and is easy to use (Figure 7).[15]

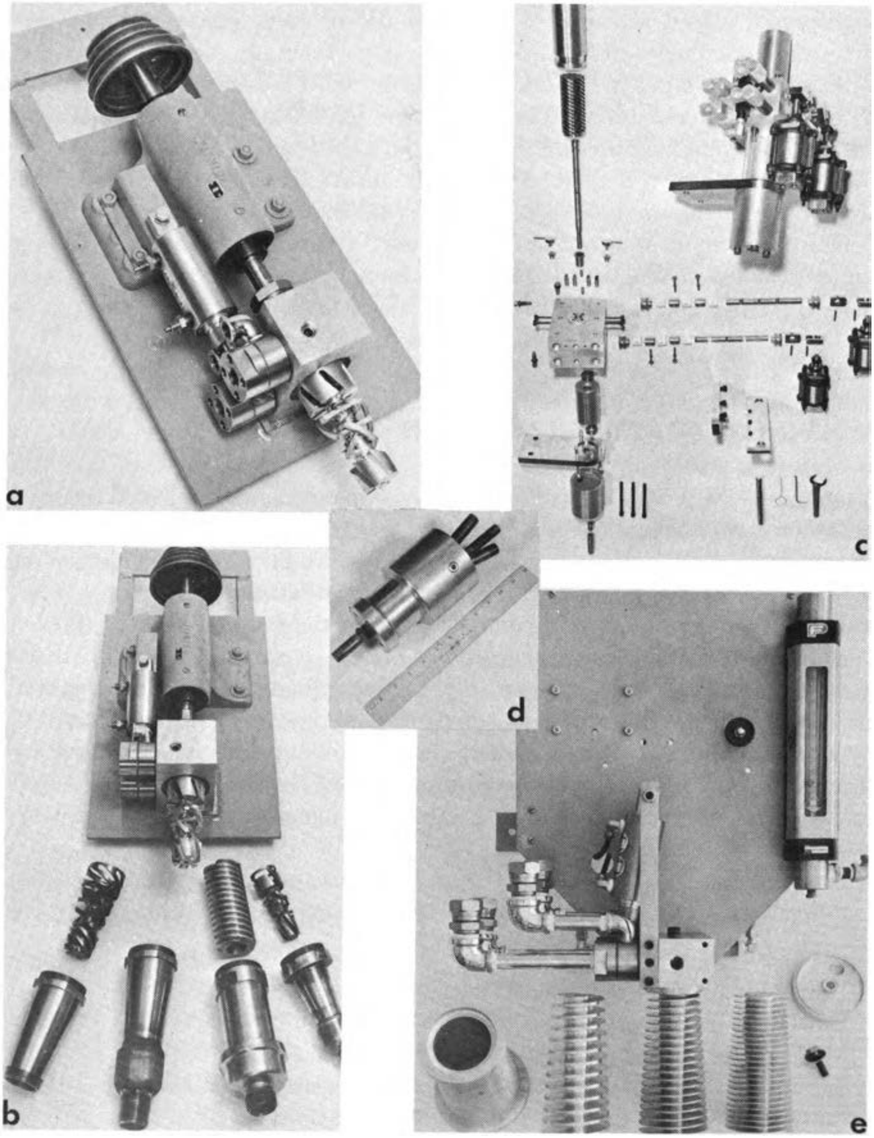

FIGURE 4

a. Power-driven three-stage mixer assembly.

b. Power-driven mixers.

c. Mixer assembly—exploded view.

d. Helix mixer.

e. Helix mixer assembly.

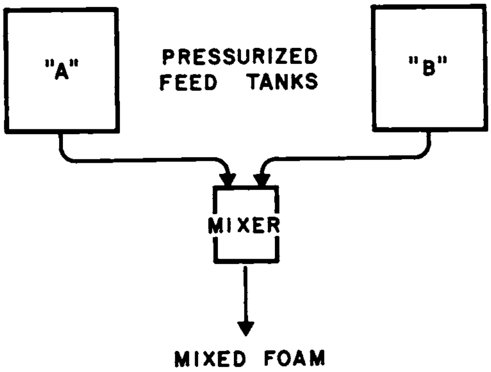

Figure 5
Prepackaged froth unit.

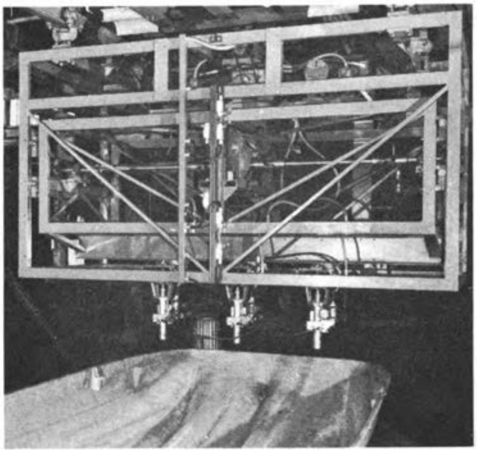

Figure 6
Multiple-head foaming equipment.

Figure 7
Insulating trailer with frothed foam.

FIELD APPLICATION

Although the same foaming processes previously described are applicable in the field, changes in equipment are required since the auxiliary services readily available in the factory are not always present in the field. Additionally, the field equipment used for pouring must be simple, rugged, portable, and reliable.

Field machines are used to apply urethane foam to an object or structure at the point of use of the finished product. The output may vary from 1 lb/min up to 500 lb/min or more. The larger units may be built onto pallets or truck trailers or broken up into segments for movement and reassembled at the next job site. "Back pack" foaming units are being used for small pour foaming applications.[16]

For field applications, the raw materials are usually preblended at the chemical producer's factory to minimize the number of components transported and mixed on the job. Special drum pumps are used to transfer the

FIGURE 8
Field pour.

chemicals by hose to the foaming equipment. The metering pumps may be a few feet or several hundred feet from the mixing head. The mixing head may be hand held, mounted on a boom, or overhead-trolley mounted. The metering unit optionally may include temperature and recirculating flow control. Figure 8 shows a typical field pour application.

FACTORY SLAB PRODUCTION

The technology and equipment developed for resilient urethane foam production is applicable to rigid-foam production. The basic difference is the pressures generated during foaming. This problem is overcome by the use of conveyors equipped with moving sides. The technology developed is well documented and need not be discussed in great detail here.[2,3] The production of slabstock is usually continuous (although it need not be). The primary objective is to produce a rectangular bun to provide a maximum volume of usable foam. Examples of the equipment used for slab production are shown in Figure 9, a—c.

SPRAYING

The spray applications of rigid urethane foam are diverse.[11] The equipment used to spray foam has been developed to the point that it is rugged,

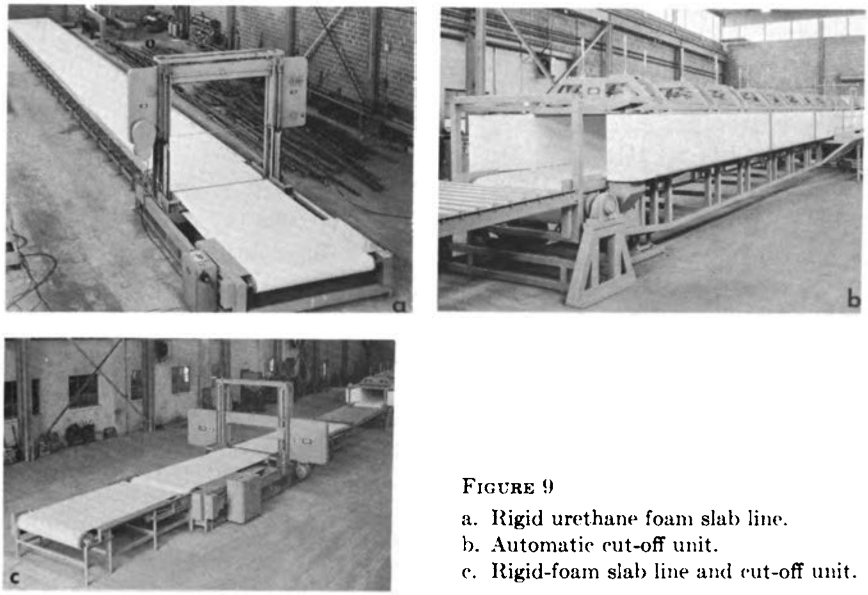

FIGURE 9
a. Rigid urethane foam slab line.
b. Automatic cut-off unit.
c. Rigid-foam slab line and cut-off unit.

portable, reliable, and easy to operate. The heart of the system is the pumping units and the mixer.

Current equipment utilizes pumps (either piston, gear, or submerged types) whose output rates are variable, but can be fixed or interlocked to assure a constant ratio of feed streams. Thus the output can vary, but the feed streams will always be in the correct ratio.

Spray equipment is used to apply foam, in a largely atomized condition, onto a vertical, horizontal, or curved surface. Flow rates of the hand-held units are normally restricted to 1 to 8 lb/min. Machine-mounted "spray" heads have been operated at flow rates as high as 40 lb/min.

The following types of mixers are used for foam spray applications:

External-mix air-atomization guns (Figure 10) pass the foam components through the gun under pressure and eject them in separate streams. Mixing and atomizing are accomplished simultaneously in an air blast from a specially designed nozzle, just as the components leave the gun.

Internal-mix air-atomization guns (Figure 11) mix the two reactant streams internally by an air-driven agitator. On discharge, a blast of air atomizes the single stream of mixed ingredients.

Internal-mix airless atomization guns (Figure 12) mix the component streams under high pressure. Atomization is accomplished on discharge by pressure drop through the mixing zone and across the nozzle.

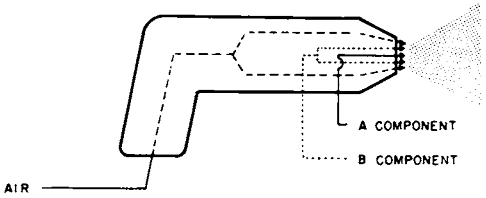

FIGURE 10
Rigid urethane foam spray gun: external-mix air-atomization type.

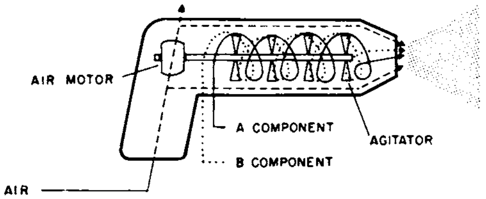

FIGURE 11
Rigid urethane foam spray gun: internal-mix air-atomization type.

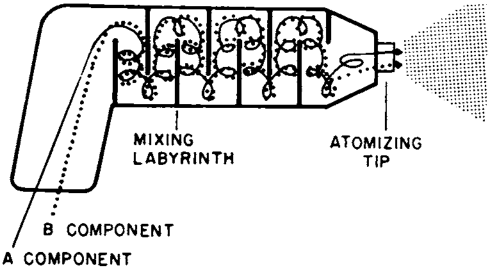

FIGURE 12
Rigid urethane foam spray gun: internal-mix airless atomization type.

In froth spraying (Figure 13) the material is mixed internally and deposited on target, not as a liquid, but as particles of froth of shaving cream consistency. The froth stream is made particulate by the external application of moderate velocity air jets.

Field application equipment should be capable of being easily converted from spraying to pouring.

The froth spray system is adaptable for either pouring or spraying.[11] Froth spraying has several unique features; these include:

Minimized foam run-off from vertical surfaces
Sprayed foam thickness more easily judged
High deposition rates
Ready application to cold surfaces
Low overspray
Efficient utilization of expanding agent
Uniformly applied foam density

Simple low-cost froth spray units are now available for field application (Figure 14).[14,17]

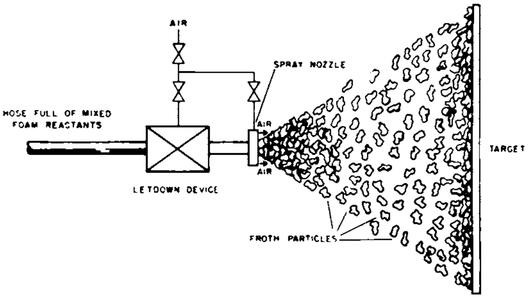

Figure 13
Preferred froth spray system.

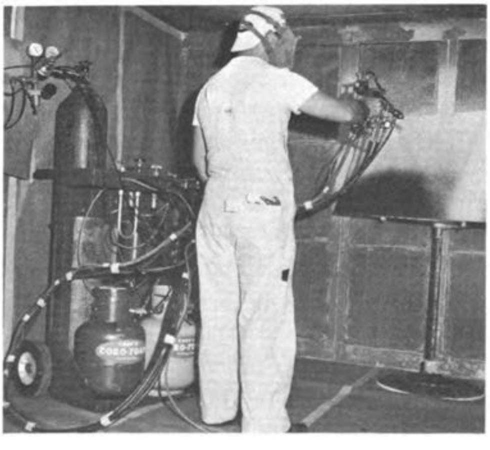

Figure 14
Prepackaged froth unit.

TRENDS

The equipment and basic application techniques described will continue to be used for the production of rigid urethane foam. There will be refinements in the basic application techniques. These improvements will include the further development of portable equipment capable of operating in the field under adverse conditions, increased use of automatic and remotely operated equipment to ensure a high degree of reproducibility and reliability in the end product, and increased use of prepackaged systems for foam application in the field.

Equipment refinements are expected: for example, increased use of rapid temperature response, in-line heat exchangers for minimum feed-stream heat exposure, and pumps that will deliver the reactants with greater metering accuracy. To improve metering accuracy, the use of pumps operated in series, the first to maintain pressure and the second to meter, can be expected.

No major changes are expected in mixing equipment although refinements will occur. For example, development of nonplugging units and units capable of maintaining constant feed-line pressures, particularly for highly viscous materials, is needed. The design of mixers continues to be largely empirical. When mixing theory is refined sufficiently to predict mixing efficiency, low-power mixers with low heat generation will be developed. The use of electromagnetic wave energy to mix polyurethane foam has been reported[18] as a means of improving cell uniformity. Several refinements in froth generation equipment have been recently reported.[19]

Molding applications will continue to increase with a definite trend toward highly instrumented and automated equipment. This will improve reliability and reproducibility in the end product.

In terms of equipment and technique, only minor changes are expected to occur in slabstock production. An increase in the utilization of slabstock is expected in a variety of end applications, particularly in the use of sandwich panel or laminate construction. However, continuous foamed-in-place laminates may replace slabstock in many construction applications.

The spray equipment now being used appears adequate; however, increased emphasis can be expected in the use of compact reliable units that are capable of operation under adverse field conditions. Electrostatic spraying has been demonstrated.[20] It does not appear to have major significance at this time in light of the advances being made in the current spray application methods.

Urethane foam components, being liquid and generating heat to form an *in situ* foaming process, have not been utilized in processes such as are used for polystyrene production, i.e., extrusion and beads. There is no fundamental reason to assume that urethane foams could not be produced by extrusion techniques or in the form of free-flowing beads. The production of shaped products by the simple extrusion of product through an orifice, although not demonstrated, is of continuing interest because of the elimination of molds.

Postforming, i.e., shaping of urethane foam into finished form, has been demonstrated.[21] This process takes advantage of the thermoplastic qualities of rigid urethane foam before final foam cure. An extension of this technology might be adapted to the spiral generation process[22] now used for polystyrene foam.

The rigidization of flexible structures with rigid urethane foam is being investigated by the University of Michigan.[23] This represents a potential application area for urethane foam.

There will be continuing efforts to complement the equipment and application techniques by developing foam formulation systems or new raw materials that are specifically designed for the end application.

APPLICATION AREAS

The most significant future trends that are anticipated to occur in the rigid urethane foam field will be in the utilization of the foam after it has been dispensed from mixing equipment.

The following discussion will cover the current uses of rigid urethane foam (Table 1) and the changes that are anticipated.

TABLE 1
Uses for Rigid Urethane Foam

Portable refrigeration	Refloatation
Semipermanent freezer rooms	Miscellaneous field applications
Refrigerated transportation	Mine sealing
Laminate structures	Pipeline applications
Structural insulation	"Building in barrels"

Portable refrigeration units range from small coolers (2–3 cu ft) up to 20–25 cu ft in size. This represents the largest current use of rigid urethane foam. Figure 15 shows typical equipment for a foamed-in-place application. Portable refrigerators utilize foamed-in-place, cut slabstock, premolded panels, or frothed foam.

The improved thermal efficiency, strength, and processibility of rigid urethane foam has enabled the refrigerator manufacturers to utilize new design and styling concepts. For example, the most recent development in refrigerators is the "side-by-side door"—one side a freezer and one a

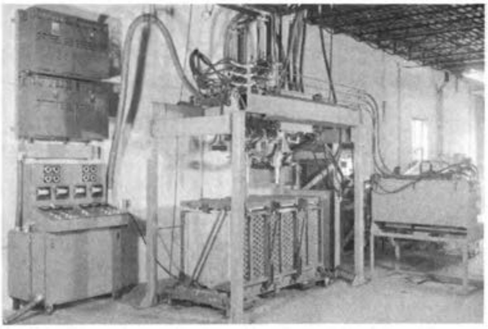

FIGURE 15
Equipment for foaming refrigerators.

refrigerator. These units are designed for foaming-in-place and utilize the strength of the metal–foam panel. The sealed foamed-in-place technique produces the most efficiently insulated units.

Semipermanent freezer rooms include the walk-in type and large warehouses for frozen-food storage. Rigid urethane foam is used in these applications because of the combination of strength and insulating properties, making possible factory premolding of foamed-in-place panels which are designed to interlock. The interlocking system facilitates field erection, disassembly, and movement. Panels of this type may also be manufactured

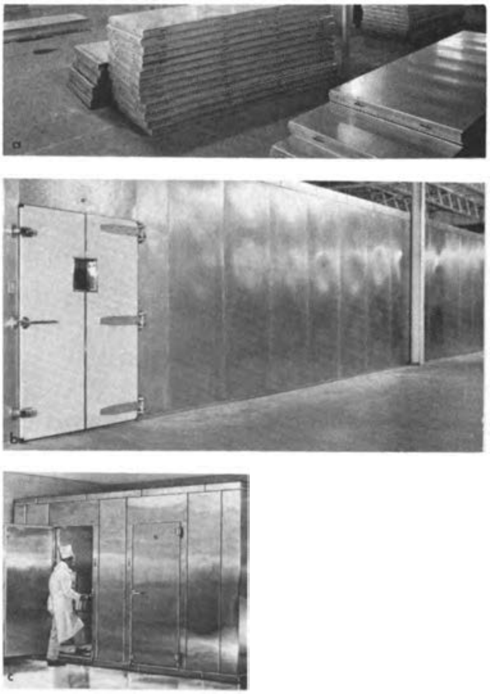

FIGURE 16
a. Prefoamed panels.
b. Freezer room assembled from prefabricated panels.
c. Walk-in freezer prefabricated urethane panels.

using cut slabstock and laminated skins, but some of the unique features of the foamed-in-place interlocking system may be lost.

The prefabricated interlocking technique lends itself to preinsulated living quarters. This could include movable or fixed barracks or even the residential home construction market. Figure 16, a–c, shows molded panels and an assembled unit utilizing the interlocking technique.

Refrigeration transportation includes trucks, commonly called reefers (Figure 17a); liquid chemical tanks (b); railroad cars (c and d); and ships (e).

Stringent regulations govern the transportation of frozen foods. Rigid urethane foam has found general acceptance because of its insulating properties and strength, leading to thinner wall construction which increases the container's usable volume and payload. The following illustrates

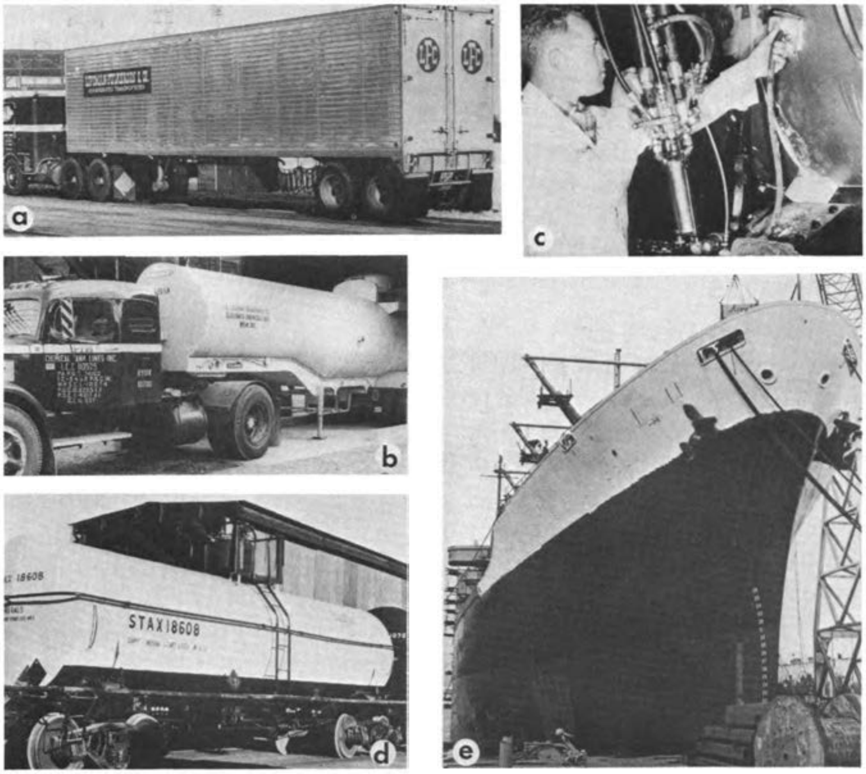

FIGURE 17

a. Truck trailer insulated with rigid urethane foam.
b. Urethane foam insulated tank trailer.
c. Froth filling a railroad tank car.
d. Finished urethane froth-foamed insulated car.
e. Urethane foam insulated refrigeration compartments.

the increase in insulating efficiency resulting from the use of urethane foam in reefers.[24]

	Urethane	Nonurethane Insulation
Rate of heat loss through walls Btu/hr at 100°F	5–6000 (4-in. insulation)	12–14,000 (6-in. insulation)
Air leakage rate, ft^3/min	1.5–3	25–50
Rate of insulation weight gain, lb/hr	0.2–0.4	2.5

Urethane foam insulated trailers retain their efficiency as the following illustrates:

	Heat Loss, Btu/hr/100°F	Air Leakage Rate, cu ft/min
Original	5,400	4.5
Aged 3 years	6,800	4.5

Air leakage minimization is important since an air leakage of 10 cu ft/min represents a heat loss of ~2,000 Btu/hr/100°F.[25]

LAMINATES

Rigid urethane foam panels are finding increasing use in the building industry. Foam lamination is the production of rigid urethane foam having a facing material. The laminate can be formed by bonding the appropriate facing material to cut slabstock or it can be formed *in situ* in a continuous molding operation.

Rigid urethane foam is a good laminate or structural panel material. It can be made in low density having fine cell structure and good strength properties. Structural or sandwich panels were developed in the early days of the Second World War primarily by the U.S. Forest Products Laboratory in connection with honeycomb wing construction of fighter planes. A structural sandwich is defined as a layered construction formed by bonding two strong thin facing materials to a thick low-density core. While the latter must provide sufficient shearing resistance, the primary purpose of the foam is to hold the facings parallel.

Several patents and published articles attest to the current interest in rigid urethane foam in sandwich panel applications.[26] Rudkin and Gallagher have recently described a continuous process for sandwich panel production.[27] The process developed takes advantage of the pour-in-place technique and adhesive qualities of urethane foam to laminate continuously various types of skins to a urethane foam core. The foam is sprayed or poured in place between two facing sheets. The foam rises to fill the space between the facing sheets and the adhesive characteristic of the urethane foam securely bonds the skins to the foam core. The sandwich is then cured in an oven and finally it is cut to size at the end of the line (Figure 18).

This process can utilize almost any type of skin. Sandwich panels have been produced with various types of surfaces, such as paper, metal foil, asphalt felt, and plastic. Metal skin sandwich panels are being produced in Canada and Europe.[28] Typical applications for sandwich panels are given in Table 2.

Interest continues in the architectural and structural application of rigid urethane foam. Crandall has recently reported on the use of paper-laminated urethane foam as a structural material.[23] Oberdick has demonstrated the practicability of using spray-applied rigid urethane foam in simple or complex geometric designs. Reinforced structures can be readily formed without the use of molds.[29] A new concept in mass-produced low-cost housing has been introduced.[30] The new type of house comprises two one-piece sections which, when joined together, form the roof and walls of the building. The sections are made of rigid urethane foam faced on both sides with bleached Kraft paper and a coating of white polyethylene. This fold-out rigid urethane foam house is assembled in a reported 45 min.

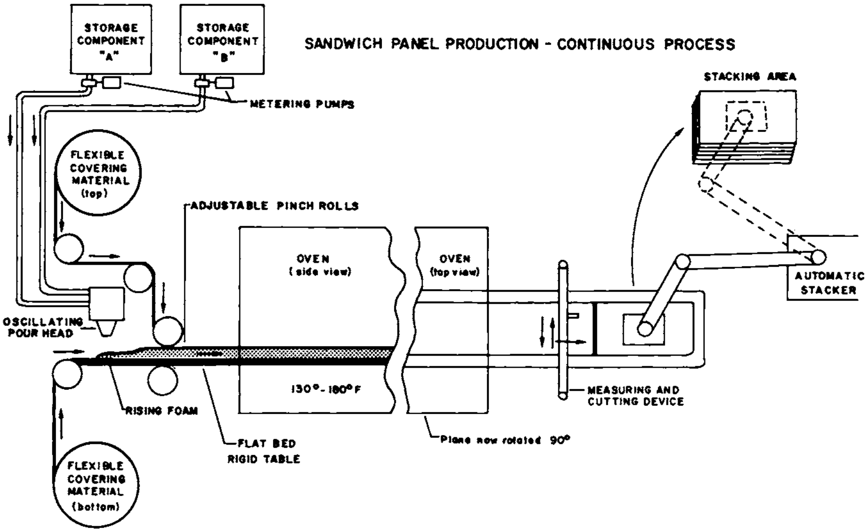

FIGURE 18
Sandwich panel production—continuous process.

TABLE 2
Typical Applications for Sandwich Panels

Application	Skins
Roof insulation	Asphalt–Chipboard
Plaster base	A lathing paper
Dry wall base	A dry-wall paper
Dry wall	A dry-wall paper
Perimeter insulation	Asphalt–Kraft
Duct insulation	Steel foil–Aluminum
Sheeting	Foil
Form board	Chipboard
Drop-in ceiling tile	Chipboard
Packaging	Decorative acoustical
Acoustical board	Depends on type
Display board	Acoustical
Low temperature	White Kraft
Insulation	Brown Kraft
Core material	Kraft–Chipboard

STRUCTURAL INSULATION

The use of structural insulation represents a large growth area for rigid urethane foam. Kennedy and Bennett have classified 11 general areas of application.[31] These range from cavity wall to roof insulation (Figure 19). Frothed rigid urethane foam has been used as perimeter wall insulation in several high-rise buildings.[32] The CBS Building in New York City utilized frothed-in-place rigid urethane foam.

Figure 20 illustrates another application of foam-in-place techniques. The studs in this application are cut urethane slabstock. To the studs are

FIGURE 19
Roofing insulation laminated board stock.

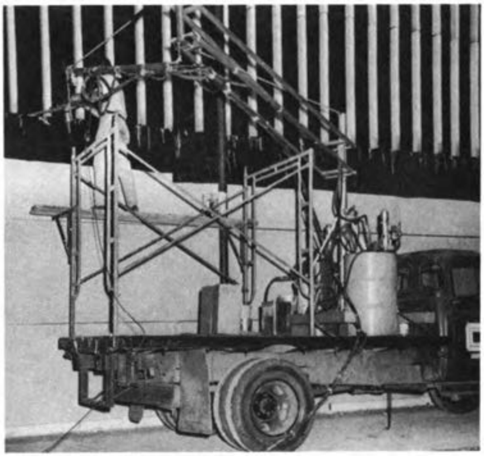

FIGURE 20
Urethane foam insulated warehouse.

secured the interior skin, and foam is then poured in place. The floor and roof also use foam to ensure maximum insulation efficiency.

Rigid urethane foam has been used for residential insulation. The technology is already developed to utilize spray-in-place, cut slabstock, and laminated panels.

An interesting concept in the structural–insulation uses of urethane foam is the development of plastic cargo containers reported by Reeves and Scollay.[33,34] The containers are formed from rigid urethane foam blocks, faced with glass fiber sheets and then bonded into an integral internally reinforced unit by a resin polymerized *in situ*. The resulting reinforced containers are strong efficiently insulated units which have found utility in military applications (Figure 21, a and b). Perhaps the most interesting aspect lies in the possibilities of fabricating very large units for commercial transportation applications.[35]

The commercial production of building panels by spray techniques has been reported by Ratto.[36] The uniqueness of this operation lies in the uniform distribution of foam on corrugated and curved surfaces. Uniform thickness is achieved by maintaining a constant distance between the spray nozzle and the panel. The constant distance is maintained by a servomechanism which raises and lowers the spray nozzle as it reciprocates across the panel face (Figure 22, a and b).

REFLOATATION

The Department of the Navy has been supporting feasibility studies on the use of urethane for refloatation. The Atlantic Research Corporation concluded that "a foamed salvage method is estimated as taking less than

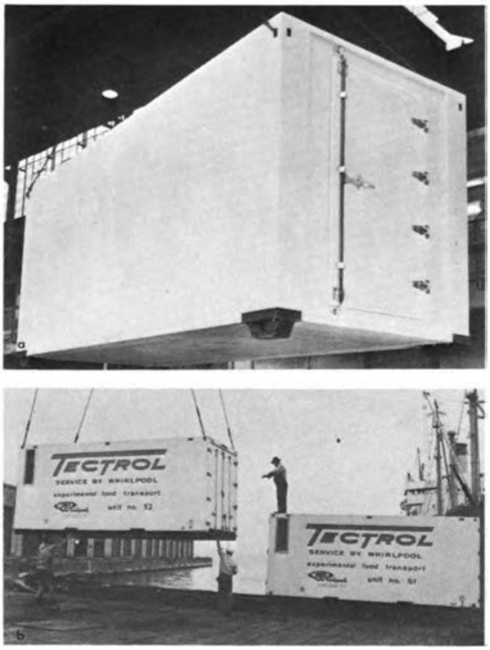

FIGURE 21
a. Reinforced foam container.
b. Foam-reinforced plastic portable freezers.

one half of the time and costs less than one half of a conventional salvage operation."

In 1964, a 500-ton barge was recovered in California from a depth of 60–80 ft, where it had been a hazard to navigation. In this instance, 60,000 lb of rigid urethane foam was poured in place through 150 ft of hose.

About a year later, the Destroyer 455 (*Frank Knox*) was grounded near Hong Kong. When conventional deflooding proved inadequate, urethane foam, in combination with conventional hauling and tugging, freed the ship.[37] It is the current belief that it is now feasible to salvage sunken vessels from depths as great as 375 ft with foamed materials.[38]

MISCELLANEOUS FIELD APPLICATIONS

Mine Sealing

For many years various techniques have been evaluated for sealing mines. Rigid urethane foam may provide a solution to this problem.

Quoting from a recent Department of Commerce review on foam technology and applications:

> The uses of foam seem to be almost unending. Polyurethane foam has been found to increase the safety and productivity in mines. Lining the walls with foam im-

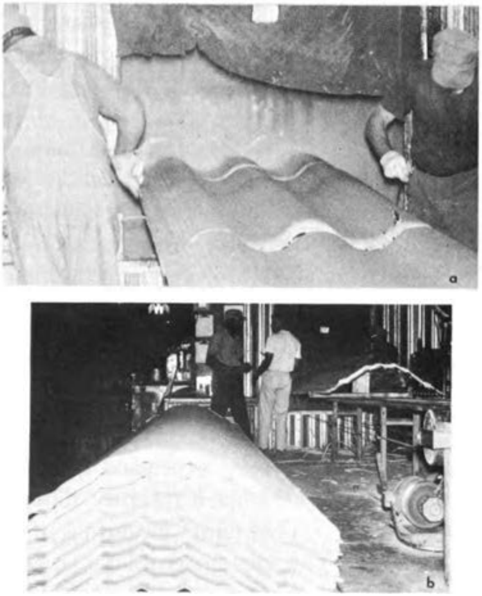

Figure 22
a. Spraying corrugated surfaces.
b. Completed foam spray insulated panels.

proves the mine ventilation, reduces the weathering of mine rock and steel, provides seals in fire areas and serves as thermal insulation.

The foam's attributes, in such applications, are that it is easy to apply to unprepared surfaces, expands to seal joints and cracks and the perimeter, and has good stability.[39,40]

Pipeline Applications

A system for insulating pipelines with rigid urethane foam to permit long-distance underground pumping of heavy fuel oil has been demonstrated.[41] Heavy fuel oil is used primarily in steam generation applications. The material at room temperature is extremely viscous; however, when heated above 100°F, the material can be pumped. The material previously was not transported by pipeline because of excessive heat loss. Insulating with rigid urethane foam has overcome this problem.

The original full-size field-test installation was in England, connecting the Fawley refinery to the Marchwood power station of the Central Electricity Generating Board, a distance of 8 miles where 20,000 barrels a day were transported. The success of this original installation established the feasibility of the concept. Subsequently, a complex of three buried pipelines, extending a distance of 66 miles, has been completed in northwest Italy. The longest section is 48.5 miles from the refinery to the Turin area and is in current use. This project would not have been successful without rigid urethane foam plus some ingenious application methods. To make the installation feasible, it was necessary to insulate the pipe in the field. A foaming station was set up to froth-fill the space between the pipe and the casing. A foaming station was regularly moved as the pipeline laying progressed.

In the United States, urethane foams have been used to enclose pipes used by the petroleum industry where they pass under roadways. In these applications, the foam is used to reduce vibration and to minimize temperature changes, corrosion, and maintenance. The pipe casing is urethane froth-filled at 60-ft intervals. Premolded rigid urethane foam spacers are used to position the pipe within the casing.

BUILDING IN BARRELS

The military has long expressed interest in the field application of rigid urethane foam.[7] Swensen recently reported on the erection of buildings in remote areas.[42] This effort is unique in that sandwich panels can be made in the field. The system employs froth foaming and a unique "nesting" of molds such that each mold provides restraining support to the other. An interlocking panel system for rapid erection of panels using unskilled labor has also been developed.

SPACE APPLICATIONS

Numerous articles have been published covering the use of urethane foam in space applications. These range from space vehicle rigidization, to meteorite protection, and to re-entry.[5,7,43]

SUMMARY AND CONCLUSIONS

Rigid urethane foam is an established and fast-growing segment of American industry. Equipment and techniques have been demonstrated for the large-scale production of rigid urethane foam, both in the factory and the field.

The basic technology already demonstrated is expected to satisfy future requirements for use of this material. No major changes are expected in the equipment and techniques used to store, pump, meter, and mix the foam components. Major changes and innovations are expected in foam utilization. Increased emphasis is expected in field applications and the use of urethane foam in combination with other materials for structural and building application use.

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REFERENCES

1. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology*, Vol. II, Interscience, New York (1964).
2. T. H. Ferrigno, *Rigid Plastics Foams*, Reinhold, New York (1963).
3. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology*, Vol. I, Interscience, New York (1964).
4. *Aerospace Expandable Structures, Conference Transactions*, sponsored by AF Aero Propulsion Laboratory, AF Flight Dynamics Laboratory, Dayton, Ohio, October 1963.
5. J. C. Stuebner, *J. Cellular Plastics, I* (4), 491 (1965).
6. *The Potential Use of Foam Plastics for Housing in Underdeveloped Areas*, Architectural Research Lab., Univ. of Michigan, ORA Research Project 05215.
7. *Foamed Plastics*, Proceedings of a Conference, April 22–23, 1963, PB 181576, U.S. Department of Commerce, Office of Technical Services, Washington, D.C.
8. R. E. Knox, *Chem. Eng. Progr., 57* (10), 40 (1961).
9. W. J. Neary, *Plastics Technol., 11*, 50 (March 1965).
10. W. R. Brooks, *J. Cellular Plastics, I* (3), 419 (July 1965).
11. R. E. Knox, *Chem. Eng. Progr., 59* (7), 74 (July 1963).
12. R. E. Knox, *Chem. Eng. Progr., 60* (11), 84 (Nov. 1964).
13. *Urefroth*, Polytron Corp., Richmond, Calif.
14. Editorial, *J. Cellular Plastics, II* (1), 14 (Jan. 1966).
15. U.S. Pat. 3,208,958.
16. W. W. Connoly, *Operating Management's Chem. Processing, 29*, 124 (Feb. 1966).
17. *Urethane Industry Digest, II* (26), 360 (Feb. 20, 1965).
18. U.S. Pat. 3,209,056.
19. U.S. Pat. 3,178,157; U.S. Pat. 3,181,839; U.S. Pat. 3,181,199; *Urethane Industry Digest, II* (20), 279 (Nov. 28, 1964); *Resin News, IV* (9), 3 (Sept. 1964).
20. U.S. Pat. 3,147,137.
21. U.S. Pat. 3,079,641.
22. E. E. Ziegler, *J. Cellular Plastics, I* (4), 494 (Oct. 1965).
23. J. S. Crandall, *J. Cellular Plastics, I* (4), 497 (Oct. 1965).
24. W. W. Seary, Budd Co., Report to Common Carrier Conference, Miami, Florida, Jan. 6 and 7, 1966.
25. G. Heffner, Trailmobile, Report to Common Carrier Conference, Miami, Florida, Jan. 6 and 7, 1966.

26. U.S. Pat. 3,158,529; Australian Pat. 42,072; U.S. Pat. 3,166,454; Australian Pat. 18,974/62; U.S. Pat. 3,170,827; U.S. Pat. 3,174,887.
27. G. O. Rudkin, Jr., and H. P. Gallagher, *J. Cellular Plastics, I* (4), 484 (Oct. 1965).
28. Brit. Pat. 997,086.
29. W. A. Oberdick, *J. Cellular Plastics, I* (4), 503 (Oct. 1965).
30. *Plastics World, 24* (2), 41 (Feb. 1966).
31. R. N. Kennedy and R. B. Bennett, *J. Cellular Plastics, I* (4), 465 (Oct. 1965).
32. James C. Stuebner, *J. Cellular Plastics, I* (4), 491 (Oct. 1965).
33. Wayne State University Polymer Conference Series, Cellular Plastics, May 24–28, 1965 (not published).
34. R. Scollay, British Railways Board, Report to 1966 Antel Mtg., "Structural Uses of Reinforced Plastics," Montreal, Canada, March 8, 1966.
35. F. G. Heinman, Fruehauf Report to Common Carrier Conference, Miami, Florida, January 6–7, 1966.
36. J. J. Ratto, *J. Cellular Plastics, I* (4), 472 (Oct. 1965).
37. *Bureau of Ships J.*, 20 (Dec. 1965).
38. Atlantic Research Corp. TR-PL-6993-00-0 (Mar. 26, 1965).
39. Foam Technology and Applications, Rept. of Investigation 6366, U.S. Dept. of Commerce, July 1965, OTR-121.
40. D. W. Mitchell, J. Nagy, and E. M. Murphy, *Rigid Foam for Mines*, Bureau of Mines Rept. RI-6366.
41. *Chem. Processing, XI* (11), 98 (Nov. 1965).
42. S. B. Swensen, USA ERDL, Ft. Belvoir, Va., Report to 2nd Aerospace Expandable Structures Conference, Minneapolis, Minn., May 26, 1965.
43. *2nd Aerospace Expandable Structures Conference*, Minneapolis, Minn., May 26, 1965, Air Force Propulsion Lab. Tech. Rept. 65-108 (Mar. 1966).

Enclosing Space by Spiral Generation

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For generations man has protected himself, his domesticated animals, and his equipment, as primitive or as sophisticated as the latter may have been, by fashioning structures from a wide variety of materials. Most of these structures have been based largely on straight lines and flat planes. There is much historical background, however, for the use of curved lines and contoured shapes. For example, extremes of climate and availability of materials have resulted in variations of domed structures such as snow block igloos in the Arctic, adobe huts in the arid plains, and thatched roofs in the tropics.

Domed or spherical roof sections can be graceful as well as highly practical. They are inherently strong and efficient. Nature has shown this in skulls and in the shells of turtles and eggs. Engineers have long known of these characteristics and have taken advantage of them in their design of pressure storage tanks and deep sea research vessels.

Now, a novel and interesting development has taken place wherein the talents of inventor, scientists, and engineers have been combined to create a new concept of dome construction. It involves the use of electromechanical equipment together with a modern synthetic cellular plastic known as Styrofoam brand polystyrene foam to form domed structures, the shape of which has been known for centuries. We call this concept "Spiral Generation."

We start with a shape which is inherently strong and efficient and use a foam which is at once light weight, rigid, formable, and a permanent thermal insulator. We take advantage of the fact that this material, being a thermoplastic, can be easily and quickly heat welded to itself without chemical degradation.

With Spiral Generation it is possible to create a free-standing form of considerable strength which, for some uses, would require little or no interior finish and only a light weather-protective shield on the outside. On the other hand, it is also possible to use this strong shell as a form board for the subsequent application of plaster on the inside and reinforced concrete on the outside to create a well-insulated, fireproof, load-bearing structure of unquestioned strength and permanence.

Figures 1–5 photographed on one specific construction job illustrate the equipment, progress at various stages of construction, and appearance of the finished building.

As can be seen in these illustrations of the formation of a dome, a machine head is mounted on a boom which swings around a pivotal center

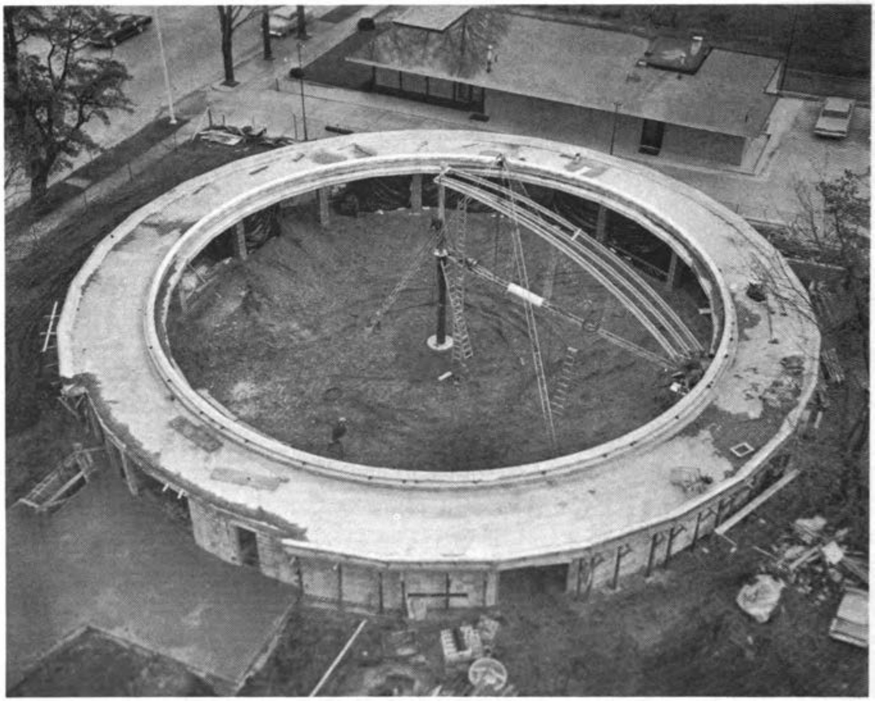

FIGURE 1
Masonry walls were built on the periphery of a 100-ft-diameter circular area. Brick columns were erected on an 80-ft-diameter circle to support the flat roof deck and the base of the 80-ft-diameter dome. This project was undertaken for the Park Place Motor Inn, Traverse City, Michigan. The architect was Paul Hazleton.

FIGURE 2

A flat concrete roof deck was cast to connect the base ring for the dome to the circular wall. A continuous angle iron hoop was lagged to the concrete curb to act as the base (tension) ring for the dome. The first course to Styrofoam FR insulation was then bolted to the ring. All additional boards of Styrofoam FR were welded into place with the Spiral Generation equipment.

point, bending and bonding layer upon layer of foam board in a rising spherical form.

The concept of Spiral Generation is, of course, much broader than this simple illustration and description would imply. Many variations have been considered. Some have already been worked on; others will be in the future, as part of Dow Chemical Company's continuing research and development program.

From the standpoint of military interest, there are several obvious advantages to this concept of construction.

Speed of Erection. A domed roof 40 to 80 ft in diameter can be erected by a few men in 1 day.

Light Weight. If properly supported, these buildings can easily be moved by men or machines.

FIGURE 3
With each revolution, the operator and sealing head were raised the height of the board stock (4 in.). As the spherical shape neared completion, the diameter of the opening became smaller and approached the maximum height of the dome.

Permanent Insulation. Of value in hot or cold regions.

As Permanent as Required. They may vary from practically "disposable" buildings of foam to permanent structures of concrete covered foam.

Electronically Transparent. Suitable for weather protection of radar equipment.

Low Labor Requirements. Relatively automated.

Advantageous Shape. Casting little or no shadow and providing for ease of camouflage.

Of course, there are also some potential disadvantages which must be considered. For some uses, a spherical shape may be unsatisfactory. The logistics of supplying lightweight foam might be difficult. The fact that special equipment and trained operators are required could be a localized problem.

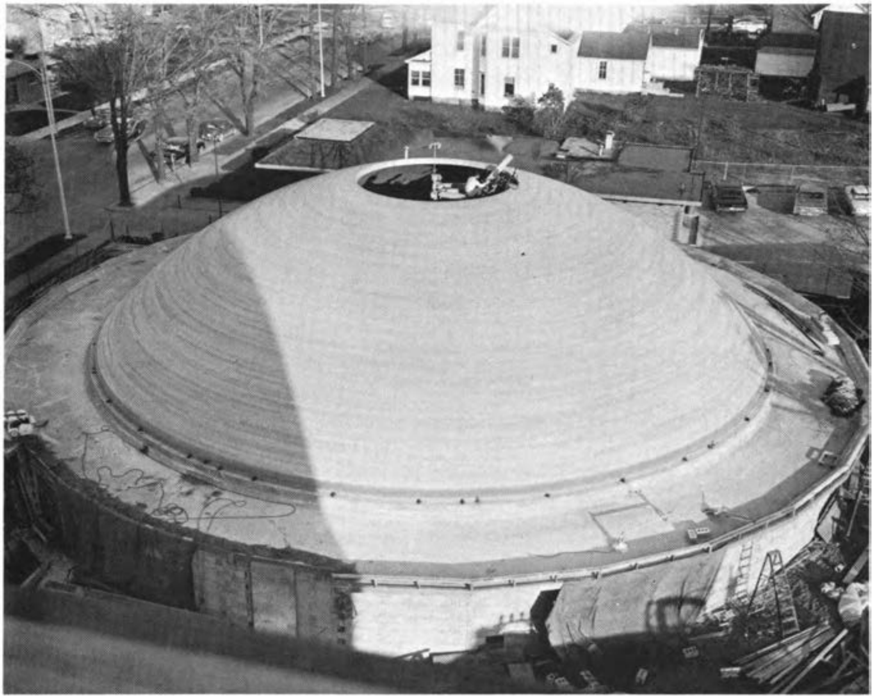

FIGURE 4
The equipment spun the opening to a diameter of approximately 8 ft. The final closure was accomplished with a prefabricated plug made of Styrofoam polystyrene foam and a ventilator.

A number of potential military uses suggest themselves for both domestic as well as foreign use. These include barracks, commissaries, meeting centers, recreational buildings, electronic equipment housing, and refrigerated food storage. Additional uses of potential interest in such areas as Vietnam also come to mind. They include native housing, village meeting centers, warehouses, mobile equipment maintenance shelters and hangars, field hospitals, and first aid stations.

[At this point a colored motion picture of Spiral Generation in action was shown.]

There are several spirally generated buildings already in use, including a medical clinic in Lafayette, Indiana, comprised of seven intersecting domes.

We have learned a great deal during the past few years' experience with this type of construction, and we fully appreciate the fact that we do not

FIGURE 5
The structural foam dome was covered with a skim coat of latex-modified concrete to meet the Class B fire rating. The roofing material was an experimental plastic sheet, cut into pie-shaped segments and solvent-welded together to form a continuous contoured membrane.

yet have all the answers; much additional work needs to be done. We do believe that this Spiral Generation is an intriguing development that takes advantage of trends toward prefabrication, automation, and the growing use of thermal insulation to make efficient use of cellular plastic materials in creating domed enclosures. We believe its future is unlimited.

A Process for Field Erection of Rigid Urethane Foam

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Let us back into our discussion of rigid urethane foams by talking football.

You are all familiar with the huge bonuses that are being commanded by rookie football players today. These bonuses amount to buying a pig in a poke, in the harshest terms. A ball player is being paid huge sums to sign with a team with only his *potential* worth to judge from. If he produces under fire—if he can pass in the pro leagues—then this potential worth has been realized. If he can't produce in the third-down-and-two-to-go situation, that huge bonus no longer looks like such a good investment.

Generally, the ability to produce under pressure, to carry the team through the turning point in a game is a function of maturity—maturity through age and experience. When the brilliant rookie gains maturity, he is able to utilize his great potential and produce game-winning performances.

Think, if you will, of rigid urethane foam as a rookie with great potential and greatly in need of maturity—maturity through age and experience.

At its inception about 1958, rigid urethane foam presented great potential for use in many diverse applications. The unique chemistry of urethane foam opened new vistas for designers and manufacturers in many industries.

Today, we find urethane foam and foam products being utilized in many applications where steady growth is anticipated. However, the great potential growth of urethane into other uses will depend largely upon two things: the development of a wide range of new products which will have properties that are unavailable now and the development of technology to permit on-site application of foam.

The previous papers should have pointed out to you that the rigid urethane chemist is constantly developing new information about the urethane reaction and myriad products that can be made with it. Even the most outspoken advocate of urethane foam still must recognize that the growth of the market is about 50 percent of what it was expected to be 5 years ago. The chief explanation for this is that laboratory technology has far outstripped application technology.

If you take a look at where this growth is (Table 1) you will note that the greatest penetration has been made where the foam process is a highly controlled "factory" operation, much like laboratory conditions. Little penetration has been made in the areas where precise control is difficult and where both foam and equipment must be adaptable to many uses.

TABLE 1

Present Markets for Urethane Foam

	1965 Sales in Millions of Pounds	Sales Forecast[a] for 1965 in Millions of Pounds	Applied in
Appliance	22	34	Plant
Transportation	24	29	Plant
Marine and government	9.5	20	Plant, field
Construction	16	100	Plant, field
Mining	2	—	Field
Miscellaneous	2	10	

[a] Forecast made in 1960—Dow Market Development—generally accepted in industry.

The most brilliant passer in professional football is severely handicapped without a good running game. In the same manner, the great potential of urethane foam is severely handicapped by the lack of application equipment and techniques which are adaptable to new uses.

It is the development of such equipment and application techniques which is the subject of this paper.

The recent development of SCUFA foam applicator, we believe, represents an effective connecting link between the creation of a system in a laboratory and application of the system in the field.

SCUFA is a developmental item which will find initial use in the mining industry for the erection of ventilation stoppings in coal mines. The principles that are involved in this field erection technique are, however, applicable to many other field situations. We invite you to consider the demands of your projects and see if some answers are provided here.

A primary method used by the mining industry for reducing ventilation costs has been the construction of cinderblock ventilation barriers to seal off worked-out underground mine tunnels. The Dow Chemical Company felt that rigid urethane foam would be an excellent substitute for cinderblocks in erecting these ventilation barriers. A urethane barrier seemed to offer:

1. A cost which was less than the cinderblock method
2. A nonporous airtight barrier which prevents transmission of working air into worked-out areas and seepage of methane-contaminated air into working passages
3. Barrier erection in one fourth of the time required for a cinderblock barrier, thus freeing men for other jobs
4. Less storage space for barrier material: the liquid chemicals expand 30 times in volume when applied
5. Less ventilation is wasted, hence, less total ventilation is needed
6. Urethane barriers resist earth movements and help withstand explosion percussions

These were the advantages envisioned for a urethane foam barrier. However, the foams were required to satisfy the following basic specifications in addition to those generally attributed to urethane foam:

1. That 1 in. of foam could withstand a 1,950°F propane flame for 10 min
2. That the foam not thermally deform at 450°F
3. That the foam adhere to the surface of most rocks

Such a foam was supplied to the U.S. Bureau of Mines for its evaluation in 1961 by Dow and was rated as permissible by the Bureau. This project resulted in new understanding and insight into problems of flame spread, fire retardancy, possibilities of spontaneous fires, and the toxicological aspects inherent in field application of sprayed urethane foam systems. These subjects could each be the basis of a separate paper.

However, the capability of producing a foam to these strict specifications was not enough. Two primary questions remained: Could urethane foams be successfully applied on-site in an underground mine where temperature and humidity vary greatly? Would such a new construction technique be economically attractive?

To answer these questions, a feasibility study was undertaken by Dow and the Anaconda Copper Company with the cooperation of the U.S. Bureau of Mines. Although these studies showed that urethane foam would perform well in this application, it also became overwhelmingly obvious that available equipment was not suitable because it:

1. Required skilled applications technicians
2. Was too bulky
3. Required an external power source, sometimes hard to find
4. Was expensive

A foam barrier seemed superior to conventional barriers, but cumbersome to erect. At this point, our promising rookie was in danger of being cut from the squad; his good points did not outweigh the bad.

If you look at the growth of urethane foam in mining since 1961, you will see it has succeeded only to a point—the large projected gowth has not been realized. Once again, a good product had been created in the laboratory, but it could not be brought to market easily.

To meet this need, Dow developed the SCUFA foam applicator. The significance of the SCUFA foam applicator is that it is self-contained, easily carried to any location in the coal mine, and will produce a high-quality urethane foam. It replaces large and cumbersome equipment which, until now, required an external power source to process the chemicals necessary to make the foam.

Utilizing SCUFA, a rigid urethane foam barrier can be constructed in one fourth the time it takes to erect a cinderblock barrier, and skilled workmen are not needed to do the job. One unskilled workman can erect the urethane barrier with SCUFA, thus freeing other employees for additional work. The raw materials necessary for SCUFA production of the urethane foam stopping are liquids which, when mixed, expand to 30 times their original volume. Therefore, only one thirtieth of the volume of a cinderblock barrier material need be handled and stored in the mine employing rigid urethane foam. The SCUFA foam applicator was designed for erecting ventilation stoppings; however, it can be adapted simply to a wide variety of formulation ratios for different applications. The equipment can also be used with a froth-type system.

The SCUFA foam applicator has been tested at Dow's Midland, Michigan plant, the U.S. Bureau of Mines experimental mine in Pennsylvania, and in approximately 25 mines in the Appalachian region of the United States.

The SCUFA foam applicator consists of two aluminum tanks which hold two Dow products: ET-897 activator and ET-898 resin. Regulated air pressure is supplied to these tanks from a third bottle holding compressed air. The liquid in the two tanks is under pressure and is forced through a positive displacement proportioning device which maintains a constant ratio between the two reactant streams over a wide range of temperatures (40–110°F) and viscosities. This patented proportionating device is the heart of the SCUFA system.

If anything does change in the system, it will be the throughput, not the ratio. The reliability of the system is shown by the data in Table 2.

We settled on the positive displacement system after working with the pressure orifice concept as a method of developing ratios. This is significant because we also developed a 1:1 ratio foam system of equal viscosities—the ideal situation for the pressure orifice metering technique. However, in most cases, such pressure orifice systems were dramatically affected by

TABLE 2
SCUFA Control of Ratio

Operating pressure, psig	Operating Temperature, °F	Ratio[a]
40	38	1.40
40	60	1.40
40	80	1.41
72	20	1.45
72	40	1.42
72	60	1.42
100	60	1.44
72	60	1.42
40	60	1.39
100	20	1.39
72	20	1.45
40	20	1.47

[a] Desired ratio is 1.42 ± 0.02.

temperature, viscosity of components, and simple fluctuations in orifice size, and we questioned their reliability in different "field" situations. There have been many creative engineering efforts to overcome these problems so that the pressure orifice ratio could be used. However, experience in field applications convinced us that a direct proportioning concept has wider application and a better safety factor.

In operation, the two proportioned streams are passed through a tube to the gun where they are mixed and propelled by an airstream as a spray. The airstream is drawn from the compressed air bottle which is also used to pressurize the liquid tanks. The gun air pressure is regulated independently of the pressure applied to the liquid tanks. In addition, the compressed-air cylinder may be used as a source of breathable air for the operation.

The mixing–spraying gun is a unique part of the SCUFA system. The gun is inexpensive and easy to use, requires little maintenance, and has a disposable mixing chamber.

Many rookies have come up and demonstrated all the potential in the world on the practice field. However, what really counts is the game. In the game, the rookie has to prove that he can spot the receiver, anticipate the receiver's moves, and remain poised while those friendly, lovable, 300-lb linemen are bearing down on him. Our rookie, once in danger of being cut from the squad, now has shown that he *can* complete the pass in a game. He still isn't the pro. He needs perfection and a variety of different pass plays.

Similarly, SCUFA in the mining industry has shown that urethane foams can be applied successfully on-site. The SCUFA foam applicator was also used successfully to insulate on-site process equipment in the Dow Chemical Company plant on an experimental basis. But like our rookie who has now shown he can pass in a game, our SCUFA equipment needs to find other areas of usefulness.

To use the SCUFA, the following items should be considered:

1. A need or reason for field application
2. The availability of a mold to froth into, or a surface to spray upon
3. The temperature of the components can be limited to a range of 40 to 110°F
    (a) Upper limit is not clear, but some vapor locking is noticeable above 110°F
    (b) Lower limit is established by viscosity and tube size. Surface sprayed upon can be as low as 32°F
4. Water is a problem. We can foam under it, upon it; but we lose adhesion when spraying on a wet rock surface.

Some of the potential areas of use for SCUFA are shown in Table 3.

These applications can also be classified in a number of categories based on use.

1. Urethane foam—can be sprayed on a surface to give structure. The surface can be anything from a solid to 1/4-in. hardware cloth.

In our southwest United States this concept is used as an economical way of repair for rusting metal roofs. The idea is that a roof lasts only 10

TABLE 3

Other Potential Areas of Use for SCUFA

- Construction
  - Thermal insulation
  - Temporary shelters
  - Tropical hut replacement
  - Rigidizing
- Packaging
  - Cushioning
  - Corrosive environment protection
  - Encapsulation and flotation for transportation by water
  - Thermal insulation for frozen food
- Caulking and Sealing
  - Fumigation
  - Flood damage control
  - Ground stabilization
- Military
  - Shelters
  - Pontoons
  - Foxhole liners
  - Encapsulation of parachuted articles

years in this corrosive atmosphere. Urethane foam lasts half that time but costs only one fourth of the price for a new metal roof.

The most obvious use of this idea is for shelters. These can be built easily by spraying on:

(a) any curtain fabric with 1/4-in. or smaller openings,
(b) metal,
(c) natural materials, such as hay and bamboo,
(d) any inflatable fabric.

Think of camouflage uses—wall and roof sections can be made by spraying foam on the ground or sand and then lifting these into place after hardening. The framework can be sealed by a spray foam caulk technique. The outside of the structure will have a surface exactly like the natural terrain.

2. The second category of potential uses is to mold a part. The mold can be prepared, or in emergencies could be made in the ground. In this way, pontoons, for example, can be made in the field.

3. The third category is packaging. Urethane foam, either sprayed or poured in place, provides good insulation characteristics as well as offering a protective cushion.

4. The fourth category is sprayed foam on the ground. Urethane foam can be used to provide soil stabilization, foxhole liners, and ground hardening; to eliminate the weathering of rock, i.e., "sluffing;" and for the enclosing or caulking off of an area.

All these applications are now much more practical because of the SCUFA concept of equipment and urethane formulations.

As I mentioned previously, the SCUFA foam applicator is still a developmental item—our rookie is studying plays and gaining maturity, but we feel that when he gets into the ball game soon, he will win some games for us.

Foams in Packaging

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INTRODUCTION

I have been asked to cover the application and use of foams in the area of packaging. To do this, let us first review those materials that can be foamed and have been used in packaging. Rubber, epoxy, polyvinyl chloride, silicone, phenolic, cellular acetate, ureaformaldehyde, polyurethane, polyethylene, as well as polystyrene and its copolymers have been used. Some have been found wanting, others have enjoyed a good measure of success.

Rather than delve into a discussion of specific properties of each material, it will suffice to identify those materials that have commercial importance and talk about only those properties that are important from the packaging standpoint. The most significant properties are light weight, cushioning ability, moisture resistance, ease of fabrication or molding, chemical inertness, nonabrasiveness, no dusting, thermal insulation, useful temperature range, and competitive cost.

The foamed materials that have best met the test in the marketplace and are now commercially important are polyvinyl chloride, polyethylene, polyurethane (both rigid and flexible), and expanded polystyrene; with the workhorse of the packaging industry being the latter—polystyrene.

Packaging techniques using these materials vary with the utilization of the property most desired for a specific application: product volume, value of the product, and ease of fabrication. Specific applications will be covered later.

In any discussion of packaging we must first determine the necessity for packaging at all. If we manufacture a product worthy of our customer's acceptance, we must try to achieve a package that will get this product safely to our customer at a minimum cost. Therefore, the needs of the packaged product itself must be determined.

Let us first take a look at how we in packaging presently categorize packaging.

Consumer Packaging

This is the packaging that is market and sales oriented and is directed to the consumer in the area of foods, soft goods, hard goods, materials for which there is an immediate need, materials that can be impulse sold, and items that, after manufacture, cycle through distributors and dealers to the ultimate customer.

Industrial Packaging

This group includes all materials that are basically oriented as industrial products or items that will be sold directly to an industrial consumer. For example, the materials may be goods, in a large volume and at times very bulky, that go into the manufacture of a consumer item. The items themselves are large, delicate, and fragile or have some peculiarity that sets them aside from a direct consumer product.

Military Packaging

This category encompasses all those items that are procured for use by the various military services.

Export Packaging

We can export any or all of the items in the three preceding categories, and, therefore, we must determine yet another method of packaging.

From the above we note that the needs of the various packaging methods can and will be different. If we were to pick the most important feature of the many requirements of these packages, in consumer packaging it would be the graphics for sales appeal. In industrial packaging, utility would be selected for the ease of decasing. In both military and export packaging, the most important feature would be protection. By definition then, and after meeting the customer's needs, we must design the package to fit the sophistication of the distribution system, at a balanced cost. Package development therefore is hinged to knowledge of the basic environments that will be encountered in any given distribution system. The properties of foams have contributed to meeting these needs. The package then can in effect be looked at as the interface between product and environment and between manufacture and ultimate use.

Before we look at specific illustrations of cellular plastics and their applications in packaging, I should like to say that packaging requirements have dictated using the best material for the job at any given point in time. Historically, glass, metal, and forest and animal products have had their use. As new forms of materials were developed, they were studied for use in packaging. Very few, other than exotic materials, have not been used in some way in packaging. As cellular plastics became available at costs consistent with good packaging practices based on expanded technology, their place was assured in the field of packaging.

Specific examples of foams for packaging will now be considered.

POLYVINYL CHLORIDE

Foamed polyvinyl chloride is presently being used to coat large-volume products that have surfaces needing protection. The material, which con-

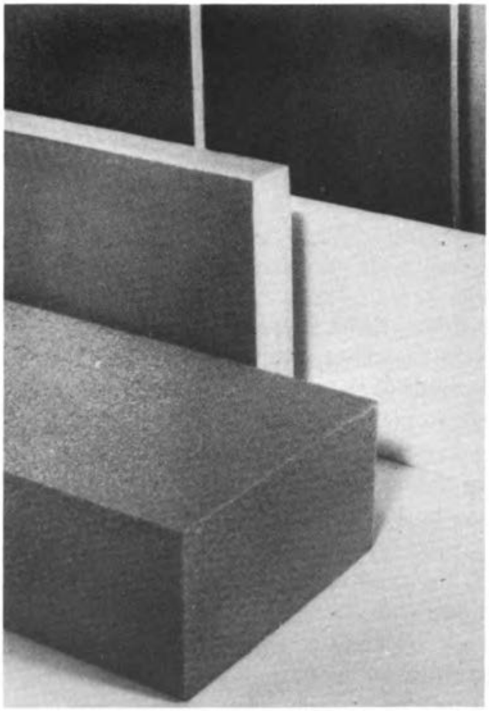

FIGURE 1
Foamed polyethylene is available in slabs and billets. It is also available in round stock.

tains a heat-activated blowing agent, is applied to parts such as bezels, automotive trim, and tools by a curtain coater. Coated pieces are then conveyed through an oven where the material foams and cures, increasing its thickness about 20 to 30 times. The pieces can now be bulk handled. This eliminates the need for individual wrapping. This system is interesting because it is virtually scrapless.

POLYETHYLENE

Polyethylene foamed in slabs, rounds, and billets (Figure 1) is fabricated into packaging components using conventional woodworking equipment, hot wire, or heated forming dies. For examples of fabricated packages see Figure 2, a and b.

We have used this tough and resilient material to block and brace high-value low-volume products in wooden boxes as well as other types of containers. Sheets and slabs have been used between the journal and V-block supports on large rotors.

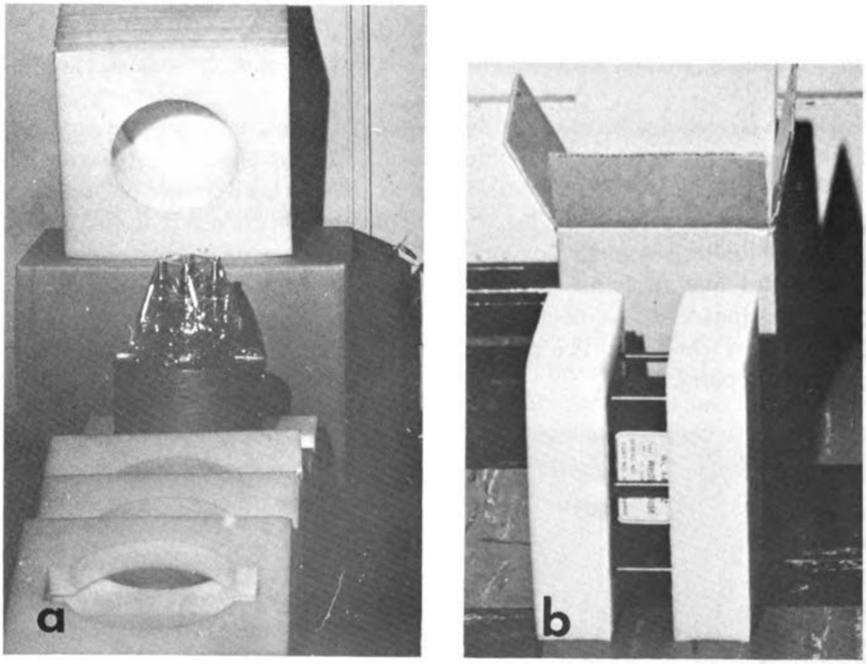

FIGURE 2
a. Fabricated polyethylene foam packaging components for a small power tube.
b. Fabricated polyethylene foam end bells for a small microwave device.

As we develop this paper, please note the classic shapes and techniques for capturing the geometry of the various products for positioning in the package. These shapes take the form of trays, rails, end bells, and corner blocks which also can be used in combination with each other.

POLYURETHANE

The next foam material, polyurethane, is available in two forms, rigid and flexible. Rigid polyurethane may be cast in slabs and then fabricated. It may be molded or foamed-in-place. It may also be sprayed in place.

Fabricated or molded pieces of rigid urethane have been found to be of little use in packaging. Foam-in-place has enjoyed some success, but the anticipated use of this packaging technique has not yet materialized.

Rigid urethane foam has captured the area of containers (Figure 3) used for the transport of frozen food, usually referred to as containerization. Nevertheless, the basic function of a box, large or small, is to deliver the goods. The *k* factor is the important feature in these units.

Flexible polyurethane material has contributed much to packaging. It may be fabricated by contour cutting. It may be molded. Sheets may be used as wrappers. Several proprietary corner devices have been developed for cushioning effects. Bonded shredded scrap has also been used successfully.

Figure 4a shows a form of urethane foam fabricated by contour cutting; Figure 4b is an example of molded flexible polyurethane; and Figure 4c illustrates the use of a flexible urethane which has been manufactured and is used as a corner block device, one which can capture a box-in-box situation, cushioning the inner box sufficiently for the needs of the product.

I should like to point out that flexible urethane (sheets) used as a wrapping material has been misused in many instances. Indiscriminate use by those who feel it is a panacea is at fault. It can be expensive if not utilized properly.

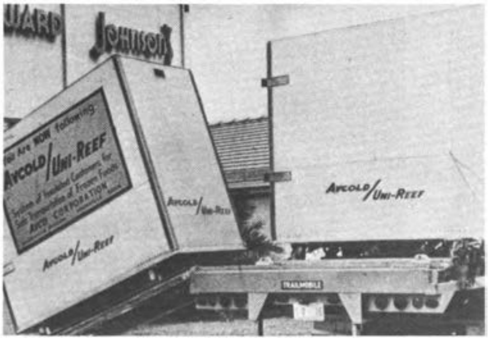

FIGURE 3
Frozen food container, urethane foam wall construction.

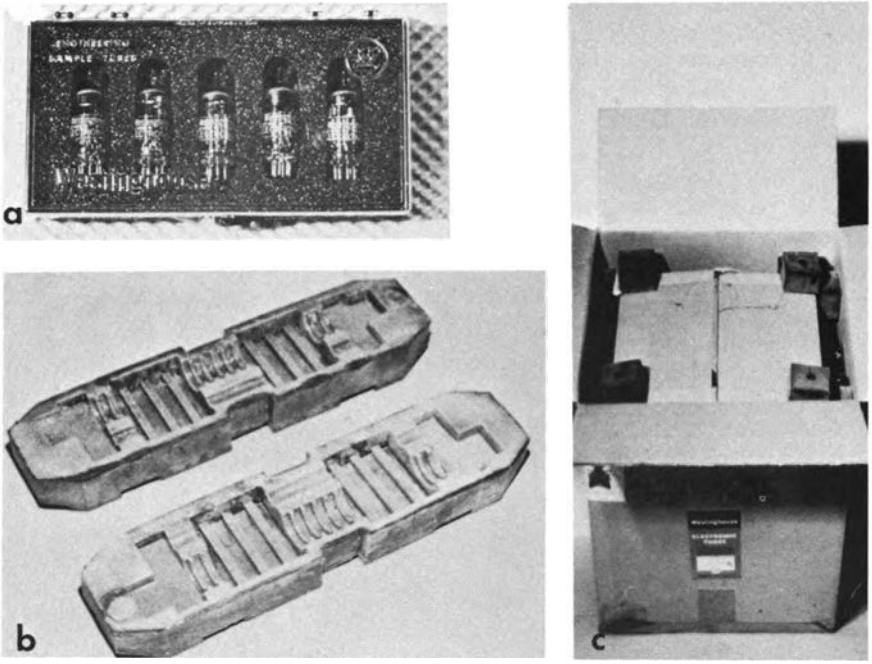

FIGURE 4

a. Sample package with contour-cut flexible urethane insert. Receiving tubes nested in insert.

b. Molded flexible urethane device. The two halves encapsulate an electronic device.

c. Corner devices for cushioning a box in a box.

POLYSTYRENE

As stated before, polystyrene in its various forms has been the workhorse of the cellular plastic packaging materials. The available forms used for packaging are: (1) parts and components fabricated from bead board and expanded polystyrene; (2) parts and components molded from beads; (3) parts and components pressure formed from expanded extruded sheet (this sheet can also be used as a wrapper); (4) loose fill material which can take several forms, e.g., as extruded strands which can be expanded. Chopped, slit, or ground scrap may also be used.

The first packaging use of polystyrene was by fabrication of packaging components from slabs and blocks. This expanded material can be easily worked with conventional woodworking equipment and hot-wire cutting devices.

Incidentally, the majority of molded prototype samples are constructed in this manner today. This procedure is advantageous in that samples can be fabricated from material of known density, can be weighed, and can be analyzed very accurately for material costs. Because of the peculiar geometry of some devices, this method is the simplest way to get the desired data. Examples of polystyrene used in some typical fabricated packaging applications are shown in Figure 5, a–c.

Up to this point we have talked basically about small items. Now if we look at Figure 6, we will see a large wooden skid with two expanded poly-

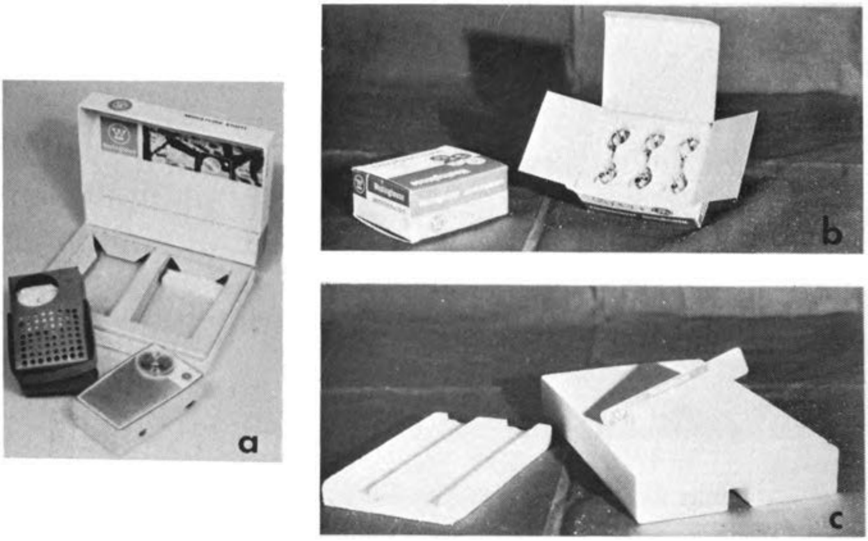

FIGURE 5

a. Small EPS block used to position transistor radio in package.

b. Insert made by heat-deforming expanded polystyrene.

c. Two fabricated pieces, the one on the left is a routed tray. The one on the right is fabricated by using saw cuts. You will note that there is a small carded item which slides down into each individual saw cut. This piece is a shelf package from which the product can be dispensed.

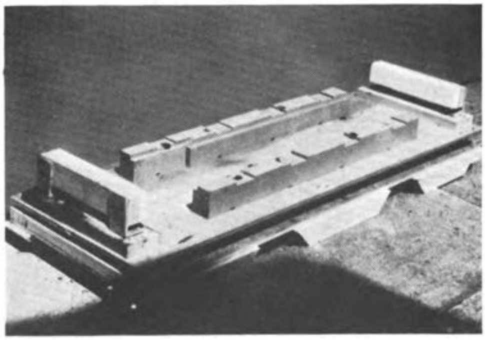

FIGURE 6
Skid with polystyrene headers.

styrene blocks assembled on each end. The skid is for the packaging of a large military transmitter. The blocks cushion and position the transmitter on the skid and are more economical than shock mounts.

In many instances, fabricated pieces have been used for the initial packaging of start-up low-volume items. When the demand for the product increased sufficiently, a change was made to the lower-cost molded pieces. This transition is illustrated in Figure 7. The product packaged in these trays is a solid-state device used in automobile alternators.

Westinghouse first used molded EPS in 1959. The packaging component for a breaker switch was changed from conventional corrugated rat traps (see Figure 8a) to molded end bells (Figures 8b and 8c).

Figure 9, a–d illustrates the progressive development of packaging for refrigerator compressors from a wood crate through an all-corrugated container to a corrugated container with expanded polystyrene components.

Figure 10 illustrates a packaged portable hand mixer, the first foam and shrink-film package developed for a portable appliance. Both foam and shrink wrap were in their infancy during the development of this package, and many things were learned. First, we discovered that with molded pieces, packaged and sealed in corrugated cases, the residual steam condensate was trapped and could not escape and thus was detrimental. It became necessary to dry the parts. Today, most molders make some provision to dry molded pieces and use ventilated containers. Wet foam with the hand mixer encased in a shrink wrap would certainly have been catastrophic.

Next, we became aware of the problem of migration of plasticizers. In this project, a pink foam was used and the body of the hand mixer was made from an acetate. It was noted that where the beads of the foam were in contact with the body of the mixer, there was a transference of pink color—giving the various colored mixers (yellow, white, green, and pink) pink freckles. We solved this problem by placing a piece of polyethylene film between the mixer body and the foam tray. Another problem was the unsightly "fish eye effect" caused by the shrunk film over the uneven surface of the mixer body. This problem was eventually solved by dusting

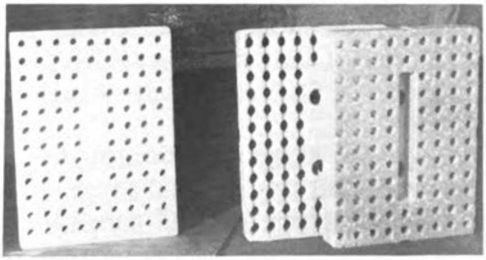

FIGURE 7

Trays for solid-state devices. The one on the left was fabricated by heat deformation from expanded polystyrene. The two on the right were molded from polystyrene and are color coded positive and negative.

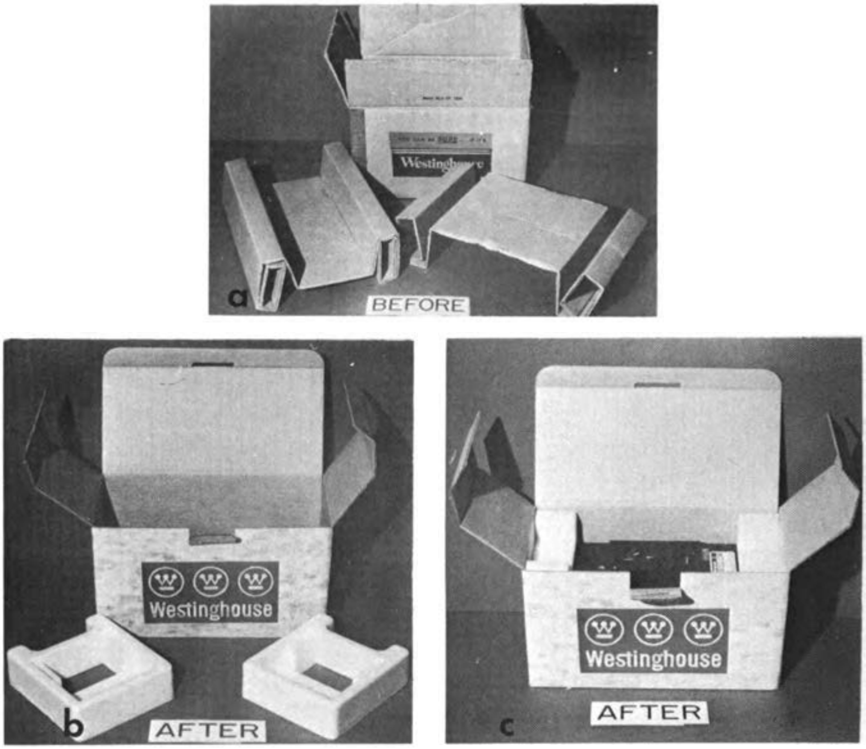

Figure 8

a. This illustrates "the before;" the corrugated rat traps that were used to secure a large electrical switch in a container.

b. The molded pieces that replaced the rat traps in a.

c. The switch packed ready for closure.

talc on the body of the mixer; this, in effect, leveled the surface and thereby gave a better optical attribute.

Applications needing little or no explanation are illustrated in Figure 11, a–e.

Let us now look at combinations of materials in which the best properties of each material are used advantageously.

The use of corner posts for refrigerators was standard for years (Figure 12a). Top rails were developed and after much testing were adapted (Figure 12b).

Foam end caps and a corrugated tube replaced a five-panel folder, two corner-cut inserts, and two pieces of wadding formerly used to package wallboard heating units (Figure 13). Better stacking and protection resulted from this development.

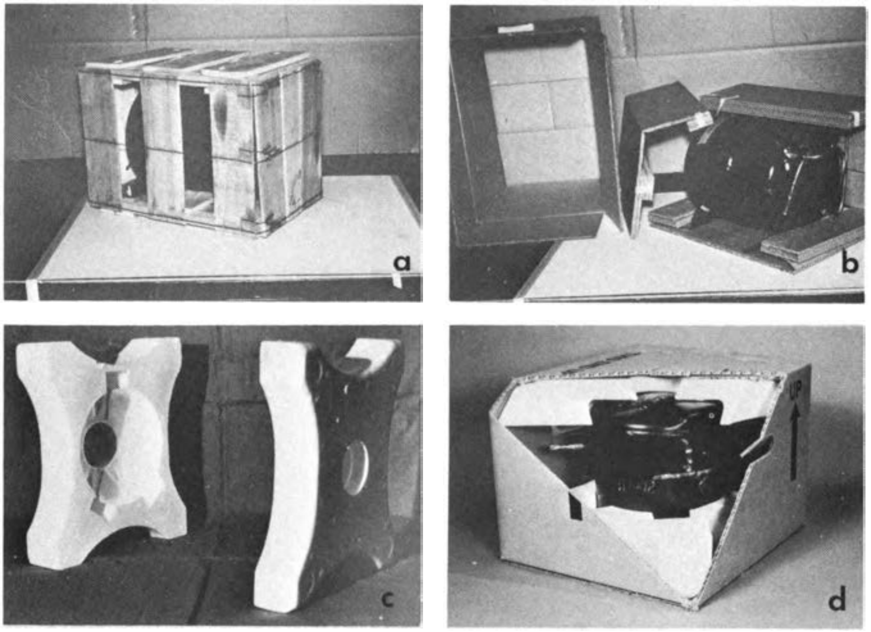

FIGURE 9

a. Wire-bound crate for refrigerator compressor.
b. All corrugated package for refrigerator compressor.
c. Foamed trays for refrigerator compressor.
d. Foamed trays with compressor assembled in container.

Figure 14, a and b shows a special electronic tube package developed for shipping and storage. The shipping container is corrugated. The "top hats" molded urethane components position and cushion the expanded polystyrene molded case. The case can also be used as a storage unit.

The potential of expanded extruded sheet is just now beginning to emerge. High-volume applications such as pressure-formed trays for produce and meat are gaining acceptance in the marketplace (Figure 15).

In another application, a clam shell packaging component is used to cushion and position a fragile projection lamp in its carton (Figure 16).

The last method of packaging with polystyrene is the use of loose fill material made from expandable extruded strands as shown in Figure 17. This material is used in shipping rooms mostly for nonstandard low-volume fragile items.

The preceding foam packaging applications have demonstrated how foam, if properly applied, can be used to fit the needs of both the customer and the distribution system. In all cases, the packaging costs were reduced. Costs here mean total costs. In other words, the foam packaging component

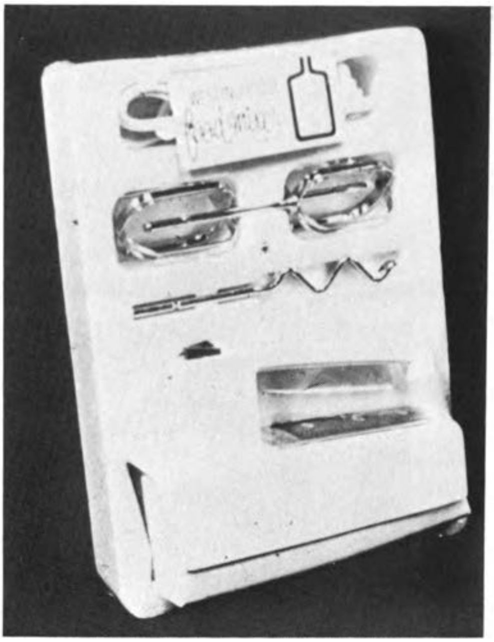

FIGURE 10

Portable hand mixer—first foam and shrink-film combination package.

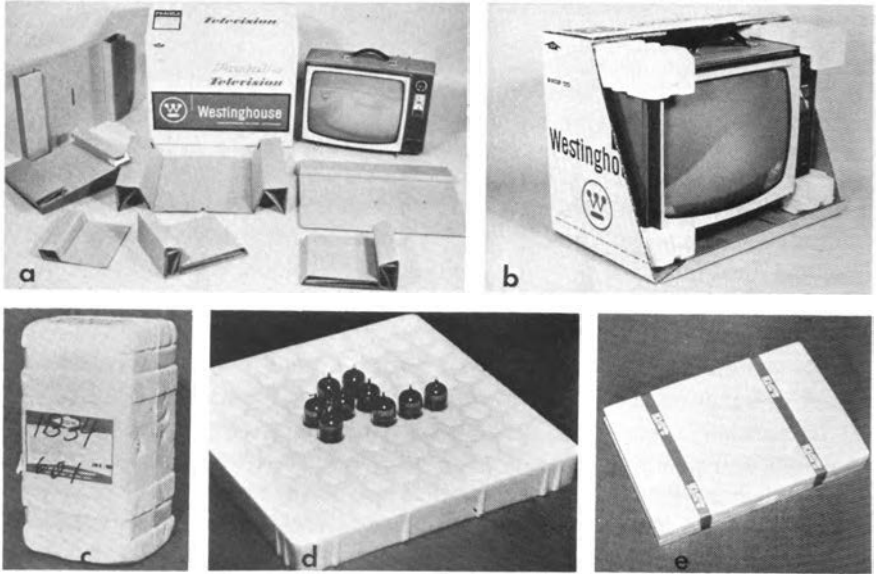

FIGURE 11

a. Portable TV pack—seven corrugated pieces required.
b. Foam TV pack—four foam rails required.
c. One-quart bottle pack.
d. One-half tray for receiving tubes.
e. Two trays containing small electronic gear sealed with plastic tape.

may have been more expensive than the paper component replaced, however, the accompanying and substantial reduction in labor requirements lowered the total cost of the package. Package performance has almost always improved with the use of foam. In addition, foam packaging imparts the connotation of quality. Because of these important contributions,

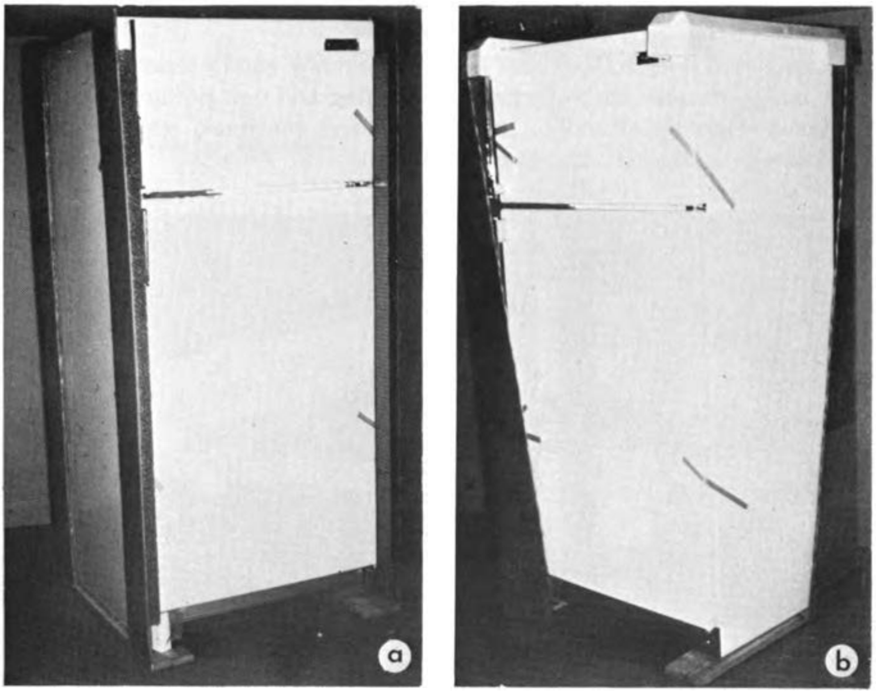

FIGURE 12

a. Refrigerator with corner posts.

b. Refrigerator with two foam top rails, which replaced the four corner posts on many models.

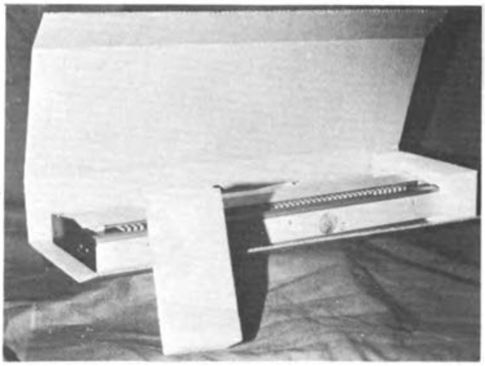

FIGURE 13

Baseboard wall heater package—end bells with a corrugated sleeve.

the production of flexible foams for packaging has grown from 5 million pounds in 1962 to 10 million pounds in 1964, with a forecast of 20 million pounds in 1967–1970.

At the same time, rigid foams have grown from 25 million pounds in 1962 to 35 million pounds in 1964. The experts are projecting the use of 50 to 200 million pounds in 1967–1970. This increase does not appear to be unreasonable.

Since foams offer the package designer so many good properties, he will continue to increase their use for both existing and new products. The use of these materials is still in its infancy and continued growth at the present prodigious rate is anticipated.

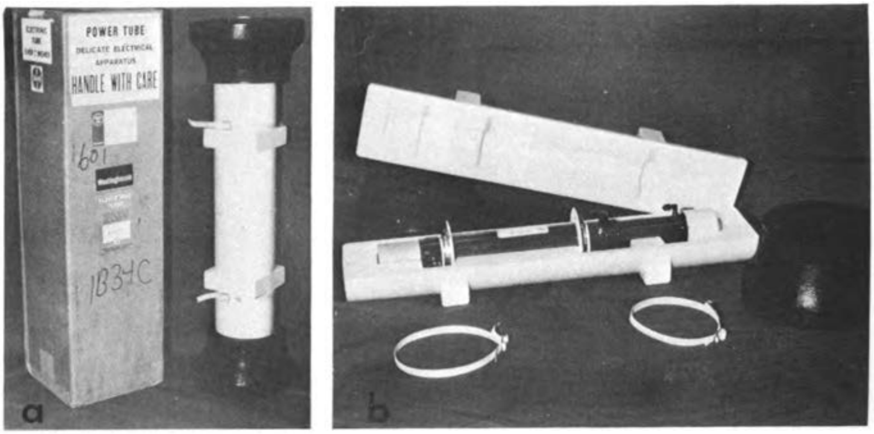

FIGURE 14

a. Combination of materials in this package includes EPS, flexible molded urethane, and a corrugated box.
b. Foamed unit can be used for storage and bench rest.

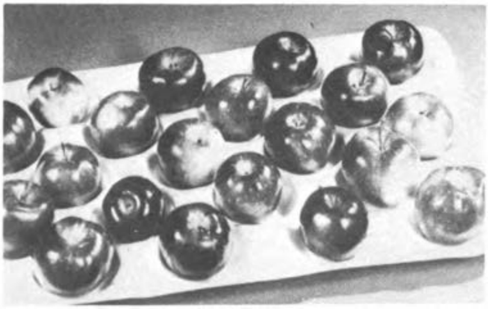

FIGURE 15
Apple tray.

Figure 16
Clam shell package for projection lamp.

Figure 17
Loose fill material.

Research on the Potential of Foam Plastics for Housing in Emerging Nations

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In July 1962, the University of Michigan received a research grant from the Agency for International Development (AID), U.S. Department of State, to explore the potentials offered by foam plastics, alone or in combination with other materials, for the resolution of housing problems abroad. AID had come to the conclusion that the use of traditional building materials and techniques alone could not resolve the housing problem confronting the emerging nations.

The Michigan project began with a feasibility study having a stated objective—the determination of "the potential use of foam plastics for housing in underdeveloped areas."

The feasibility study established the desirability of investigating further the use of foam plastics as a structural material, in the belief that such development could contribute toward a resolution of housing problems throughout the world—directly, by providing building materials that can upgrade housing, both quantitatively and qualitatively; indirectly, by contributing to the establishment of industrial facilities in the developing countries, which are both a necessity for their economic growth and a prerequisite for the adequate production of new housing.

It was evident from the outset that the project could not be conducted with any reasonable chance of success unless it could elicit active response from the plastics industry. Industry has the specialized know-how for resolving through chemistry and technology many of the problems involved in the application of foam plastics to building, and its active participation will be required to introduce and apply the findings of research in countries abroad. It has been a primary objective of this research program to demonstrate to industry what can be done with these new materials structurally and to present the potentials of an overseas housing market in the hope that industry will contribute its resources toward international development in its own enlightened self-interest.

Government likewise is a necessary resource in conducting this program of research and development. The program itself could not have originated from any individual company or even from the plastics industry as a whole. By keeping a proper balance between the interests of our foreign aid program and that of the plastics industry, government can open up a new area for the use of foam plastics and greatly assist in the successful introduction and establishment of a new building technology abroad.

Industry has to be presented with the performance specifications that can serve as guidelines in furthering the development of foam plastics in a direction that will better serve the needs of building. In many instances, the industry also needs to broaden its concept of the building market, and to be shown how materials should be approached for their own intrinsic merit in building construction.

It is in these areas that the current research project has offered its own resources to industry, and this has resulted in a close collaboration between the project staff and a number of plastics producers.

In a sense, the project has acted as a catalyst between government and industry in trying to advance the kind of technology that hopefully will be of value to the emerging countries and to our own national development as well as that of the plastics industry.

Although several prototype structures have been erected, the main effort of the project staff has been to conduct broad research in structures, not to design a specific kind of dwelling unit or a universal type of structure. Consideration has been given to the quantitative and qualitative aspects of the spaces created and to certain problems of total enclosure, but these are being treated on a fairly abstract basis until such time as a specific case study can be set up in a specific location to meet specific living conditions.

The main research goal can therefore be considered to be the development of total systems involving the design, production, and marketing of foam plastic structures in which adjustments can be readily made to cover the widest possible range of housing requirements in each developing country.

While techniques have played a major role in the research program, they do not constitute an end in themselves. Although novel, they have not been conceived for the purpose of creating structural innovations, but rather as means for the realization of better housing in the emerging areas of the world within a framework of industrial and international development.

It is believed that a new type of building industry in the developing countries, based on foam plastics, should accelerate the production of new dwellings, introduce new skills, and advance industrialization generally. For the people living in these countries, this would mean better housing, new jobs, and more buying power. Thus, any effort to alleviate the existing housing shortage in any country would not constitute a drain on the national economy, but would be a boost to it.

Foam plastics have been explored for what they can do in their own right as structural materials, rather than as substitutes for other materials. Figure 1 shows the basic pattern underlying the project's approach to structure.

In investigating and developing structural systems, the project has concentrated on the use and application of polyurethane foam. This should not be construed as an indication that the potential of other foam plastics materials in building construction has been ignored or minimized. The decision was based on the specific needs of the project. Polyurethane foam offered two major advantages: (1) versatility in methods of production which permits flexibility in the way they can be introduced abroad and (2) interest on the part of a large segment of the plastics industry in the development of this material for building use both here and abroad. Active collaboration could therefore be anticipated between various producers and the project.

At the time this decision was made, polyvinyl chloride (PVC) and epoxy foams did not seem to have the same potential as polyurethane foam for

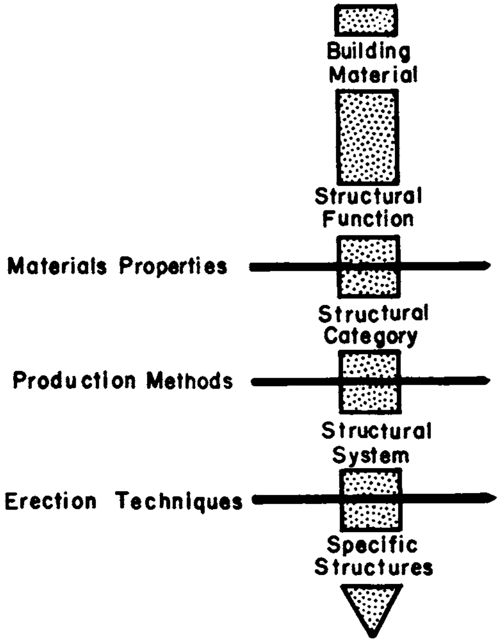

FIGURE 1
Basic pattern of structural investigation.

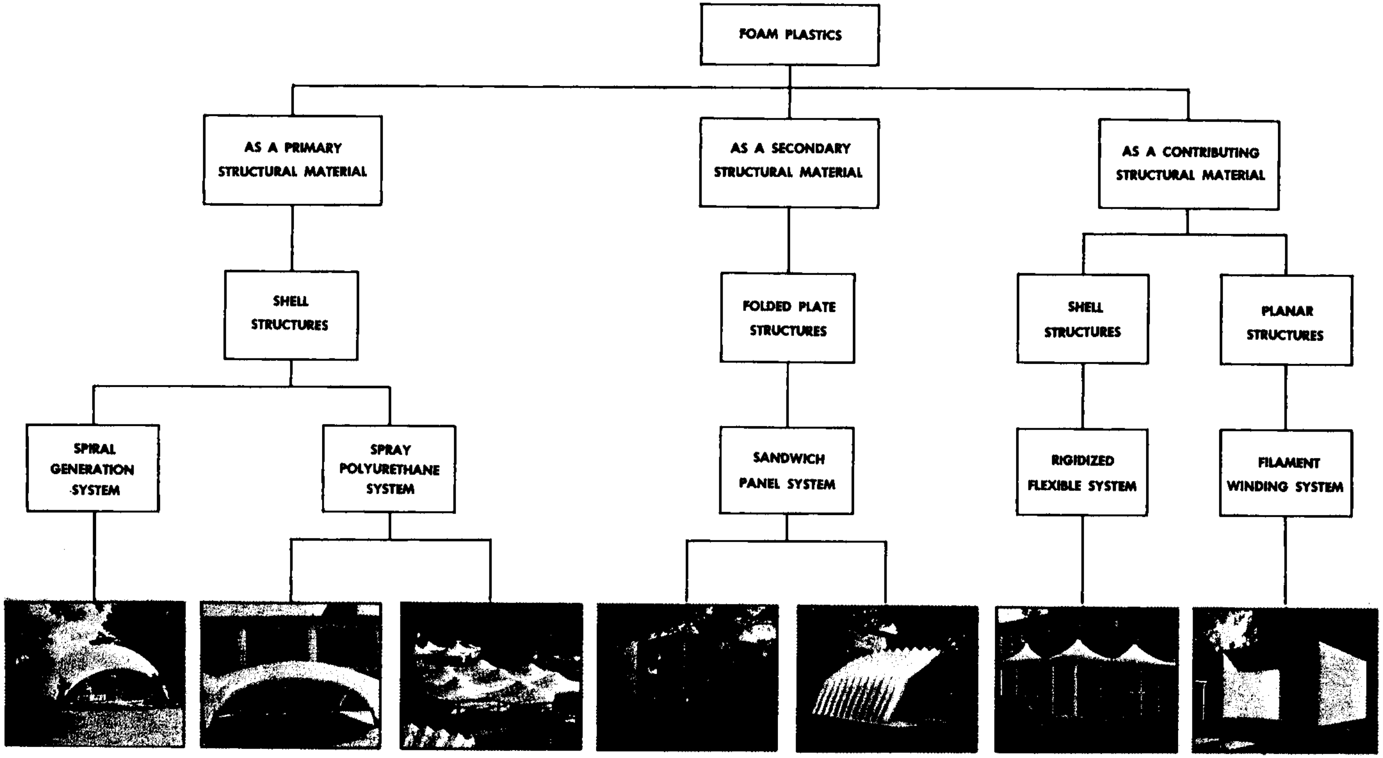

FIGURE 2
Guide to systems investigated.

early introduction in the emerging nations because of their cost and their limitations from the standpoint of properties and production and because of the limited interest of the plastics industry in this area. Breakthroughs in technology have recently occurred with the PVC foams, however, and this may put them in the forefront with other foam plastics as having a high potential for the near future.

The reason no further work was done with polystyrene foam is that the material is already well developed, especially in the form of Styrofoam, and the techniques governing its use as a structural material, as developed by the Dow Chemical Company, left very little room for any substantial contribution by the project staff.

There are many possible combinations of structural concepts, production methods, and erection techniques that can lead to logical and economical cellular plastics structures. Within the framework of this approach, our project staff has developed a variety of structural systems—the folded-plate system (in collaboration with Union Carbide), the spray–polyurethane system (in collaboration with Wyandotte Chemicals), the rigidized flexible system, and the filament wound system (in collaboration with Hercules Powder). It has also explored the application of other structural systems like the Dow Spiral Generation system and the Plydom folded-plate system, which are both in commercial production. The structural forms are illustrated in Figure 2.

Furthermore, the project staff has conducted research on appropriate structural shapes and testing methods which should prove valuable in the development of new structural systems, either by the project staff or by others.

From our analysis of structures, we find that there are three ways in which foam plastics can be used as a structural material: (1) as a primary structural material which carries the principle loads and stresses of the structure; (2) as a secondary structural material which takes secondary stresses while allowing another material to carry the principle stresses; (3) as a contributing structural material, either as a form-giving device which allows a production technique to be utilized or as a tertiary structural material which braces another material acting as a secondary element.

Figure 2 also illustrates the relationship between the use of material, structural type, production system, and structure development. It is intended to serve as an introductory guide to the systems investigated by the project staff which are described in detail in our recently published report, *Structural Potential of Foam Plastics for Housing in Underdeveloped Areas* (for AID by the Architectural Research Laboratory, University of Michigan, Ann Arbor, November 1965).