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PHYSIO-CHEMICAL STUDY OF SMOKE EMISSION BY AIRCRAFT INTERIOR MATERIALS

Part II

Rigid- and Flexible-Urethane Foams

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FINAL REPORT

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16. Abstract

A study was conducted by personnel of the University of Utah's Flammability Research Center to determine the flammability characteristics and thermal degradation of urethane cellular plastics used in aircraft interiors.

Initially, model urethane polymers, representative of systems used in aircraft interiors, were prepared, and the effect of the chemical structure of isocyanates and ployols on performance during fire exposure were studied. A series of non-fire-retarded rigid-urethane foams was synthesized and evaluated to serve as the basis for further research directed toward the synthesis of fire-retarded systems. Following this, a series of fire-retarded rigid foams was synthesized incorporating reactive and non-reactive fire retardants in various concentrations.

The flammability characteristics of these cellular plastics were evaluated using test methods for the ease of ignition, flame propagation, fire endurance, smoke emission, and oxygen index as criteria.

Based on the information obtained, a series of optimized rigid foams, which incorporated reactive and auxiliary fire retardants, was prepared and evaluated. The optimized rigid foam systems exhibited substantial improvements in the ignition, flame propagation, and fire-endurance characteristics, and a moderate reduction in the tendency to produce smoke.

Similar studies were carried out using formulations representing flexible urethane foams. Improvement in those properties governing ignition and flame propagation were realized at the expense of increasing the smoking tendency of these flexible systems.

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PREFACE

This report was prepared by personnel of the Flammability Research Center, College of Engineering, The University of Utah for the Federal Aviation Administration. The work was part of a program of the Systems Research and Development Service, Washington, D. C. The work was administered under the direction of Mr. J. F. Marcy.

Many people within the Flammability Research Center, the College of Engineering, the Division of Materials Science and Engineering, and the Federal Aviation Administration contributed to the technical success of this project. The excellent cooperation of NAFEC personnel has dramatically helped to attain the research objectives of this project.

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Purpose

The purpose of this project was to determine those parameters which govern the smoke emission characteristics of polymeric materials. Special emphasis was directed toward the development of a fundamental understanding of the parameters, both chemical and physical, which lead to smoke development and, subsequently, light obscuration during the pyrolysis and combustion of polymeric materials.

The project was divided into six separate phases of study:

1. A review of the chemical literature pertaining to smoke development in polymeric materials.
2. The determination of the physio-chemical nature of the selected polymeric materials which cause emission of smoke particulates and aerosols during pyrolysis or actual fire exposure.
3. A study of the effect of fire-retardant structure and concentration on the smoke emission of urethane foams.
4. The measurement and, where possible, the prediction of the response of the selected polymeric materials during actual fire exposure.
5. The development and synthesis of test samples for NAFEC evaluation of smoke-development characteristics of urethane polymers.
6. Analysis of the modified polymeric materials to ensure that they do not produce an intolerable toxic situation.

Background

Federal Aviation Regulations Part 25 - Airworthiness Standards for Fire Protection specified four separate materials categories depending upon their intended use or location in the aircraft. In order of decreasing severity of application, these are listed as follows: (1) fireproof, (2) fire-resistant, (3) flame-resistant, and (4) flash-resistant. The first two categories are for materials either completely or largely non-combustible in composition such as metals, glass and asbestos. The organic materials used in aircraft interiors are basically combustible. The maximum burn rate permitted under Federal regulations adopted in 1947 for rating materials as flame-resistant was 4 inches per minute as tested in the horizontal position. A 1966 revision of the Federal Standards required that certain types of interior materials used for wall, ceiling, partition, and floor construction be self-extinguishing in the vertical position within an 8-inch char length.[3] The revised standards also eliminated the lowest category of flash-resistant materials which permitted a burn rate as high as 20 inches per minute for seat-cushioning materials. Further upgrading of the standards as contained in the FAA Notice of Proposed Rule Making (PRM 69-33) issued in July 1969 and adopted as a regulation in May 1972, increases the severity of the test and decreases the allowable char and/or burn limit to 6 inches for some materials such as panels and 8 inches for upholstery fabrics and other cabin furnishings.

Marcy and Johnson[4] listed 5 major factors related to fire which may provide useful data in rating material as follows: (1) minimum heat, temperature, and time required for ignition, (2) rapidity by which flames propagate following ignition, (3) tendency for flash fire to suddenly erupt, (4) tendency for flaming to become self-extinguishing upon removal of the ignition source, and (5) rate and total heat generated by the combustion process. Other factors of increasing interest in aviation safety are measurements of smoke and other combustion product concentrations as these affect either visibility or indicate a toxic hazard.

The physiological and toxicological aspects of smoke during fire exposure have been discussed by Einhorn.[5] Consideration of those parameters affecting the combustion of plastics has led the authors to list the hazards to life support in the following order of decreasing importance for a typical airplane crash fire:

1. Flame propagation
2. Smoke development
3. Attack by superheated air or gases (maximum survivable temperature)
4. Asphyxiation - caused by rapid depletion of available oxygen
5. Toxicity hazards of combustion products.

A sixth factor must be considered which probably outweighs the factors mentioned above. It is the combined effect of the first five factors. Smoke develops very rapidly and reaches a level, even in the event of small fires, which hinders evacuation during early stages of flame propagation. Toxic hazards are listed last due to the time factor evolved in physiological damage.

Thus, considering the possible hazards encountered during the combustion of plastics in confined spaces, the chemist may elect to modify the basic polymer structure or he may incorporate fire retardants, either reactive or inert, into the plastic in order to modify the rate of combustion. Either route tends to produce a more incomplete combustion thereby resulting in greater smoke generation accompanied with an increase in the concentration of toxic byproducts.

Recent studies conducted by Einhorn, et al.,[5] have confirmed the relative hazard by the combined action of carbon monoxide and temperature in reducing the survival capability of laboratory animals subjected to the combustion products of fire-retarded plastics. Further effort is being directed toward the evaluation of the effects of individual gaseous degradation products and the potential interactions caused by exposure to multiple gaseous products.

SMOKE DEVELOPMENT IN POLYMERIC MATERIALS

The burning of many polymers is accompanied by smoke development. The term "smoke" has eluded a precise and widely-accepted definition. A dictionary definition of smoke is "the volatilized products of the combustion as an organic compound, such as coal, wood, etc., charged with fine particles of carbon or soot; less properly, fumes, steam, etc."[6]

Perhaps the most common definition of smoke is that adopted by the ASTM[8] with regard to air polution. They define smoke as "finely divided particles of microscopic size resulting from incomplete combustion. The particles consist mainly of carbon and other combustible material." The ASTM differentiates among smoke, fume, fog, mist, dust, fly, ash, and vapor. They define soot as an agglomeration of smoke particles. With respect to the subject of flammability, it is suggested that the ASTM definition of smoke is either too restrictive or that a new term is necessary. A preferred practical defination is that of Hilado,[9] that "smoke is the gaseous products of burning organic materials in which small solid and liquid particles are also dispersed; smoke can also be defined as solid particles, such as carbon and ash, suspended in air."

Based on its more restrictive sense, the measurement of smoke from burning polymeric materials has been based only on its affect on light transmission. This is the detection basis used in the ASTM E-84 Tunnel Test,[10] the NBS Chamber,[11] the LRL Chamber,[7] and the Rohm and Haas XP-2 Chamber.[12] In all of these methods the detection is made by a light-beam photocell arrangement. With some of these test methods, it is possible to vary the ignition source and the degree of ventilation. The LRL Chamber permits the exposure of materials to heat fluxes varying from 2.5 to 25 watts/cm^2.

While the measurement of light obscuration is a direct way of determining one of the important effects of smoke during a fire, other studies are required in order to answer the fundamental questions pertaining to the formation, nature, and possible dimension of smoke. This includes the important question of the possibility of retarding flammability without increasing the tendency to smoke.

An important group of compounds in most smoke from burning polymers includes the carbonaceous particles which may vary in size from on the order of 0.01 to 1.0 or more microns. Particles of this size have a terminal settling velocity of less than approximately 0.0001 ft./sec., which is so small that the particles settle hardly at all. Interest in carbon-forming reactions has existed for many years because of commercial applications to partial-oxidation processes for producing carbon black.[13] Raw materials for these processes include natural gas, oil, coal tars, and acetylene. Commercial carbon black consists of nearly spherical particles which tend to associate in loose chains in a semi-graphitic structure. Chemically, the particles are mainly carbon, but they may also contain hydrogen and oxygen, with the latter being confined mainly to the particle surface where oxidation occurred.

Some experimental studies of the mechanism of carbon formation have been reported. Of importance is the careful work of Homann and Wagner[14] on premixed carbon-forming flames of acetylene and benzene at low pressures. Based on this and previous work, they conclude that the formation of carbon particle nuclei takes place in the gas phase by free-radical combination, dehydrogenation, and polymerization reactions of acetylene and polyacetylenes (mass range of 26 to 146), polycyclic aromatic hydrocarbons (mass range of 78 to $\sim$300), and reactive polycyclic hydrocarbons (mass range $\sim$150 to $\sim$550), regardless of whether the gaseous or liquid fuel is aliphatic or aromatic in nature. The nuclei grow and agglomerate to produce the particles actually observed.

Colored gaseous components may also contribute to the opaque qualities of smoke. However, most gases are colorless. Exceptions include Br_2, Cl_2, NO_2, N_2O_3, as well as certain organic compounds (dyes) which contain conjugated chains and chemical groups which intensify color. In addition, the opaque nature of a smoke may be partially or wholly caused by liquid or solid condensation products. In studying the nature of smoke, it is essential to differentiate among these various materials which may be responsible for the observed opaqueness.

In studies on the tendency of various fuels to smoke, Minchin[15] and Clark, Hunter, and Garner[16] found that the tendency of paraffins to smoke increased with the molecular weight. On the other hand, for olefins, diolefins, materials of the benzene series, and materials of the naphthalene series, the tendency to smoke was found to decrease with molecular weight. However, these materials have a far greater tendency to smoke than do the paraffins. Figure 1 shows a summary of the findings of these investigators.

Gaydon and Wolfhard[17] point out that the carbon to hydrogen ratio is an important parameter, but not the only one. Since branched chain paraffins smoke more readily than the corresponding normal isomers, they surmised that the structure of the molecule is also very important. In addition, unsaturation in the molecule increases the tendency to smoke.

Measurements of the height of the flame at which soot first appears was used by Clark, et al.[16] to study the tendency of various alcohols to smoke. Although methyl alcohol does not smoke when burned, all the other alcohols studied exhibited a tendency to smoke and this tendency increases with molecular weight as shown in Figure 2. Secondary and tertiary alcohols smoke more readily than do primary alcohols. Also, alcohols containing double bonds in their structure smoke more readily than do saturated alcohols.

Mickelson and Einhorn,[18] and Einhorn, et al.,[19] have studied urethane and isocyanurate polymers produced by varying the chemical moieties that govern polymer structure as well as the effects of incorporation of fire retardant type and concentration. They found that the principle parameters that effect the development of smoke are:

1. The nature and functionality of the monomers
2. The degree of aromaticity in the polymer backbone
3. The molecular weight per cross-link density
4. The type and concentration of additives that may be incorporated into the polymer system to retard combustion.

Further studies with other generic classes of polymers are necessary to determine if these parameters will also affect smoke development in a similar manner.

The methods used to measure the development of smoke are discussed in detail in Part I of this report and thus, the reader is referred to that discussion.

COMMERCIAL UTILIZATION OF URETHANE FOAMS

General Background

The major emphasis within the scope of this study was directed toward the development of the fundamental parameters governing the smoke emission characteristics of rigid- and flexible-urethane foams. Prior to discussing the research program, it is desirable to review the history of the development of urethane cellular plastics.

The commercial utilization of urethane foams prior to the mid-1950's was of little significance. By 1956 it was estimated that the total world-wide use of all types of urethane foams was approximately 10 million pounds.

The physical properties of urethane cellular plastics can vary widely depending on molecular weight, molecular weight distribution, and the nature of the isocyanate and polyols used in their formulation. Further property variables may be related to such processing factors as length and temperature of post-cure, surfactants used to control cell porosity, and rate and angle of the pouring operation. Generally, urethane foams are classified as either flexible or rigid. A third classification, semi-rigid (or semi-flexible), is quite often used. Considering cross-link density ($\overline{Mc}$)* as a criteria, urethane foams possessing an $\overline{Mc}$ less than 500 are considered as rigid foams; urethane foams having an $\overline{Mc}$ greater than approximately 1500 are usually considered as flexible foams. Thus, the semi-rigid (or semi-flexible) foams usually range in $\overline{Mc}$ between 500 and 1500. For the purpose of this discussion, urethane foams will be identified as rigid or flexible systems. Uses for semi-rigid (or semi-flexible) foams will be incorporated with those of flexible foams.

Flexible Urethane Foams

The flexible urethane foams were quickly developed as a potential replacement for latex foam or chemically-blown rubber sponge after their initial market introduction. Thus, the producers of flexible urethane foam were able to concentrate their research, development, and sales efforts on known areas of commercial utilization. Due to the wide variety of foam components together with a potentially easier and cheaper processing route, the urethanes were able to make rapid inroads into existing product lines.

The first significant volumes of flexible urethane foams were obtained in automotive and furniture seating. Initially, selection of urethane foams was governed almost exclusively on the basis of its lower cost which led many potential users to classify the urethanes as "cheap" replacements for a higher quality latex foam. Improvement of urethane foam properties resulted from modification of processing techniques coupled with the introduction of a wide variety of new raw materials. During the middle 1960's, the low price of flexible urethane foams permitted successful competition with accepted commodities such as cotton and curled hair.

By the mid-1950's urethane topper pads (thin sheets of flexible foam) were used in many models of automobiles produced in the United States, Canada, Scandinavia and Great Britain. These pads varied in thickness and usually ranged from 1/4" to 2" in thickness.

Other major uses for flexible urethane foams included safety applications (dash padding, arm rests, visors, etc.); household products (ironing board pads, mops, sponges, etc.); industrial uses (packaging, encapsulation, pipe covering, and gaskets); and for such miscellaneous uses as clothing interliners, toys, and flexible shoe soles. It should be noted that the lower density of urethane foams was an attractive feature leading to their replacement of latex cushioning in aircraft seating since 1960.

By 1961 total worldwide usage of flexible urethane foams was estimated at 180 million pounds, of which 61 per cent was produced and used in the United States. Table I[20] summarizes the United States flexible foam market statistics from 1960 through 1971 and includes market projections through 1980. Thus, a growth of greater than 500 per cent was realized in the United States for flexible foam markets during the past decade.

$$*\overline{Mc} = \frac{\text{Total weight of foam ingredients} + (C\,Cl_3F)}{\frac{\text{wt. of isocyanate (F-2)}}{\text{M.W. of isocyanate}} + \frac{\text{wt. of polyol } (F_1\text{-}2)}{\text{M.W. of polyol}} + \frac{\text{wt. F.R. Agent } (F_2\text{-}2)}{\text{M.W. F.R. Agent}}}$$

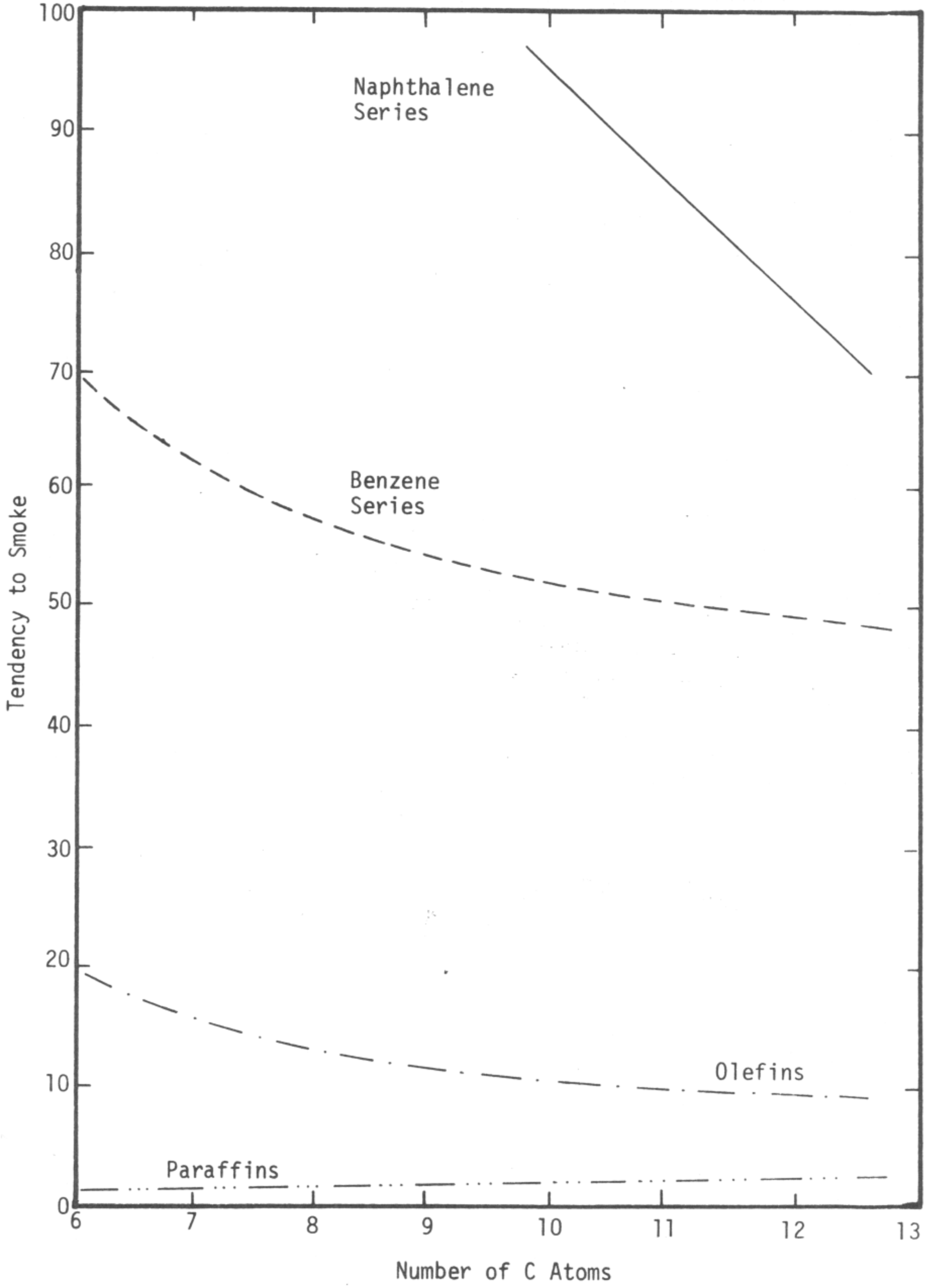


FIG. 1. TENDENCY OF VARIOUS FUELS TO SMOKE

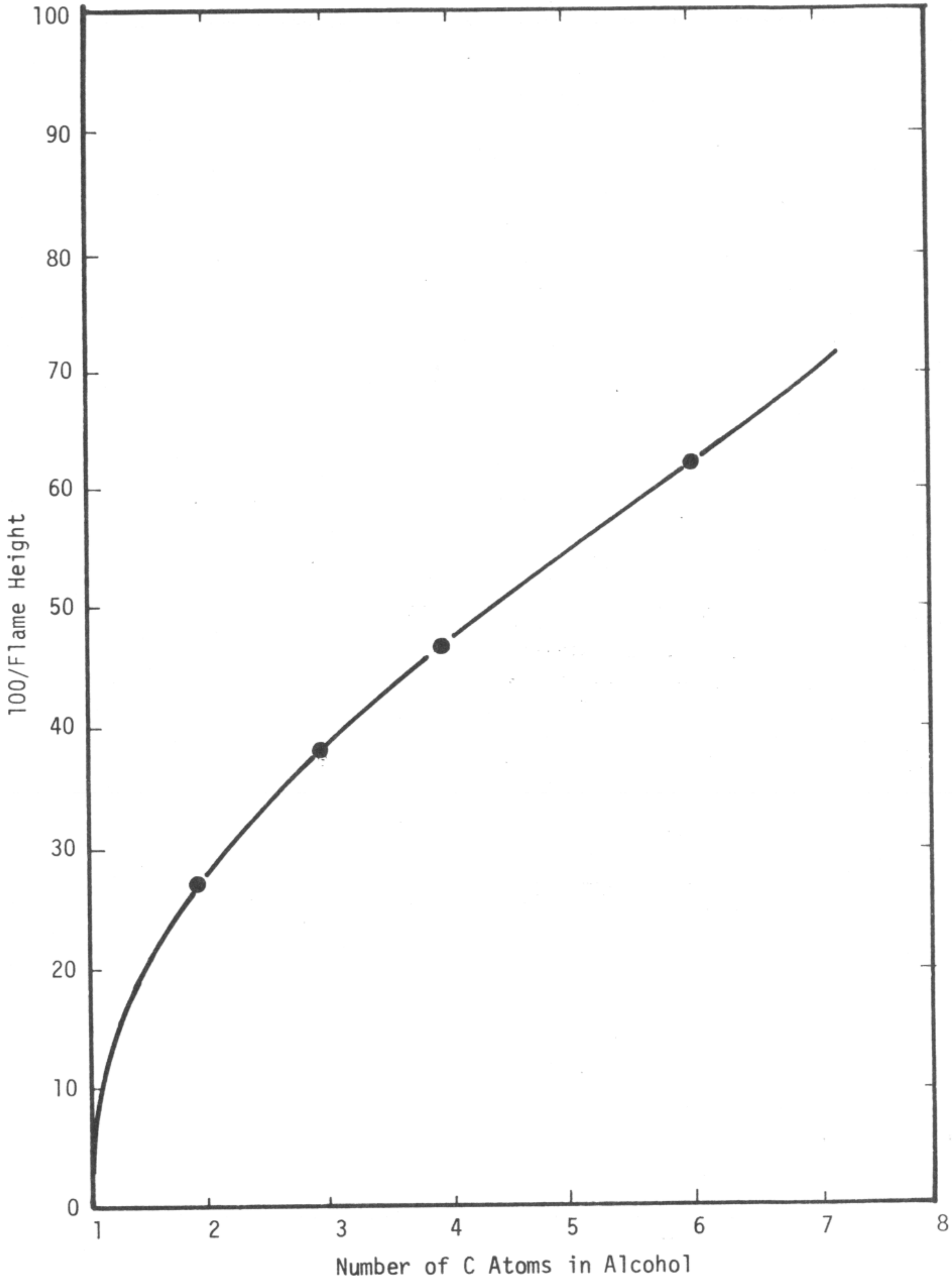


FIG. 2. TENDENCY OF PRIMARY ALCOHOLS TO SMOKE

TABLE I[20]

FLEXIBLE URETHANE FOAM MARKETS - UNITED STATES
(Millions of Pounds)

Use	1960	1965	1970	1971	1975	1980
Vehicles	--	73	170	185	360	600
Furniture	70	120	210	235	400	800
Bedding	10	35	50	60	75	100
Apparel and Textiles	--	25	44	48	50	60
Carpet Underlay	--	3	25	28	40	50
Miscellaneous	--	22	41	44	75	90
Total	80	278	540	600	1000	1700

Similar expansion in the commercial utilization of flexible urethane foams was observed in the rest of the world during the same time period. The applications for which this foam was used were roughly parallel to those in the United States. The volume of materials used in each market category varied widely and was usually dependent on local acceptance codes and the local economy. By 1971 flexible-urethane foam used in the United States was estimated to be 600 million pounds with 1.85 billion pounds estimated for world utilization. Table II[21] summarizes the worldwide statistics for use of flexible-urethane foams in 1971.

TABLE II[21]

WORLD USE OF FLEXIBLE-URETHANE FOAMS (1971)

Trading Area	Total Foam (millions of pounds)	Pounds (per capita)
European Economic Community	580	3.00
Other Western Europe	260	1.80
Eastern Europe	45	0.12
North America	615	2.70
Latin America	110	0.40
Australia, New Zealand, Japan	210	1.80
All Other Asia	30	0.016
Total	1850	

It should be noted that notwithstanding a 500 per cent growth in the United States consumption of flexible-urethane foams between 1961 and

1971, the percentage of U.S. consumption of flexible urethane foams, on a worldwide basis, dropped from 61 per cent to approximately 30 per cent during this period. This is an indication of the very rapid rate of growth in the use of flexible foams throughout the world.

New markets projected to consume large volumes of foam during the next 10 years include packaging and rug underlay. Some market forecasts predict the U.S. usage in the carpeting area will reach a total of 225 million pounds by 1981. This forecast is based on an annual market of 1.5 billion square yards of carpeting of which 10 per cent of the market will require flexible-urethane foam underlay.

It must be realized that many of the urethane products have, in the past, lagged considerably behind projections of this type. In the opinion of the authors, unless flexible-urethane foams possessing vastly improved flammability characteristics are made available, these goals will not be achieved. In fact, more restrictive regulatory standards may well diminish current sales volume if these improved foams are not forthcoming.

Rigid-Urethane Foams

The development of the rigid-urethane markets was slower than that realized by flexible foams due to the use of large volumes of materials that were required to meet more stringent product requirements. In addition, it should be recognized that flexible foams are produced mainly on high production, in plant processing lines and then cut and fabricated. Typical pouring rates range from 60 pounds per minute (batch process) to several hundred pounds per minute (slab production). While rigid foams are produced by a similar slab production, the production rates are lower due to a substantially higher processing exothermic reaction. In addition, many rigid foam applications require in-situ pouring, spraying, or frothing. Production rates for these processes may range from a few pounds per minute to a maximum of 20 to 40 pounds per minute.

Table III[20] summarizes rigid foam statistics for United States markets for the years 1960 through 1971 with market projection carried through for 1980.

TABLE III[20]

RIGID-URETHANE FOAM MARKETS - UNITED STATES

Use	1960	1965	1970	1971	1975	1980
Appliances	8	25	42	50	75	120
Construction	--	21	75	86	155	310
Marine	--	4	8	10	20	40
Vehicles	2	31	37	40	65	100
Furniture	--	--	23	35	75	160
Miscellaneous	--	5	6	6	10	20
Total	10	86	191	227	400	750

A comparison of U.S. rigid-foam markets may be made by studying the figures for European consumption of rigid-urethane markets presented in Table IV.[22]

TABLE IV[22]

EUROPEAN USE OF RIGID-URETHANE FOAM - 1971

Total Market:

Europe 100,000 metric tons
U.S.A. 90,000 metric tons

Use Area	EEC* %	EFTA** %	Other Countries %	Italy %	Ger. %	U.S.A. %
Household Appliances	51.3	42.5	69.6	83.7	35.5	25.6
Building Sector	29.4	17.8	10.1	6.9	40.0	44.4
Transportation	6.9	11.0	5.1	2.0	6.9	21.1
Technical Insulations	6.7	13.6	8.9	3.3	9.0	5.6
Others	5.7	15.5	6.3	4.1	8.6	3.3
	100.0	100.0	100.0	100.0	100.0	100.0

The properties and processing conditions pertaining to rigid-urethane foams may vary widely. Table V[20] compares these parameters for commercially-produced rigid-urethane foams.

*European Economic Community
**European Free Trade Association

TABLE V[20]

TYPICAL PROPERTIES OF COMMERCIALLY-PRODUCED RIGID-URETHANE FOAMS

Foam Type	Spray	Pour	Slab	Prepolymer
Raw Materials				
Amide-based polyol	100			
Sucrose-based polyol		70		137
Sorbitol polyol			80	
Fire retardant	30	30	20	
Blowing agent	48	30	40	42
Surfactant	1.0	1.0	2.0	0.84
Catalyst	0.5	1.5	2.0	0.84
Catalyst diluent		1.5	2.0	
Polymeric isocyanate	198	108	113	
Quasi-prepolymer, (29.4% excess NCO)				143
Foaming Characteristics				
Cream time, sec.	1-2	10	9-10	
Rise time, sec.	10-15	130-140	160-170	
Tack-free time, sec.	30	140-150	180-200	
Maximum exotherm, °F (10-14" bun)		160	156	
Physical Properties				
Density, pcf	2.2	2.0	1.8	2.1
Compressive strength (at yield, psi)				
Parallel to rise	60	31-33	25	45
Perpendicular to rise	--	16-20	15	--
Tensile strength, yield psi	--	33	40	35
K-factor, BTU/hr/sq ft/F/inch, (vertical to rise)	0.11	0.11	0.11	0.12
Moisture vapor transmission rate, perms/inch	2.77	1.5	3.5	3.0

Comparison of Total United States Cellular Plastics Market Statistics

Table VI[20] presents a summary of market consumption for major classes of cellular plastics used in the United States for the years 1960 through 1971. Projection of future markets extend through 1980.

TABLE VI[20]

SUMMARY - UNITED STATES MARKET STATISTICS FOR MAJOR CLASSES OF CELLULAR PLASTICS
(Millions of Pounds)

Foam Plastic	1960	1965	1970	1971	1975	1980
Rigid Urethane	10	86	191	227	400	750
Flexible Urethane	80	278	540	600	1000	1700
Polystyrene	50	120	300	354	582	980
Vinyl	20	85	250	280	400	600
Misc. Thermoplastic	1	12	50	70	160	400
Misc. Thermosetting	3	10	15	15	20	25
Total	164	591	1346	1546	2562	4455
Use						
Appliance	11	33	52	65	155	210
Construction	22	71	130	150	260	535
Marine	2	16	28	33	75	110
Vehicles	11	134	305	320	557	905
Furniture, Bedding	86	180	365	425	665	1300
Flooring, Underlay	2	15	85	100	140	225
Packaging, Cups and Trays	20	45	210	250	425	750
Apparel, Textiles	5	40	65	75	100	200
Miscellaneous	5	57	106	128	185	220
Total	164	591	1346	1546	2562	4455

As mentioned earlier, the rigid cellular plastics have been subjected to more severe service specifications than have the flexible cellular plastics. Within the past year a considerable increase has been noted in pending legislative restrictions which may substantially alter future market requirements. Several regulatory agencies have already introduced modified codes which limit ignition, flame propagation, and fire endurance characteristics of cellular plastics. Even more restrictive regulations governing the smoking tendency of materials and the nature and concentration of products of combustion resulting from fire exposure of cellular plastics are pending by major national and local agencies. There is doubt whether many of today's materials can be modified so as to meet the future restrictions prior to the 1980's. Several new types of rigid-isocyanurate foams, polysaccharide foams, and modified polyimide foams are now under development. These new cellular plastics may substantially replace today's materials within the next decade.

More reliable means of fire detection and suppression, coupled with a more modern engineering and systems approach to construction design and fabrication techniques as well as increased consideration directed to potential fuel loading in completed structures must be considered if rigid-cellular plastics are to meet the short and long-range goals projected by market research studies carried out by the chemical and plastics industries.

COMMERCIAL UTILIZATION OF FIRE RETARDANTS FOR URETHANE FOAMS

Rigid-Urethane Foams

Approximately 65 million pounds of flame-retardant rigid-urethane foams were consumed by 1967. Flame retardancy was achieved either with reactive systems (for about 50 million pounds of foams) or with additives (for about 15 million pounds of foam). The chief reactive systems were phosphorous - or halogen-containing polyols or other materials like phosphonate esters - that react like polyols. Consumption of these materials was about 9 million pounds in 1967.

Several companies introduced isocyanurate rigid foams during 1967. These products offer significant improvement in flame-retardant properties and service temperature range over flame-retarded rigid polyurethane foams.

Flexible-Urethane Foams

Approximately 10 million pounds of flexible urethane foams were flame retarded by 1967. New regulatory standards increased the demand for more resistant properties since 1967.

FUTURE TRENDS IN COMMERCIAL FIRE RETARDANTS

A marked change is taking place in the plastics' industry as new standards are being promulgated by various regulatory agencies. Three major factors responsible for these changes are:

1. Government and industry's self-policing regulations
2. Increasing consumer concern over product safety
3. A growing realization on the part of manufacturers that safe products are good business.

Table VII[23] presents a review of the pattern of consumption for flame retardants for the period from 1960 through 1970. Estimates for future use are projected through 1975.

TABLE VII[23]

FLAME RETARDANTS - PATTERN OF CONSUMPTION
(Millions of Pounds)

	1960	1963	1964	1965	1966
Additive Types					
Phosphate Esters	26	31	34	38	41
Antimony Oxide	10	15	15	17	20
Chlorinated Paraffins	6	8	7	9	9
Others	1	2	2	3	5
Totals	43	56	58	67	75
Reactive Types					
Chlorendic Acid and Anhydride	6	8	11	13.0	15
Phosphorus-Containing Polyols	--	1	2	3.5	6
Others	8	10	13	17.0	21
Totals	14	19	26	33.5	42
Total Fire Retardants	57	75	84	100.5	117
Intumescent Coatings (In Millions of Gallons)	--	--	280,000	300,000	400,000

	1967	1968	1969	1970	Esti-mated 1971	Editor's Estimated 1975 Market
Additive Types						
Phosphate Esters, Non-Halogenated	43.0	47.0	50.7	57.0	62.0	93.0
Phosphate Esters, Halogenated	6.5	8.5	9.5	6.0	7.0	8.0
Antimony Oxide	12.6	14.0	16.0	14.0	15.0	16.0
Boron Compounds	1.5	1.5	1.7	2.0	3.0	3.5
Chlorinated Paraffins	8.0	10.0	14.0	18.0	22.0	51.5
Others	4.6	5.0	5.7	7.0	9.0	12.0
Totals	76.2	86.0	97.6	104.0	118.0	184.0
Reactive Types						
Reactive Systems (Urethanes)	9.0	8.5	9.5	11.0	15.0	35.0
Reactive Systems (Polyesters)	15.0	17.0	19.0	23.0	27.0	40.0
Epoxy Intermediates	1.3	1.5	1.7	1.8	2.0	3.0
Others	19.0	4.5	5.0	6.0	7.0	10.0
Totals	44.3	31.5	35.2	41.8	51.0	88.0
Total Fire Retardants	120.5	117.5	132.8	145.8	169.0	272.0

EXPERIMENTAL PROGRAM

A series of model compounds were prepared representing as closely as possible the structures of commercially-available urethane polymers. Following the initial evaluation of non-fire-retarded and fire-retarded model compounds, a second series of model urethane foams was prepared, using laboratory equipment and simulating actual production techniques. Additional experiments were conducted using commercial foam systems. The purpose was to develop optimum foam systems with superior fire resistance while exhibiting minimum smoke emission properties.

Model Urethane Polymers

A study of the thermochemical, physical, and flammability characteristics of urethane polymers was undertaken by personnel of the Flammability Research Center of The University of Utah.

A series of model urethane polymers, having chemical structures representative of flexible- and rigid-urethane foams employed in airframe construction and finishing, were prepared using hexamethylene diisocyanate, tolylene diisocyanate, 4,4' diphenylmethane diisocyanate, and polymethylene polyphenyl isocyanate. Table VIII presents the structure and chemical analysis of the above-mentioned isocyanates.

The polyether polyol (a reactive hydroxyl compound) used to prepare the initial urethane polymers, was the propoxylated adduct of trimethylolpropane whose structure and chemical analysis is presented in Table IX. The polyol was heated in a vacuum desiccator for 48 hours at 80°C under a pressure of 0.25 mm to strip off excess water. The maximum Karl Fisher moisture analysis acceptable for the polyol was 0.02 per cent.

Where necessary, the isocyanates were vacuum distilled prior to polymerization in order to remove traces of microgel and any dimers and trimers which may have formed during storage.

Thermochemical Characteristics of Urethane Model Compounds

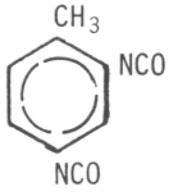
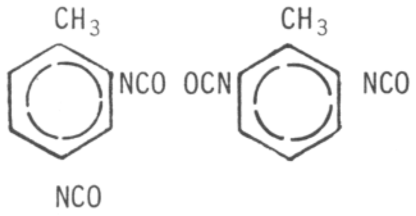
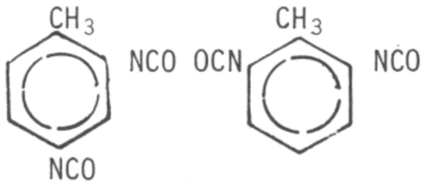
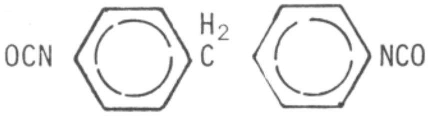
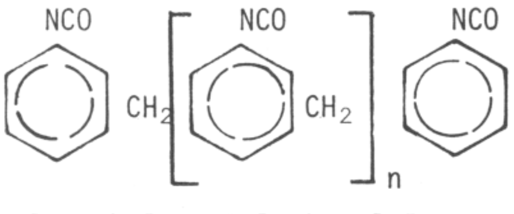
A study of the thermal characteristics of the solid castings* of the urethane model compounds was undertaken using a Dupont Model 950 Thermogravimetric Analyzer and a Dupont Model 900 Differential Thermal Analyzer, and the Mettler Thermal Analyzer. Figure 3 presents the thermograms obtained when samples were heated at a rate of 10°C per minute in an atmosphere of dry nitrogen. The polymers based on aliphatic or lightly aromatic isocyanates show no evidence of char formation as compared to those systems based on the aromatic isocyanates. Thus, the non-char forming materials burn cleanly, while those that form chars produce smoke.

---

*See Appendix D for method of preparation.

TABLE VIII

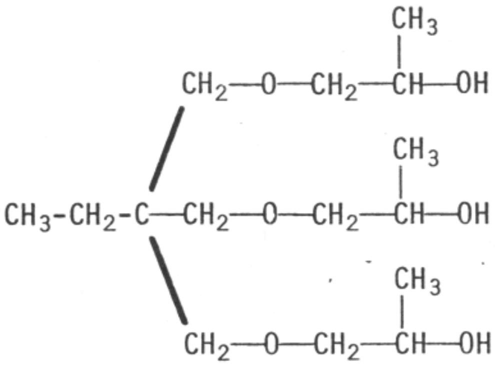
ISOCYANATE STRUCTURE AND CHEMICAL ANALYSIS

Material	Assay %	HC%*	TC%**	Acidity	Eq.Wt.	Typical Use
 Tolylene diisocyanate (2,4 Isomer)	99.5	0.01	0.10	0.01	87	Flexible Foams Rigid Foams Elastomers Coatings
 Tolylene diisocyanate (80/20 Isomer Ratio)	99.7	0.01	0.05	0.008	87	Flexible Foams Rigid Foams Elastomers Coatings
 Tolylene diisocyanate (65/35 Isomer Ratio)	99.5	0.01	0.10	0.01	87	Flexible Foams Rigid Foams Elastomers Coatings
 4,4' Diphenylmethane diisocyanate	99.5	0.002	0.10	0.002	125	Rigid Foams Coatings
 Polymethylene Polyphenyl Isocyanate	99.2	0.28	-----	-----	133	Rigid Foams
$OCN(CH_2)_6NCO$ Hexamethylene diisocyanate	98.0	0.005	-----	-----	84	Fibers Coatings

* Hydrolyzable Chlorides
** Total Chlorides

TABLE IX

POLYOL STRUCTURE AND CHEMICAL ANALYSIS



(Idealized Structure)

Average Molecular Weight	291.6
Hydroxyl Number	577.0
Water, %	0.03
Unsaturation (meg/g)	0.005
Volatiles, % by weight	0.1
Sodium and Potassium, ppm	100
Acid Number	0.4
Viscosity, cps at 25°C.	1690

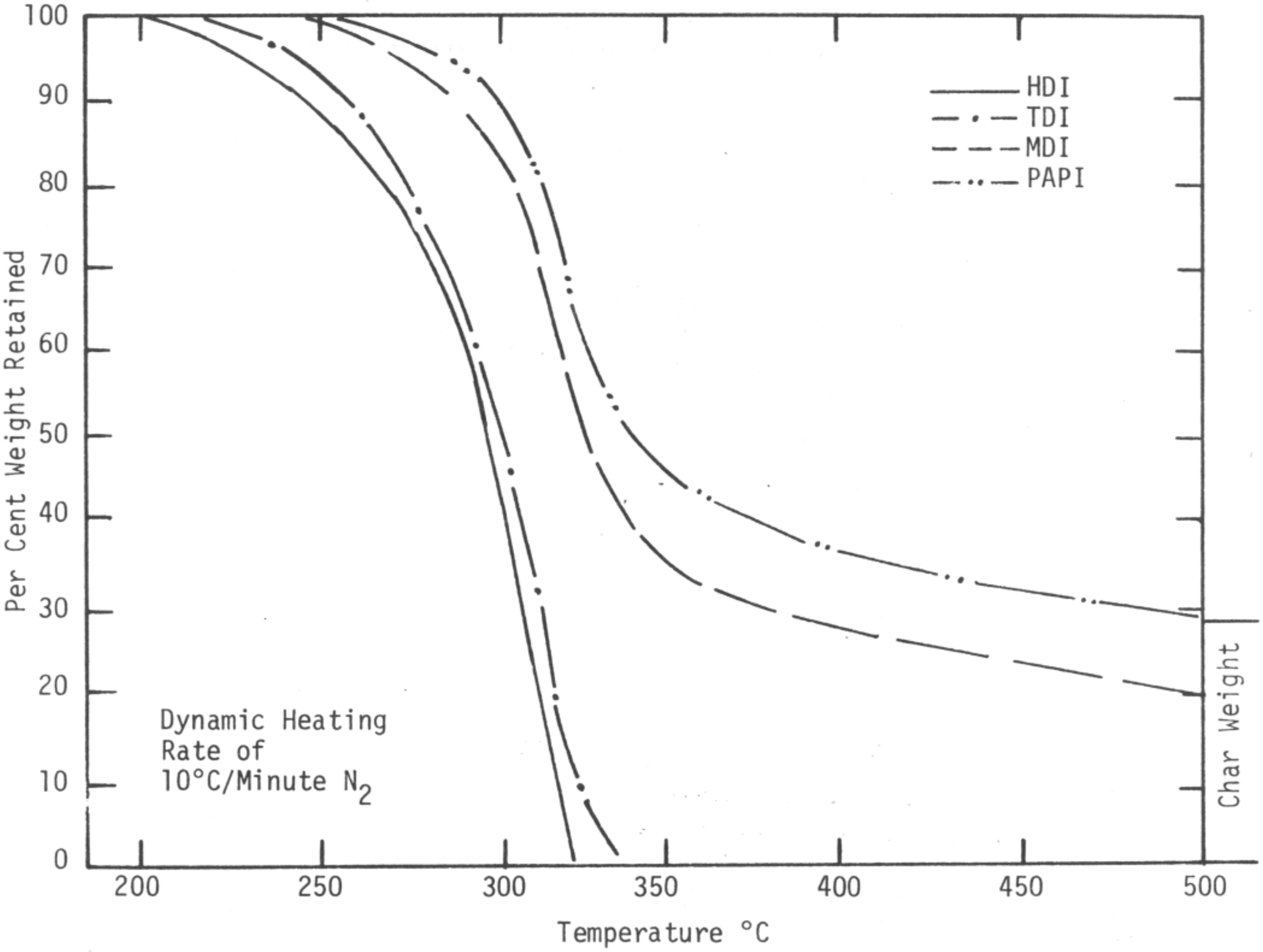


FIG. 3. EFFECT OF ISOCYANATE STRUCTURE ON THERMAL DEGRADATION OF MODEL URETHANE POLYMERS BASED ON TMP-312 POLYOL

The polymer based on hexamethylene diisocyanate and the propoxylated adduct of trimethylolpropane showed initial degradation at 185°C. The polymer based on the 2,4: 2,6 isomer of tolylene diisocyanate showed initial weight loss at 212°C. Table X summarizes the effect of isocyanate structure on thermal stability.

TABLE X

THERMAL STABILITY OF ISOCYANATE-BASED POLYMERS

Isocyanate	°C Initial Weight Loss	°C 50% Weight Loss	% Weight Remaining 500°C	Approximate Activation Energy	n
Hexamethvlene diisocyanate	188	305	0	30.6	1.10
2,4, 2,6 Isomer Tolylene Diisocyanate	212	310	0	36.2	1.10
4,4' Diphenylmethane Diisocyanate	250	327	21	53.5	1.98
Polymethylene Polyphenyl isocyanate	265	345	30	61.0	1.70

The kinetic information presented in Table X were obtained using the Maximum Point Method developed by Akita and Kase^{24} and illustrated by Equation (1) through Equation (5).

$$\frac{d\gamma}{dT} = \frac{A}{b} e \left(\frac{-E}{RT}\right) \gamma^{n} \qquad \text{Equation (1)}$$

$$\text{Where: } \gamma = \frac{W/W_o - W_f/W_o}{1 - W_f/W_o} \qquad \text{Equation (2)}$$

$T = a + bt$ = Temperature
E = Activation Energy
n = Order of Reaction
A = Frequency Factor
R = Gas Constant
W_o = Initial Weight
W_f = Final Weight
W = Weight Remaining
t = Time

The solution to the kinetic equation is given by:

$$n = \gamma_m^{\;1-n} \qquad \text{Equation (3)}$$

$$E = \frac{nR(T_m)^2}{\gamma_m} \left(\frac{-d\gamma}{dT_m}\right) \qquad \text{Equation (4)}$$

$$A = \frac{bE}{R(T_m)^2} \exp\,(-E/RT_m) \qquad \text{Equation (5)}$$

Where: m denotes "at maximum rate of weight loss."

Figure 4 illustrates how the thermogram can be used to obtain approximate kinetic information.

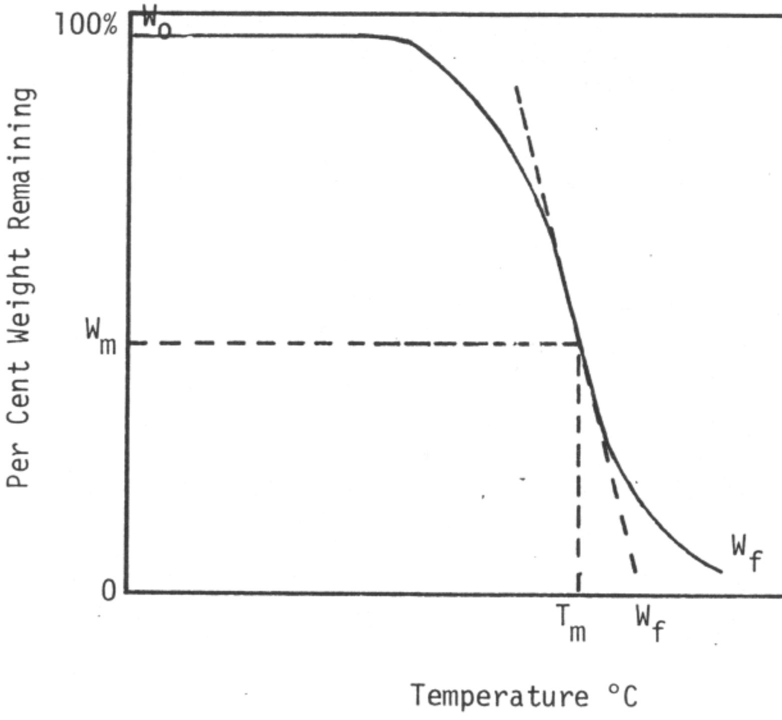


FIG. 4. SINGLE THERMOGRAM KINETIC PLOT

Effect of Molecular Weight Per Cross-Link Density

In order to show the effect of cross-link density, the earlier preliminary work of Einhorn and Mickelson[25] was repeated under the controlled conditions outlined above for distillation of the isocyanates and drying of the polyols. Table XI lists the properties of the propoxylated trimethylolpropane-based polyols.

TABLE XI

PROPERTIES OF PROPOXYLATED TRIMETHYLOLPROPANE-BASED POLYOLS

Property	Polyol				
	TP-340	TP-440	TP-740	TP-1540	TP-2540
Average Molecular Weight	312	425	732	1535	2670
Per Cent Water (as received)	0.03	0.03	0.02	0.03	0.04
Per Cent Water (as dried)	0.01	0.02	0.01	0.01	0.02
Hydroxyl Number,* KOH (g)	557	400	232	112	65.1
Unsaturation, meg/g	0.005	0.005	0.005	0.02	0.03
Acid Number	0.03	0.03	0.04	0.02	0.02

*Determined by phthalation technique.

Samples of model compounds used in this study were prepared using the same techniques as described previously in the isocyanate studies.

Figure 5 shows the effect of polyol molecular weight on the thermal degradation of urethane polymers based on the 2,4: 2,6 (80/20) isomer mixtures of tolylene diisocyanate and propoxylated trimethylolpropane polyols ranging in molecular weight from 312 to 2670.

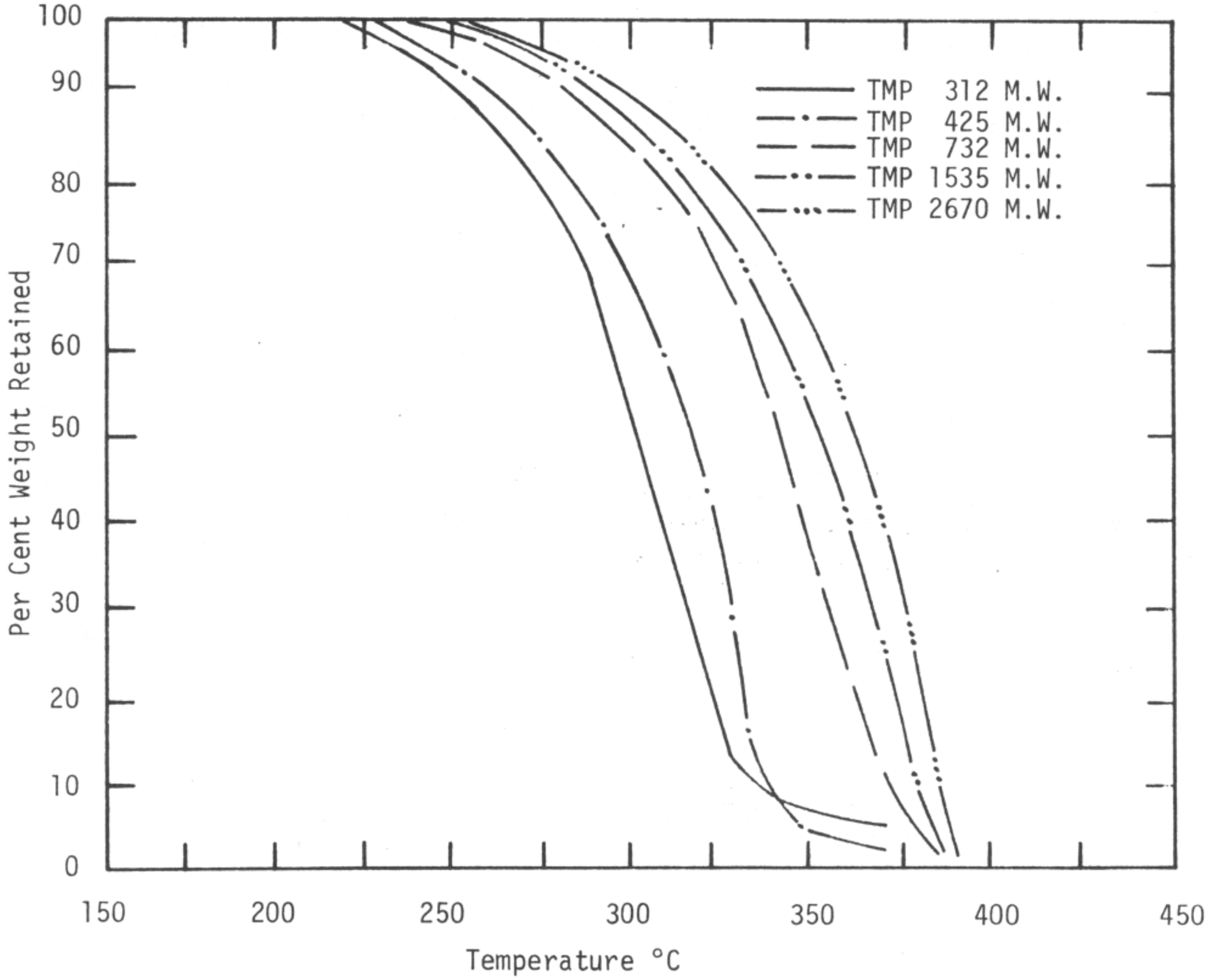


FIG. 5. EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL DECOMPOSITION (2,4: 2,6 80/20 ISOMER TOLYLENE DIISOCYANATE)

Table XII illustrates the effect of polyol molecular weight on thermal stability.

TABLE XII

EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL STABILITY (Toluene Diisocyanate)

Polyol Molecular Weight	°C Initial Weight Loss	°C 50% Weight Loss	% Weight Remaining 450°C
312	210	305	0
425	225	313	0
732	228	345	0
1535	243	355	0
2670	249	365	0

Figure 6 shows the effect of polyol molecular weight on the thermal degradation of urethane polymers based on diphenylmethane diisocyanate.

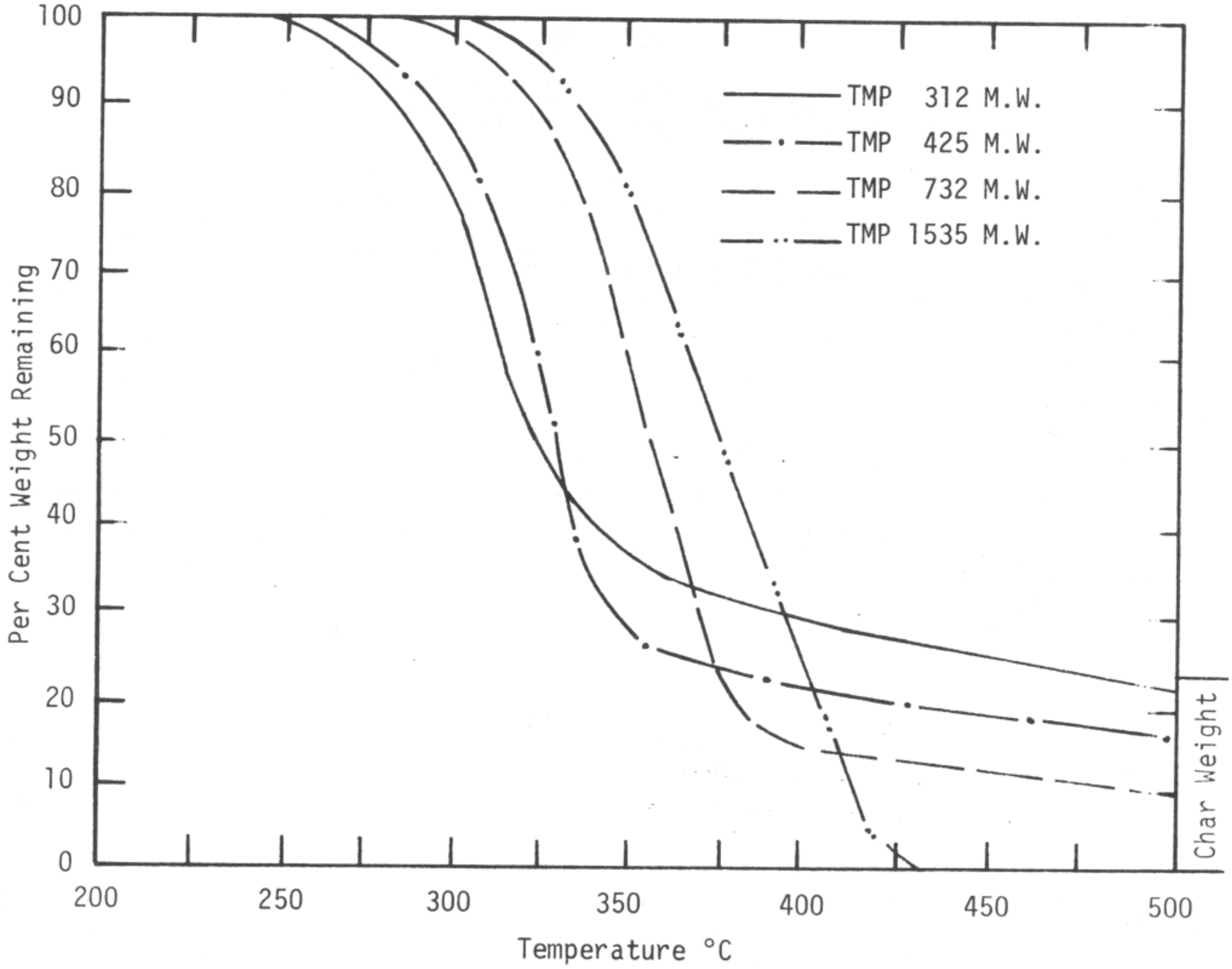


FIG. 6. EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL DECOMPOSITION (4,4' DIPHENYLMETHANE DIISOCYANATE)

Table XIII illustrates the effect of polyol molecular weight on thermal stability.

TABLE XIII

EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL STABILITY
(4,4' Diphenylmethane Diisocyanate)

Polyol Molecular Weight	°C Initial Weight Loss	°C 50% Weight Loss	% Weight Remaining 450°
312	240	320	25
425	251	330	18
732	273	355	12
1535	287	375	0

Figure 7 shows the effect of polyol molecular weight on the thermal degradation of urethane polymers based on polymethylene polyphenyl isocyanate.

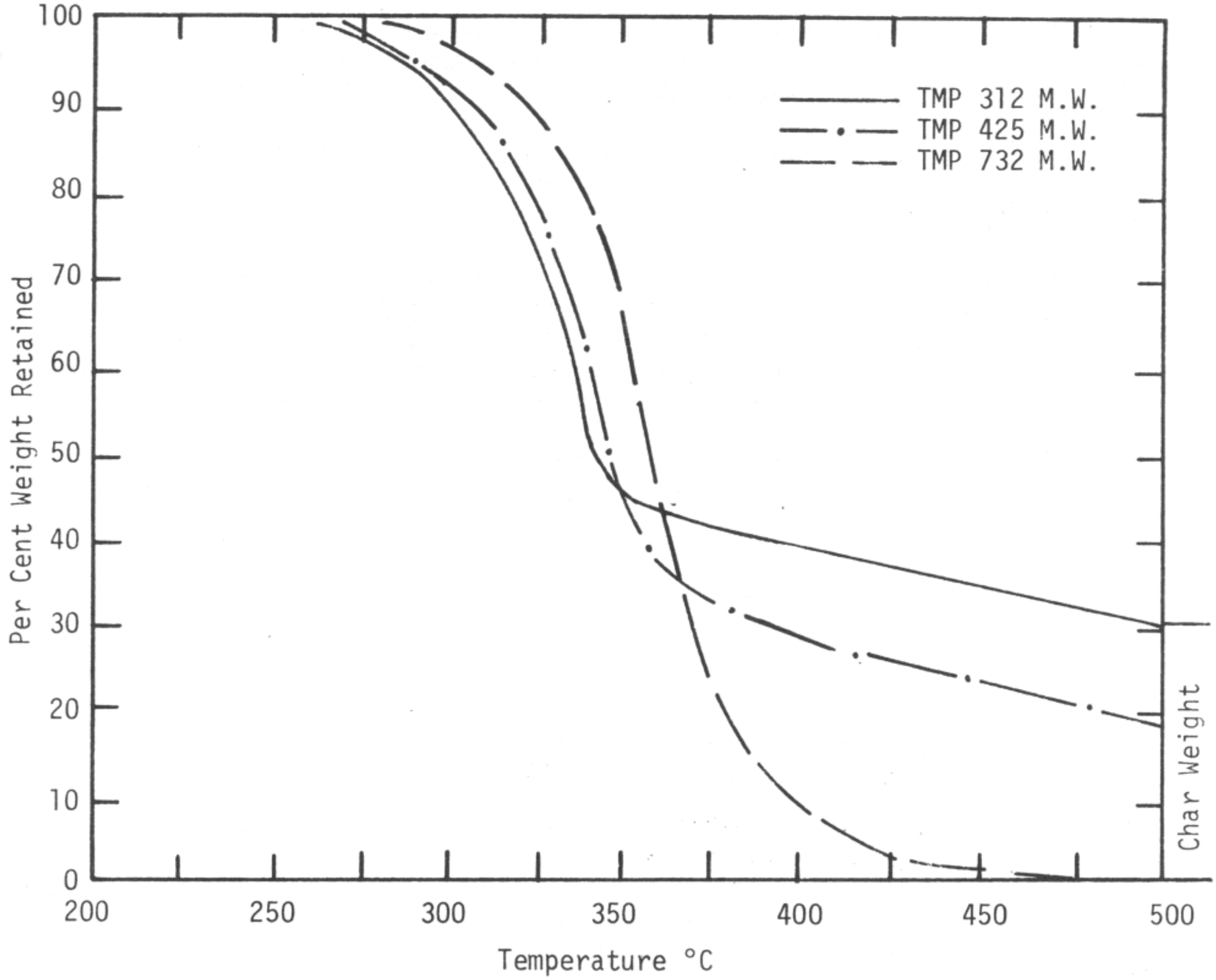


FIG. 7. EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL DECOMPOSITION (POLYMETHYLENE POLYPHENYL ISOCYANATE)

Table XIV shows the effect of polyol molecular weight on thermal stability.

TABLE XIV

EFFECT OF POLYOL MOLECULAR WEIGHT ON THERMAL STABILITY
(Polymethylene Polyphenyl Isocyanate)

Polyol Molecular Weight	°C Initial Weight Loss	°C 50% Weight Loss	% Weight Remaining 500°C
312	210	340	30
425	230	345	19
732	240	355	0

Examination of Tables XII, XIII, and XIV indicates that an increase in aromatic structure of the isocyanate moiety increased the char yield which provided a more stable foam under conditions of thermal exposure.

FLAMMABILITY AND SMOKE CHARACTERISTICS OF URETHANE FOAMS

Introduction

The combustion characteristics of urethane cellular plastics may be correlated with energy relationships within the polymer. The most important energy factors are cohesive energy, hydrogen bonding, heat of combustion, and bond dissociation energy.[26] The effect of the elemental constituents on the flammability characteristics of cellular plastics has been reported in the literature.[27,28,29,30,31] Foams containing the elements phosphorous, bromine, chlorine, antimony (preferably as an oxide), boron, and nitrogen, reduce the flame propagation of urethane polymers.

Consideration must be given to the manner in which the flame retardant is incorporated into the final polymeric structure. It is desirable to build these elements into a position pendant to the polymer backbone to prevent chain scission during their release at time of fire exposure. Evolution of small unsaturated chain segments give rise to the formation of combustible gases during heating, and if the burning process is not quenched by a fire retardant, combustion continues.

Evaluation of the Flammability Characteristics of Urethane Foams

Flammability characteristics are those properties which describe the behavior of a material in actual fire exposure. Laboratory procedures which are used to classify these characteristics may be divided into the following seven categories:

1. Ease of ignition
2. Surface flame propagation
3. Heat contribution
4. Smoke development
5. Fire endurance
6. Products of degradation
7. Mechanism of degradation

Within the scope of this contract, ease of ignition, surface flame propagation, smoke development, and fire endurance characteristics were carried out routinely for all systems evaluated, in preparation for a study relating these factors to the nature of smoke emission of materials. Those systems which proved acceptable by the combined results of these four test procedures were further evaluated to a limited degree.

Preconditioning of Test Specimens

Samples of urethane foam systems were preconditioned in a modified bell jar for a 72-hour period prior to testing at 50 per cent relative humidity and 22°C. The humidity was controlled by a 141 ml solution of 43.0 per cent sulfuric acid. This preconditioning procedure assured that all samples would have a uniform moisture content during the evaluation period.

Non-Fire-Retarded Rigid-Urethane Foams

Foam Preparation

A series of experiments were designed to show the effect of chemical structure on the flammability characteristics of urethane polymers. Five non-fire-retarded rigid-foam systems were prepared as control specimens. A second series of four foam systems were prepared substituting propoxylated trimethylolpropane, molecular weight 425, for the 312 molecular weight homologue. Table XV lists the formulations used to prepare nominal 2 p.c.f. samples representing each system. The foams were prepared in triplicate using a Martin Sweets Company Table Top Mixing and Metering apparatus. The foams were postcured in a circulating air oven at 70°C for a period of 24 hours prior to testing. It should be noted that the demarcation between rigid semi-rigid (or semi-flexible), and flexible foam systems is arbitrary. Within the scope of this report the following classification based on molecular weight per cross-link density is used:

Rigid Foam	$< 500\ \overline{Mc}$
Semi-Rigid (Semi-Flexible) Foam	$>500 < 2000\ \overline{Mc}$
Flexible Foam	$> 2000\ \overline{Mc}$

Characterization of Smoke and Flammability Characteristics of Non-Fire-Retarded Rigid-Urethane Foams

Smoke Development - ASTM D-2843T

The smoke-development properties of rigid non-fire-retarded urethane foams were studied using a modified XP-2 smoke density chamber illustrated in Figure 8. The chamber measures 12 inches by 12 inches by 31 inches high and is constructed of anodized aluminum with stainless-steel fittings. The door is cast aluminum with an inset fire-resistant plate-glass panel to permit observation of the test specimens during burning.

A quantitative analysis of the smoke density is made by the use of a Weston Barrier Layer photocell, incorporated in the walls of the chamber 11 inches above the sample support. Normally, the time necessary to reach 100 per cent light obscuration is used as a measure of the amount of smoke being produced. However, since the approach to 100 per cent light obscuration is asymptotic, it is very difficult to obtain times to 100 per cent obscuration which are reproducible. Moreover, some samples can be burned completely without ever producing enough smoke to give 100 per cent light obscuration. For these reasons, the time necessary to reach 70 per cent light obscuration was taken as the arbitrary criterion for comparing the smoke developed in the burning of various foam samples. For samples of the same material, the time to 70 per cent light obscuration can be measured within a standard deviation of 0.4 seconds.

TABLE XV

FORMULATIONS RIGID NON-FIRE-RETARDED URETHANE FOAM

Raw Materials	Foam 1 (pbw)*	Foam 2 (pbw)*	Foam 3 (pbw)*	Foam 4 (pbw)*	Foam 5 (pbw)*	Foam 6 (pbw)*	Foam 7 (pbw)*	Foam 8 (pbw)*	Foam 9 (pbw)*
Tolylene diisocyanate (2,4 isomer)	94.48	---	---	---	---	---	---	---	---
Tolylene diisocyanate 80% - 2,4 isomer 20% - 2,6 isomer	---	94.48	---	---	---	65.35	---	---	---
Tolylene diisocyanate 65% - 2,4 isomer 35% - 2,6 isomer	---	---	94.48	---	---	---	65.35	---	---
4,4' Diphenylmethane diisocyanate	---	---	---	135.9	---	---	---	93.85	---
Polymethylene polyphenyl isocyanate	---	---	---	---	134.7	---	---	---	100.00
Propoxylated adduct trimethylolpropane (M.W. 312)	100.00	100.00	100.00	100.00	100.00	---	---	---	---
Propoxylated adduct trimethylolpropane (M.W. 425)	---	---	---	---	---	100.00	100.00	100.00	100.00
Silicone Oil L-520**	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Trichlorofluoromethane	30.00	30.00	30.00	30.00	30.00	21.31	21.31	30.00	34.50
Triethylene diamine	2.92	2.92	2.92	2.36	3.53	2.48	2.48	1.94	3.00

* pbw - Parts by Weight
**Union Carbide Corporation

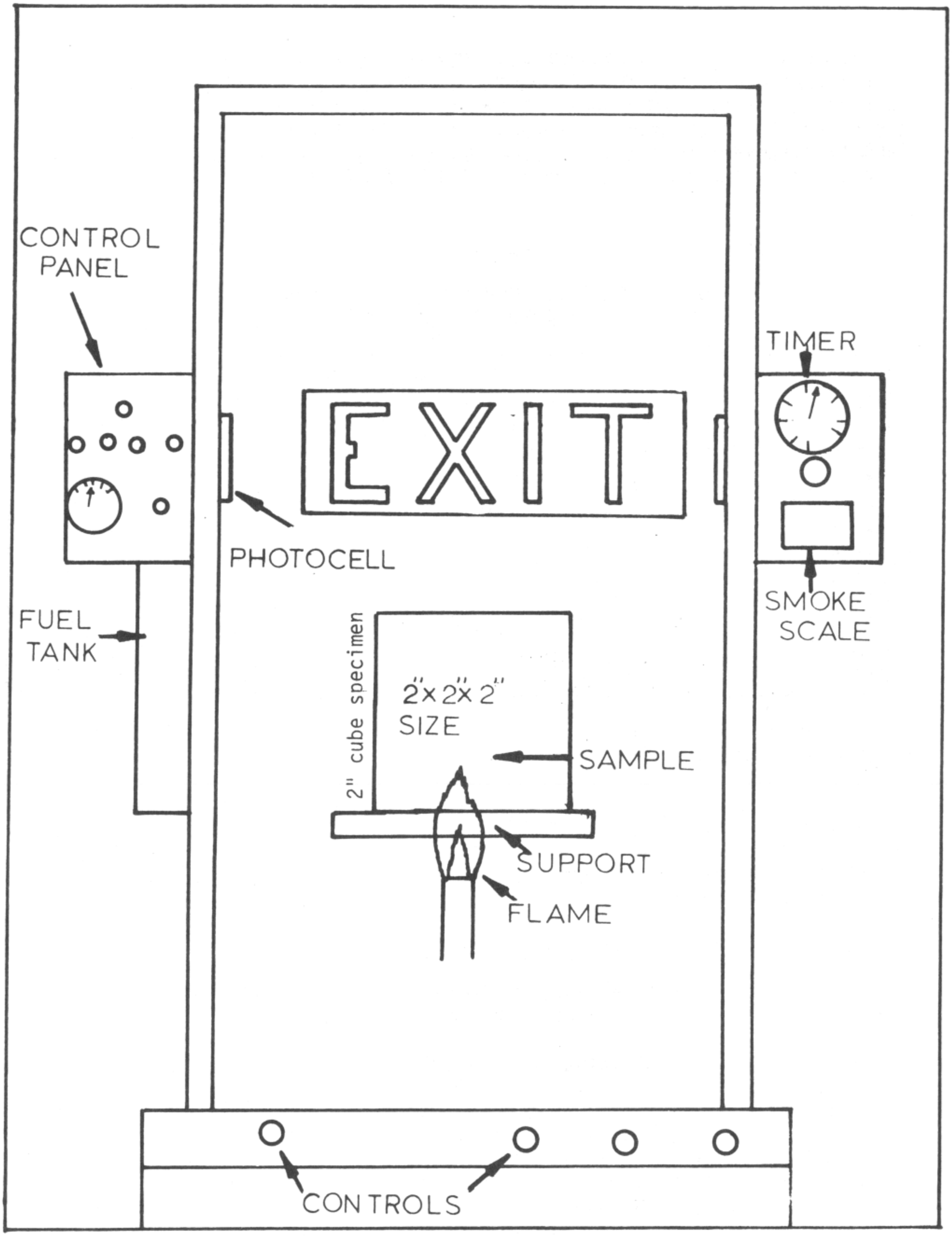


FIG. 8. SCHEMATIC DRAWING XP-2 SMOKE CHAMBER

Two-by-two-by-two inch samples of the rigid non-fire-retarded foams were evaluated using the XP-2 chamber under static conditions. The samples were supported on a 1/4-inch stainless-steel grid and subjected to the direct impingement of a propane flame (1950°F - 50 psig gas pressure). Table XVI summarizes the light obscuration data obtained during the combustion of the non-fire-retarded rigid-foam systems.

TABLE XVI

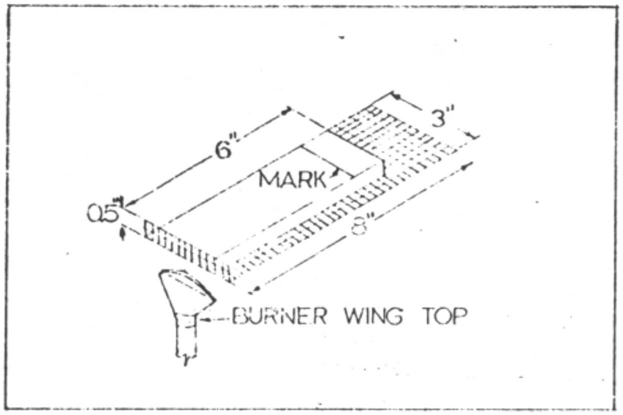
LIGHT OBSCURATION PRODUCED BY THE COMBUSTION OF NON-FIRE-RETARDED RIGID-URETHANE FOAMS

Sample	Time (Seconds) To:				
	10% L.O.	25% L.O.	50% L.O.	75% L.O.	100% L.O.
Foam 1	18.0	20.0	22.0	27.0	----
Foam 2	11.0	18.0	24.0	----	----
Foam 3	5.0	18.0	24.5	28.0	35.0
Foam 4	1.5	3.0	5.3	10.0	28.0
Foam 5	1.5	2.5	6.5	11.0	26.0
Foam 6	12.0	22.0	37.0	50.0	----
Foam 7	7.0	12.0	18.0	40.0	----
Foam 8	2.0	3.5	18.0	33.0	60.0
Foam 9	2.1	5.2	10.5	18.0	37.5

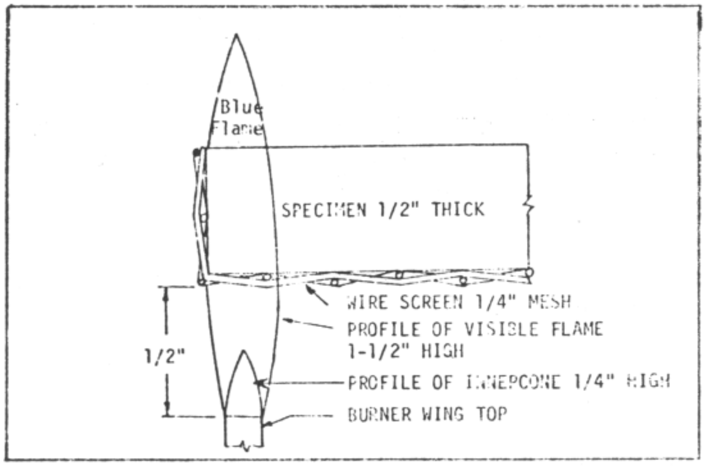
Examination of the results presented in Table XVI shows that all samples of foams evaluated produced a sufficient quantity of smoke to cause 50 per cent light obscuration in a relatively short period of time. Further study of these results shows that all samples based on the isocyanates possessing two or more aromatic rings produced 100 per cent light obscuration. Those samples which did not produce a level of smoke greater than 50 per cent were completely destroyed during the test procedures.

Ignition and Flame Propagation - ASTM D-1692

The ASTM D-1692 small-scale laboratory test has been used to determine the ignition and flame propagation of plastic materials, however, it is not a severe test. Apparatus for the ASTM D-1692 test was revised to overcome problems affecting reproducibility and to permit the testing of foam samples at horizontal, vertical, or 45° angle positions. All samples tested within the scope of this study were evaluated with the sample in the 45° position. The recommended inner cone flame height of 0.25 inch was achieved with a Tirrill burner. Uniform positioning of the burner flame was achieved by constructing a burner slide track at the base of the ring stand used to support the sample. A considerable effect of draft across the urethane foam samples was observed when the tests were conducted in the hood with varied ventilation. Therefore, a test housing was constructed which consisted of a transite box 1' x 2' x 2' high with a one-inch opening around the bottom, an open top, and a front viewing window. Final control of the draft was achieved by adjusting and partially sealing the hood control slat to obtain a draft just sufficient to carry away the pyrolysis and combustion gases. Figure 9 is a schematic drawing of the modified ASTM D-1692 apparatus. Table XVII summarizes the results of evaluation of the non-fire-retarded foam samples using the ASTM D-1692 test procedure. It should be realized that this ASTM procedure is used only as a screening evaluation test to determine the relative flammability characteristics of the specimens evaluated and should not be used to predict the flammability characteristics of these foams in large-scale fires.



9a) Relative Positions of Burner Wing Top, Specimen and Specimen Support



9b) Relative Positions of Burner Wing Top, Flame, Specimen, and Specimen Support

FIG. 9. SCHEMATIC DRAWING - MODIFIED ASTM D-1692 APPARATUS

TABLE XVII

IGNITION AND FLAME PROPAGATION - ASTM D-1692 TEST (MODIFIED - 45°)*
NON-FIRE-RETARDED RIGID-URETHANE FOAMS

Sample	Density (g/cm^3)	% Wt. Loss	Flame Travel Time - Seconds					
			1"	2"	3"	4"	5"	6"
Foam 1	0.0300	100	2.7	4.5	----	8.5	9.0	10.0
Foam 2	0.0245	100	2.2	5.0	6.0	----	8.0	9.3
Foam 3	0.0298	100	2.0	4.0	----	----	8.0	9.0
Foam 4	0.0307	100	2.6	5.0	6.0	10.5	12.0	16.0
Foam 5	0.0362	81	4.0	7.0	10.0	13.0	16.0	22.0
Foam 6	0.0239	100	3.3	5.0	10.0	----	11.3	15.0
Foam 7	0.0382	100	2.0	4.0	7.0	----	10.0	14.0
Foam 8	0.0382	100	3.5	7.0	10.1	14.0	15.5	19.6
Foam 9	0.0417	83	5.0	7.3	10.5	12.0	16.3	20.6

Note: Foam test specimens 6"x2"x1/2".
Results indicated are average of 3 tests/sample.
Flame contact continuous.
*See Table XV for foam formulations

Examination of Table XVII shows that all of the non-fire-retarded rigid foam samples were completely combusted in less than thirty seconds regardless of isocyanate or polyol structure.

Flame Penetration Test - Bureau of Mines Test (Modified)

Fire endurance or flame penetration characteristics is a measure of the resistance of a material to "burn-through" when subjected to the direct impingement of an oxidizing flame. This property of a material is important for use in localizing a fire or providing protection in critical areas.

A schematic diagram of the apparatus used for the flame penetration test is shown in Figure 10.

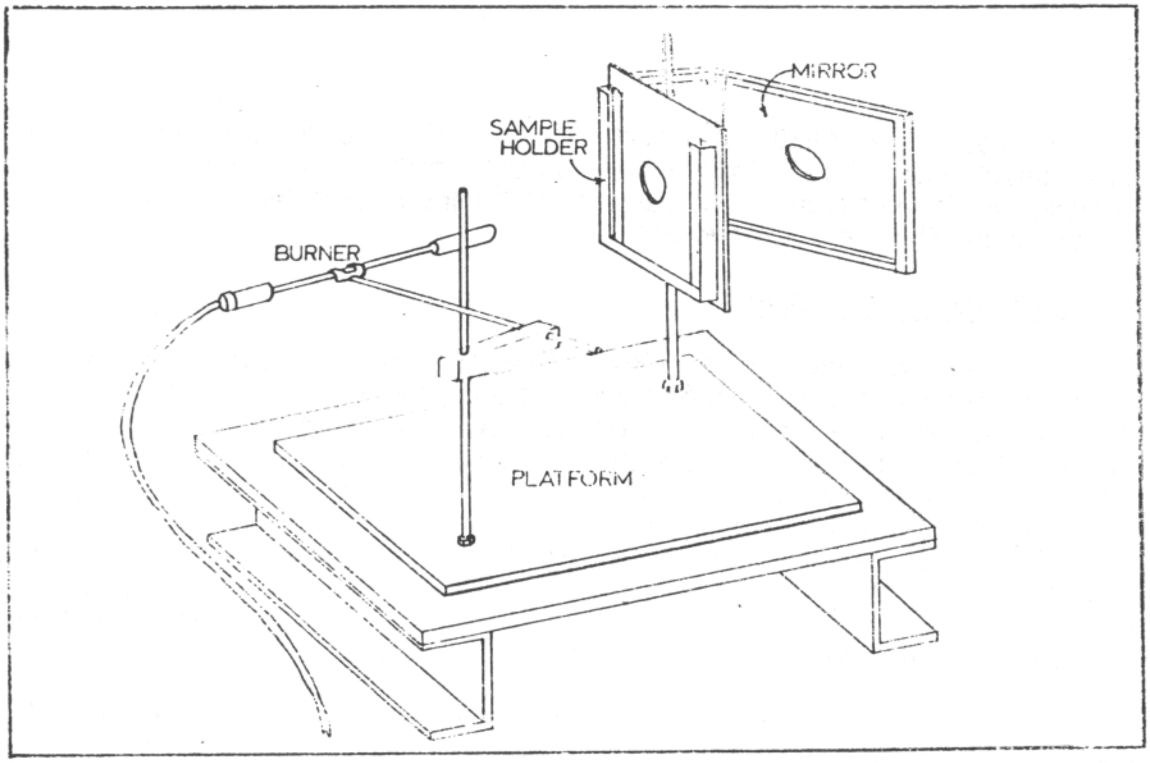


FIG. 10. APPARATUS FOR FLAME PENETRATION TEST

The flame temperature for each test sample run was measured by a chromel-alumel thermocouple which was referenced to the temperature of an ice bath using a Varian Associates Instrument Division Recorder (range of 50mv).

Table XVIII presents the results of the flame penetration studies for the non-fire-retarded rigid-urethane foam systems.

TABLE XVIII

FLAME PENETRATION TEST (MODIFIED BUREAU OF MINES TEST)

NON-FIRE-RETARDED RIGID-URETHANE FOAMS

Sample	Density (g/cm^3)	Burn Thru Time (seconds)	% Weight Loss
Foam 1	0.0300	8.1	100
Foam 2	0.0245	8.8	100
Foam 3	0.0298	8.7	100
Foam 4	0.0307	11.0	100
Foam 5	0.0362	15.3	33
Foam 6	0.0239	9.4	100
Foam 7	0.0382	10.5	100
Foam 8	0.0382	11.5	100
Foam 9	0.0417	13.1	63

*Sample Size 6"x6"x1"

The results presented in Table XVIII indicated that a greater cross-link density $(M\bar{c})$ and a higher degree of aromaticity incorporated in the polymer backbone imparted increased resistance to flame penetration as measured by this test procedure.

Limiting Oxygen Index

This test procedure describes the non-flame propagating nature of a "fuel," liberated from a substrate on heating, in any mixture ratio with the environment. In practice, most measurements are conducted in air, and hence, flame retardancy is conventionally associated with an environment containing 21 per cent O_2. The fact that many test methods used to evaluate flammability characteristics of materials stipulate self-quenching times as a criterion for rating, presupposes ignition and flame propagation by the substrate. As Stuetz, et al.,[32] pointed out, once propagation is possible, its extent depends solely on geometry factors intrinsic in the testing arrangement or in the sample.

Only inherently flame-retardant polymers fulfil the definition, i.e., they produce only non-combustible volatile gases on degradation in air.

The Limiting Oxygen Index Method (LOI)[33,34,35] has been proposed as a test that gives results which appear to be reproducible at a number of different locations.[36] The LOI is defined as the minimum concentration of oxygen in a nitrogen-oxygen mixture at which the combustion of a thin polymer rod can be just sustained in a candle-type fashion.

The General Electric Oxygen Index Analyzer was used to determine the relationship between chemical structure and the LOI for the non-fire-retarded rigid-urethane foams described in Table XVI. The results of the LOI tests are presented in Table XIX.

TABLE XIX
EFFECT OF CHEMICAL STRUCTURE ON LOI
(Non-Fire-Retarded Rigid-Urethane Foams)

Sample	Isocyanate	Polyol	LOI
Foam 1	Tolylene diisocyanate (2,4 isomer)	TMP-312*	18.23
Foam 2	Tolylene diisocyanate 80% - 2,4 isomer 20% - 2,6 isomer	TMP-312	18.25
Foam 3	Tolylene diisocyanate 65% - 2,4 isomer 35% - 2,6 isomer	TMP-312	17.90
Foam 4	4,4' Diphenylmethane diisocyanate	TMP-312	18.30
Foam 5	Polymethylene polyphenyl isocyanate	TMP-312	19.45
Foam 6	Tolylene diisocyanate 80% - 2,4 isomer 20% - 2,6 isomer	TMP-425	18.25
Foam 7	Tolylene diisocyanate 65% - 2,4 isomer 35% - 2,6 isomer	TMP-425**	18.05
Foam 8	4,4' Diphenylmethane diisocyanate	TMP-425	18.25
Foam 9	Polymethylene polyphenyl isocyanate	TMP-425	18.78

*Propoxylated Trimethylolpropane M.W. 312
**Propoxylated Trimethylolpropane M.W. 425

Although the oxygen index test should not be used as a criterion for flame propagation, it is a measure of the phenomena of combustion in the gas phase. The results presented in Table XIX indicated that the specimens evaluated will propagate, by surface burning, a flame at a high rate, at concentrations of oxygen less than that found in normal environments.

The Effect of Structural Variables on the Flammability Characteristics of Non-Fire-Retarded Flexible-Urethane Foams

The flammability characteristics pertaining to ignition, flame propagation, fire endurance characteristics, smoke development, and limiting oxygen index were analyzed and presented in Tables XVI through XIX. The following generalizations may be made:

Ignition and Flame Propagation

The degree of aromaticity present in the isocyanate moiety affects the ease of ignition and the flame propagation rate in the foamed polymers. Foams based on isomers of TDI ignite more readily than those based on MDI. The polymers based on PAPI are slightly more difficult to ignite than those based on MDI. Intuitively, one would expect an even greater resistance to ignition in PAPI-based polymers. However, it is possible that the greater steric hinderance may have reduced the degree of reaction thus negating the expected difference in properties. The flame propagation characteristics related to polymer structure followed the same general trends as those pertaining to ease of ignition. One slight result that was unexpected relates to degree of branching in the polymer network. Polymers based on the 425-molecular-weight propoxylated adduct of trimethylolpropane exhibited greater stability than did the 312-molecular-weight homologue. This may be due, in part, to a reduction in cracking resulting from greater polymer elasticity.

Fire Endurance Characteristics

The greater the degree of aromaticity, the greater was the tendency for the polymer to form a thermally stable char. Thus, foams based on PAPI exhibited greater fire endurance than those based on MDI. The foams based on TDI formed either no char or a thermally unstable char. Those polymers based on the triol having a molecular weight of 425 were more resistance to flame penetration than were the specimens prepared using the 312-molecular-weight homologue. Resistance to cracking during flame exposure was attributed to provide the extra measure of protection.

Limiting Oxygen Index

The greater the degree of aromaticity in the polymer backbone, the higher was the observed limiting oxygen index. Those polymers based on the 425-molecular-weight triol had a slightly lower oxygen index than those based on the 312-molecular-weight homologue.

Smoke Development Characteristics

The degree of smoke increased for all polymeric foams in this series as the resistance to combustion increases. Thus, foams based on the lower molecular-weight polyol or more aromatic isocyanate produced a greater smoke evolution.

Effect of Polyol Structure on Flammability Characteristics of Rigid-Urethane Foams

The functionality, molecular weight, and steric configuration of the polyols used in the preparation of urethane polymers can greatly affect the thermal stability and flammability characteristics of the resultant foam plastics. A functionality of two is required of all reactants, if the polymer is to have a high-molecular weight and useful properties.

Polyols used in the preparation of rigid-urethane foams normally contain 3 to 8 reactive functional groups. Assuming all of the reactive sights present in the reactants take part in the chemical reaction used to produce rigid-urethane foams, the greater the functionality, the greater will be the resulting thermal and flammability characteristics of the foamed polymers.

An additional factor that must be considered is the molecular weight per cross-link density. If 2 polyols, each containing 4 reactive sights are used in the preparation of a urethane polymer, the polyol having the lower molecular weight will produce a more tightly cross-linked polymer. Barring unusual steric hinderance, the more tightly cross-linked polymer will possess greater thermal stability than a polymer derived from its higher-molecular-weight homologue.

Rigid-urethane foams, isocyanurate foams, and polyimide foams were prepared using the 3 classes of polyols listed below:

1. Aliphatic polyols
2. Cycloaliphatic polyols
3. Aromatic polyols

For the present discussion, only urethane foams prepared using polyols of Class 1 and Class 2 will be considered. The aromatic polyols will be treated separately under the section covering novel foam structures. Table XX lists the polyols used to prepare the foams for this phase of the study.

TABLE XX

POLYOL STRUCTURE* AND PROPERTIES

(Representative of Commercially-Available Polyols)

Compound	Functionality		M.W.	Eq. Wt.
Trimethylolpropane	3	Aliphatic	312	104.0
Trimethylolpropane	3	Aliphatic	425	141.7
Trimethylolpropane	3	Aliphatic	732	244.0
Trimethylolpropane	3	Aliphatic	1535	511.7
Trimethylolpropane	3	Aliphatic	2670	890.0
Pentaerythritol	4	Aliphatic	426	142.0
Pentaerythritol	4	Aliphatic	484	161.3
αMethylglucoside	4	Cycloaliphatic	425	141.7
αMethylglucoside	4	Cycloaliphatic	541	180.3
Sorbitol	6	Aliphatic	529	176.3
Sorbitol	6	Aliphatic	700	233.3
Sucrose	8	Cycloaliphatic	1022	127.8
Sucrose	8	Cycloaliphatic	1138	142.2
Sucrose	8	Cycloaliphatic	1254	156.0

*All polyols used in this study are propoxylated adducts of the alcohols listed under compounds.

Table XXI presents the formulae used to evaluate the effect of polyol structure on the thermal and flammability characteristics of rigid-urethane foams. Foams 10, 11, and 12 were prepared using the "one-shot" process. These foams were selected on the basis of steric effects present in the polymer structure and are similar to rigid-urethane foams used in commercial applications.

TABLE XXI

NON-FIRE-RETARDED RIGID-URETHANE FOAMS

(Series 2)

Raw Materials	Foam 10 (pbw)	Foam 11 (pbw)	Foam 12 (pbw)
αMethylglucoside OH# 528, M_n 425	100.00	------	------
Sucrose OH# 428, M_n 1050	------	100.00	------
Sorbitol OH# 483, M_n 700	------	------	100.00
Trichlorofluoromethane	38.0	34.0	28.0
Silicone Surfactant (SF-1079)	------		1.0
Silicone Surfactant (DC-113)	1.5	1.5	------
Silicone Surfactant (DC-201)	------	------	------
Triethylenediamine	------	------	0.15
Dimethylethanolamine	------	0.2	1.0
Dibutyltindilaurate	------	1.0	------
Tetramethylbutanediamine	1.0		------
Polymethylene polyphenyl isocyanate	132.00	107.00	121.0

Table XXII summarizes the thermal and flammability characteristics of non-fire-retarded rigid foams based on the aromatic isocyanate polymethylene polyphenyl isocyanate and three highly-reactive polyols.

TABLE XXII

PROPERTIES OF NON-FIRE-RETARDED RIGID-URETHANE FOAMS

(Series 2)

Properties	Sample		
	Foam 10	Foam 11	Foam 12
Density (gm/cm^3)	0.0301	0.0318	0.0318
% Closed Cells, Corrected	89	92	90
Compressive Strength, PSI, Yield, 70°F, 0.02"/min)	40	39	41
<u>Thermal Degradation</u>			
(DTA, 10°C/Min - Air)			
Initial Decomposition	169°C	187°C	177°C
Major Decomposition	348°C	365°C	348°C
<u>% Weight Loss TGA</u>			
(10°C/Min - Air)			
10%	243°C	291°C	273°C
25%	313°C	343°C	319°C
50%	371°C	397°C	348°C
75%	524°C	552°C	451°C
<u>Smoke Development</u>			
(XP-2 Chamber)			
<u>Time to</u>			
50% Light Obscuration	1 sec.	5 sec.	1 sec.
70% Light Obscuration	3 sec.	6 sec.	2 sec.
<u>Flame Propagation</u>			
[ASTM D-1692 (45°)]			
Inches Burned/Minute	4.1	3.0	S.E.*
<u>Char Structure</u>	Moderate	Weak	Strong

*S.E. = Self-Extinguishing

A review of Table XXII shows that the cycloaliphatic polyols produce greater quantities of smoke during combustion than do the linear aliphatic polyols. The resistance to combustion, however, increases as the functionality of the cycloaliphatic structure increases.

Fire-Retarded Rigid-Urethane Foams

General Background

The preceding section of this report clearly shows that although the polymer structure may be modified with regard to the degree of aromaticity, cross-link density, and the nature of the atoms comprising the polymer backbone, the increase in stability during actual fire exposure is only slightly enhanced.

Thus, three fire retardants were selected for study in determining the effect of type and concentration on the response of rigid-urethane foams in an actual fire exposure. The fire retardants (see Figure 11) were representative of non-reactive halogen-containing phosphates and a non-halogen-containing reactive phosphate compound. The general formulations shown in Table XV were used for this study. The actual formulations used to prepare foams 13 through 69 may be found in Appendix C, Table C-I through Table C-VIII. The stoichimetry of -NCO/OH was maintained at a ratio of 1.05:1.00 by modifying the concentration of isocyanate to compensate for the incorporation of the reactive fire retardants. Within the scope of this study fire retardants used were typical of the types and concentrations employed during the production of rigid-urethane foams normally specified for commercial applications.

Characterization of Flammability Characteristics of Fire-Retarded Rigid-Urethane Foams

Smoke Development - ASTM D-2843T*

The XP-2 Smoke Density Chamber was used, as described previously, to determine the effect of polymer structure, fire-retardant structure, and fire-retardant concentration on the smoke development and light-obscuration characteristics. Figures 12, 13, and 14 respectively, compare the effect of fire-retardant concentration (for the halogenated non-reactive retardants, and the non-halogenated reactive retardant), for rigid-urethane foams based on polymethylene polyphenyl isocyanate, and the 312 adduct of trimethylolpropane. Generally, as the concentration of fire retardant increases, the time to produce a given smoke level decreases. Little significant difference was observed within these three systems.

Similar results for foams based on 4,4' diphenylmethane diisocyanate, the 312-molecular-weight adduct of trimethylolpropane, and the halogenated non-reactive fire retardants are shown in Figures 15 and 16.

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*All foam samples used to produce the data presented in Figures 12 through 23 were 2"x2"x2" in size.

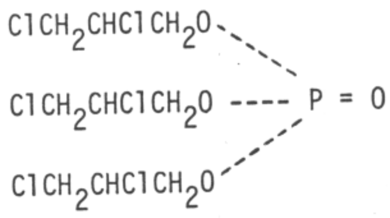
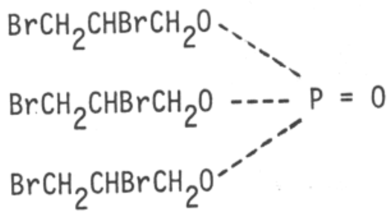
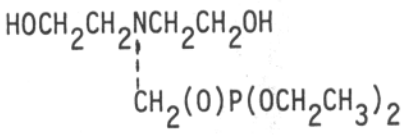
			 $HOCH_2CH_2NCH_2CH_2OH$ $CH_2(O)P(OCH_2CH_3)_2$
	Tris 2,3 - dichloropropyl phosphate	Tris 2,3 - dibromopropyl phosphate	o,o-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate
Formula Weight	431.95	697.69	255.26
Chlorine Content (%)	49.4	------	------
Bromine Content (%)	------	68.73	------
Phosphorous Content (%)	7.15	4.44	12.14

FIG. 11. STRUCTURE AND CHEMICAL COMPOSITION OF FIRE RETARDANTS

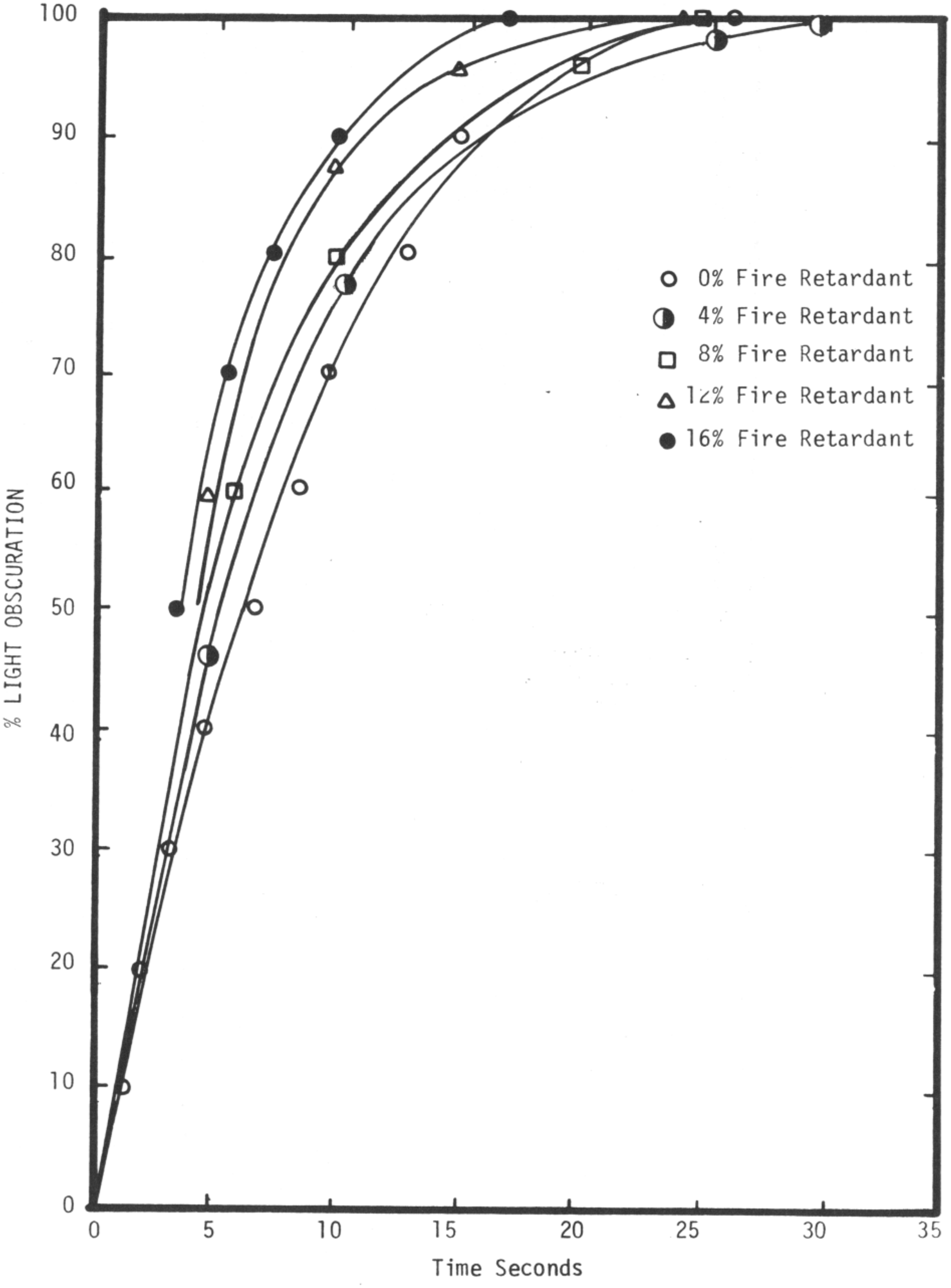


FIG. 12. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE IN TMP-312 PAPI FOAMS

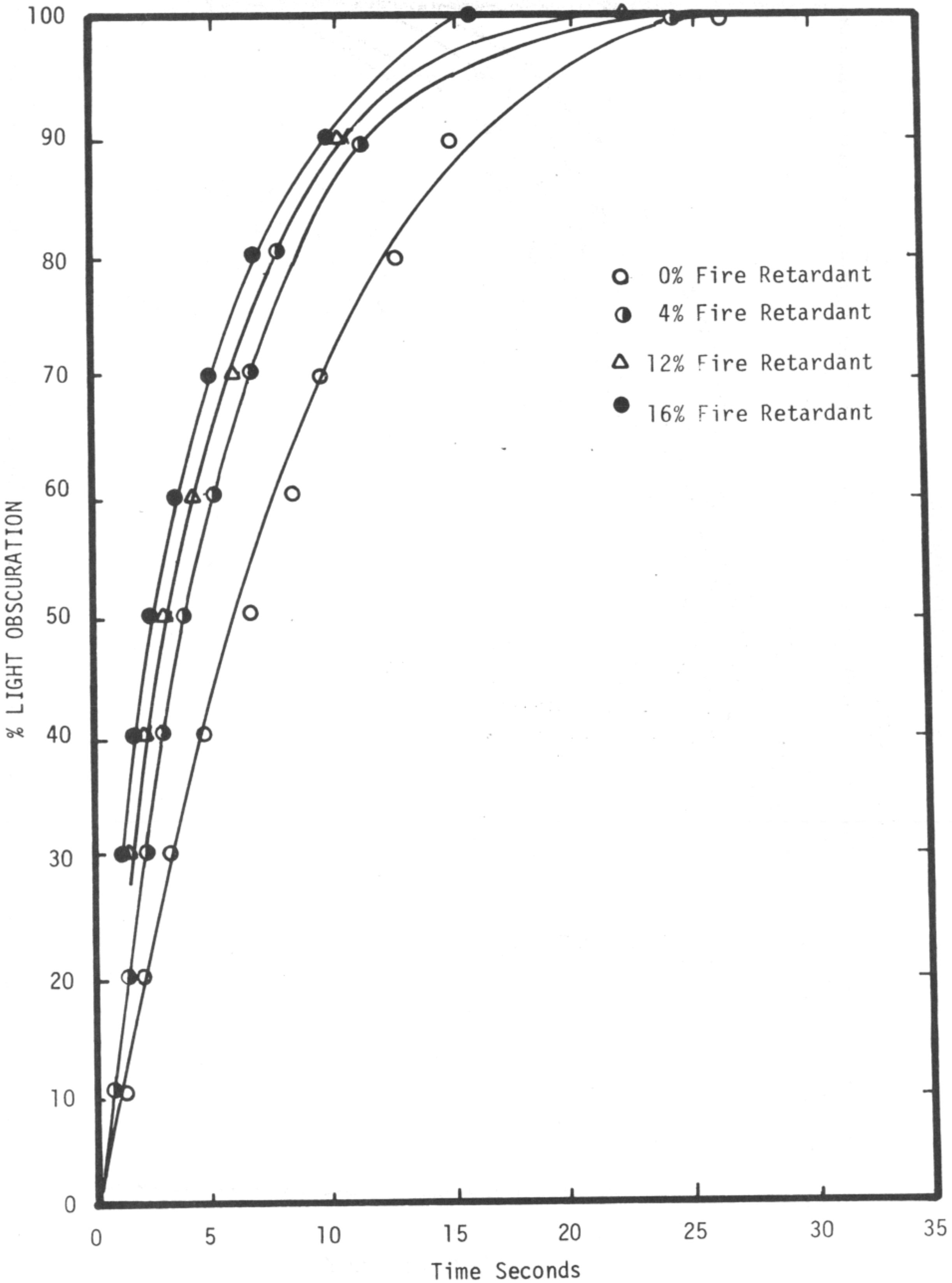


FIG. 13. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DIBROMOPROPYL PHOSPHATE IN TMP-312 PAPI FOAMS

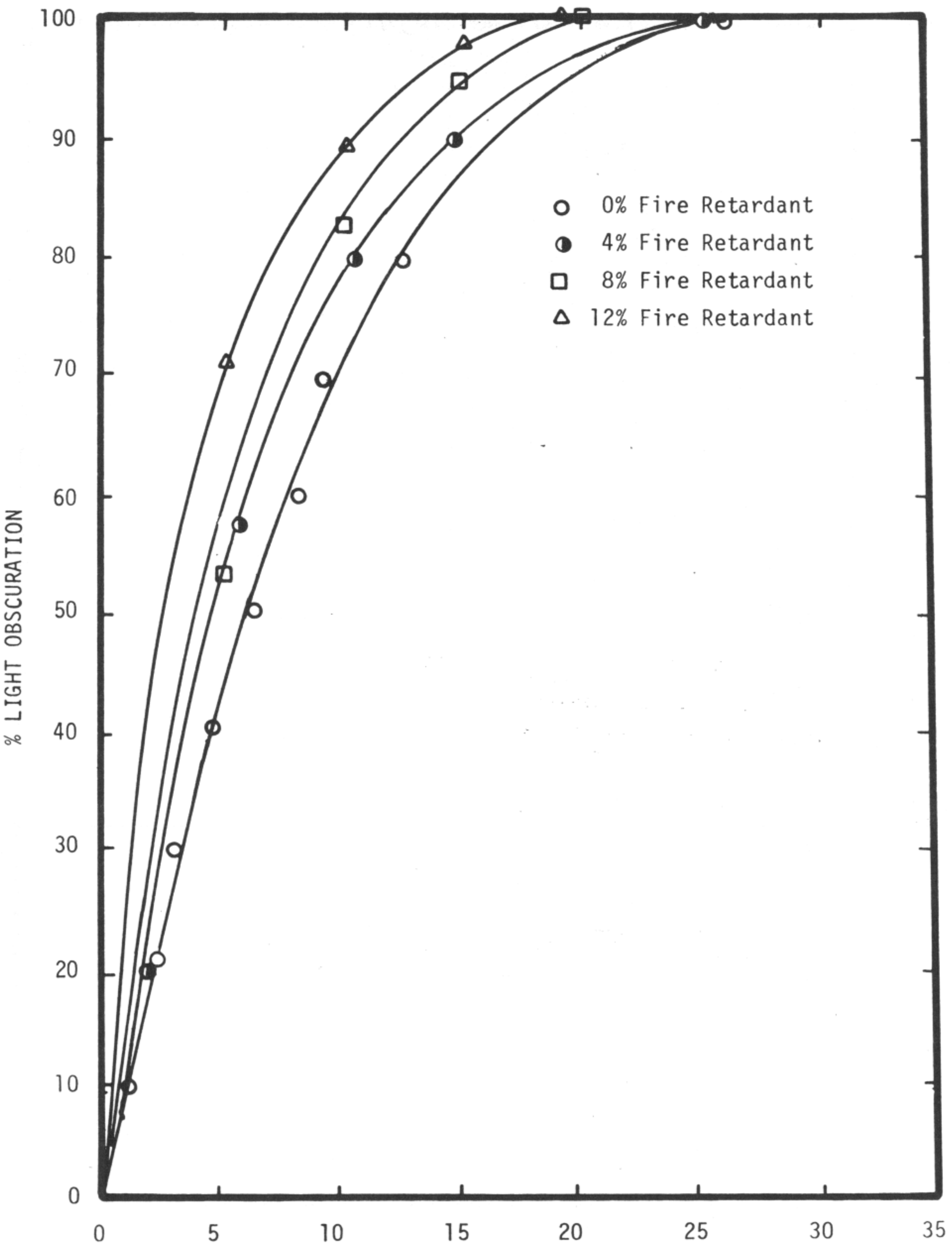


FIG. 14. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF 0,0-DIETHYL-N,N'-BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN TMP-312 PAPI FOAMS

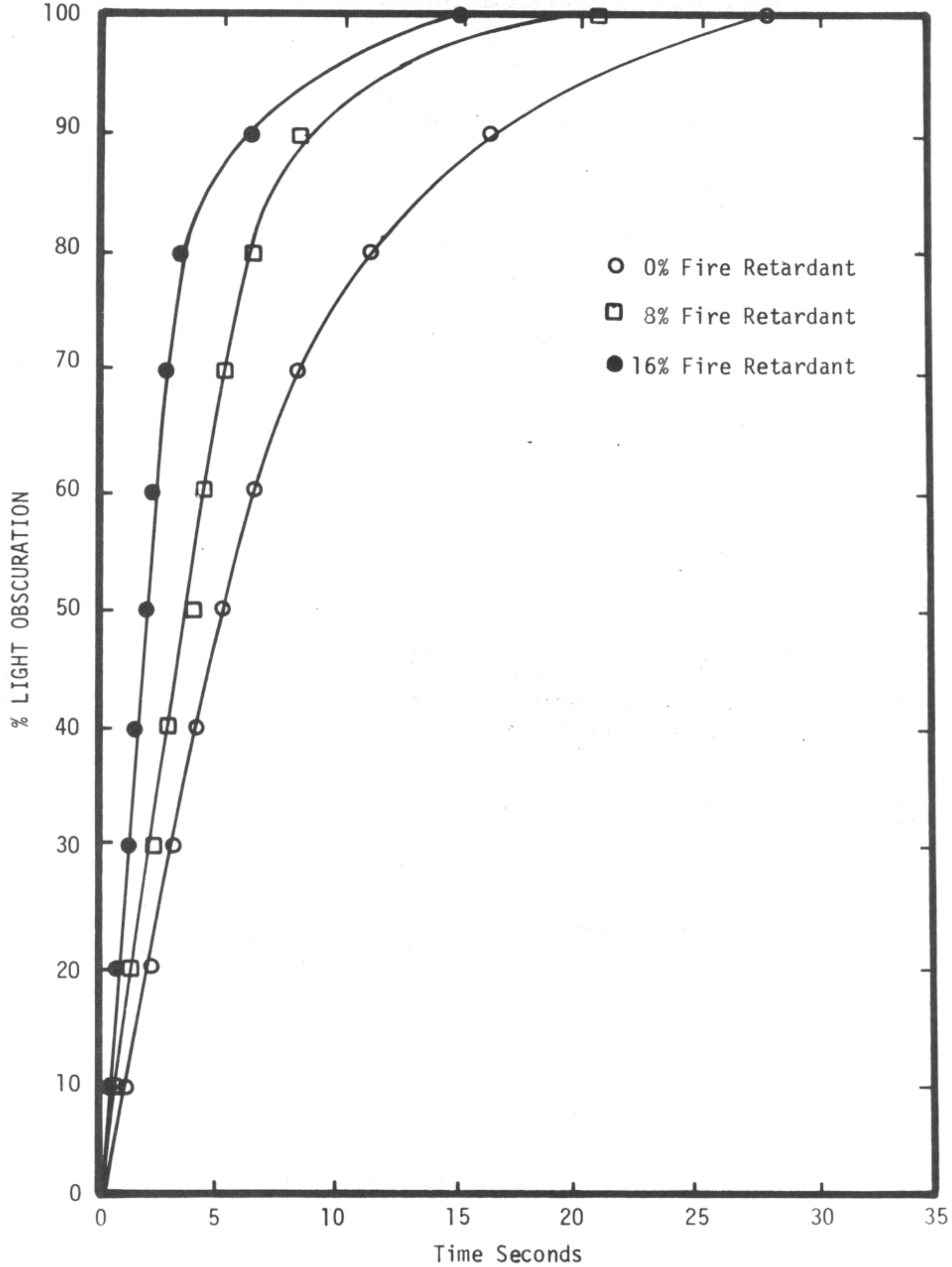


FIG. 15. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE IN TMP-312 MDI FOAMS

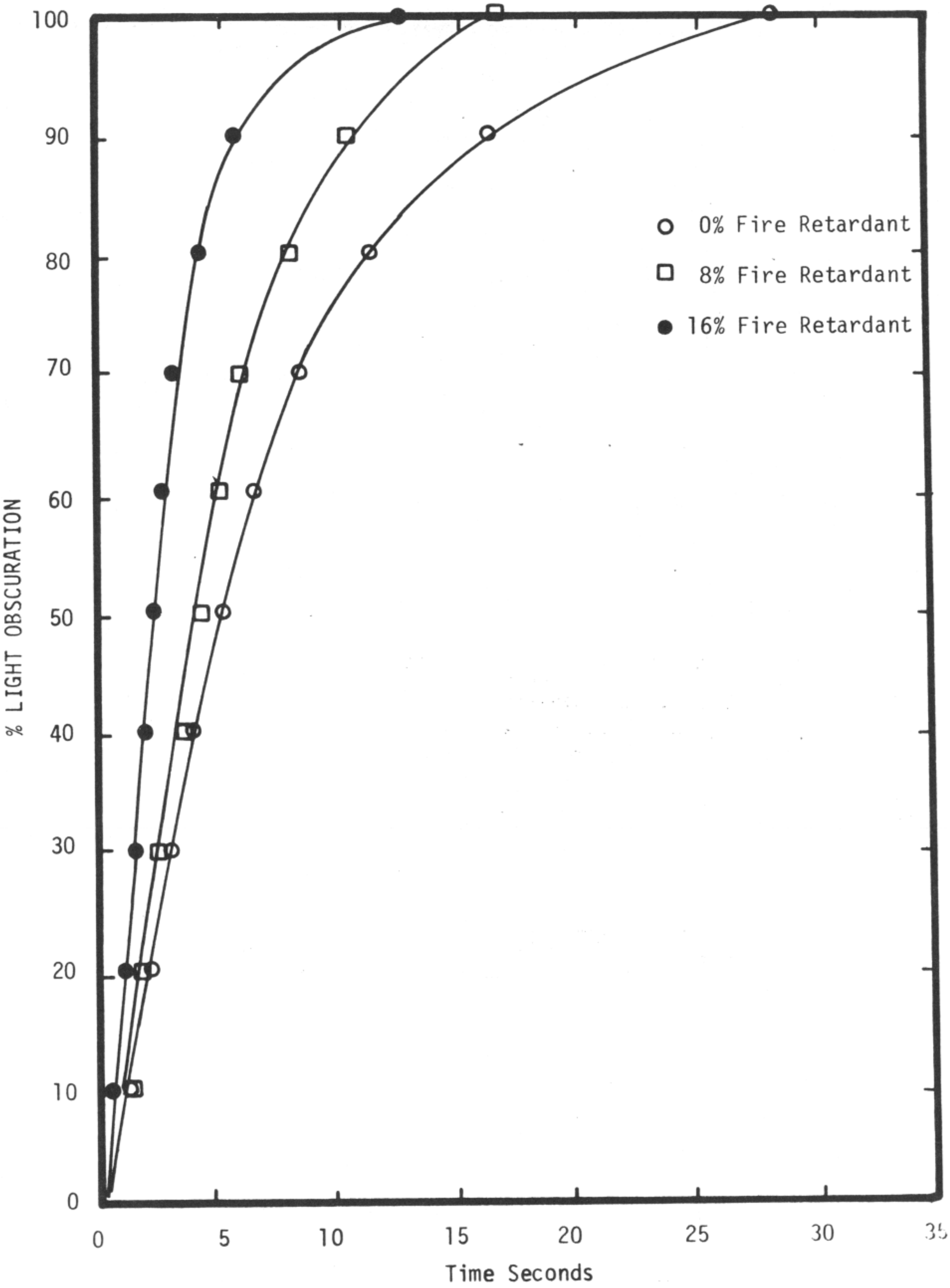


FIG. 16. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DIBROMOPROPYL PHOSPHATE IN TMP-312 MDI FOAMS

Foam test specimens based on tolylene diisocyanate exhibited erratic smoke development due to the rapid degradation of the specimen which is sometimes accompanied by a melting or dripping phenomena. The melted burning fraction usually caused isolated ignition on the floor of the test chamber. Figures 17, 18, and 19 exhibit the typical response observed during combustion of rigid-urethane foams prepared using 2 different isomers of tolylene diisocyanate, the 312-molecular-weight adduct of trimethylolpropane, and the halogenated non-reactive fire retardants containing chlorine or bromine.

Figures 20 and 21 illustrate the effect of concentration of the halogenated non-reactive fire retardants on smoke development during combustion of foams prepared using polymethylene polyphenyl isocyanate and the 425-molecular-weight adduct of trimethylolpropane. Little difference was observed in the quantity of smoke or the rate of smoke development in this series, as compared to the previous slightly more rigid foams prepared using the 312-molecular-weight adduct of trimethylolpropane.

Figure 22, the similar foam system retarded with the reactive fire retardant o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate exhibited a more rapid smoke development, and light obscuration effect, than was observed in the samples retarded with the non-reactive halogenated fire retardants.

Figure 23 illustrates the effect of fire-retardant concentration on the smoke development during combustion of systems based on tolylene diisocyanate. It should be noted that foams based on tolylene diisocyanate do not possess sufficient aromaticity to prevent total combustion and when evaluated in the XP-2 smoke chamber produce less than total light obscuration. As the concentration of fire retardant is increased, a greater degree of flame retardancy is imparted to the test specimens accompanied by a greater and more rapid smoke development.

Comparison of Figures 12, 13, 14, and 19 with Figures 20, 21, 22, and 23 shows a definite reduction in the smoke development characteristics as the degree of cross-linking is reduced, i.e., the molecular weight of the polyol is increased from 312 to 425. This is consistent with the greater ease of ignition and the more rapid flame propagation rates exhibited by the more lightly cross-linked foam specimens.

Ignition and Flame Propagation - ASTM D-1692

The ASTM D-1692 test procedure was used, as outlined previously, to determine the ignition and flame propagation characteristics of the fire-retarded rigid foams. Table XXIII presents the data obtained for foams based on the 312-molecular-weight propoxylated adduct of trimethylolpropane and polymethylene polyphenyl isocyanate and fire retarded with tris 2,3-dichloropropyl phosphate, tris 2,3-dibromopropyl phosphate and o,o-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate.

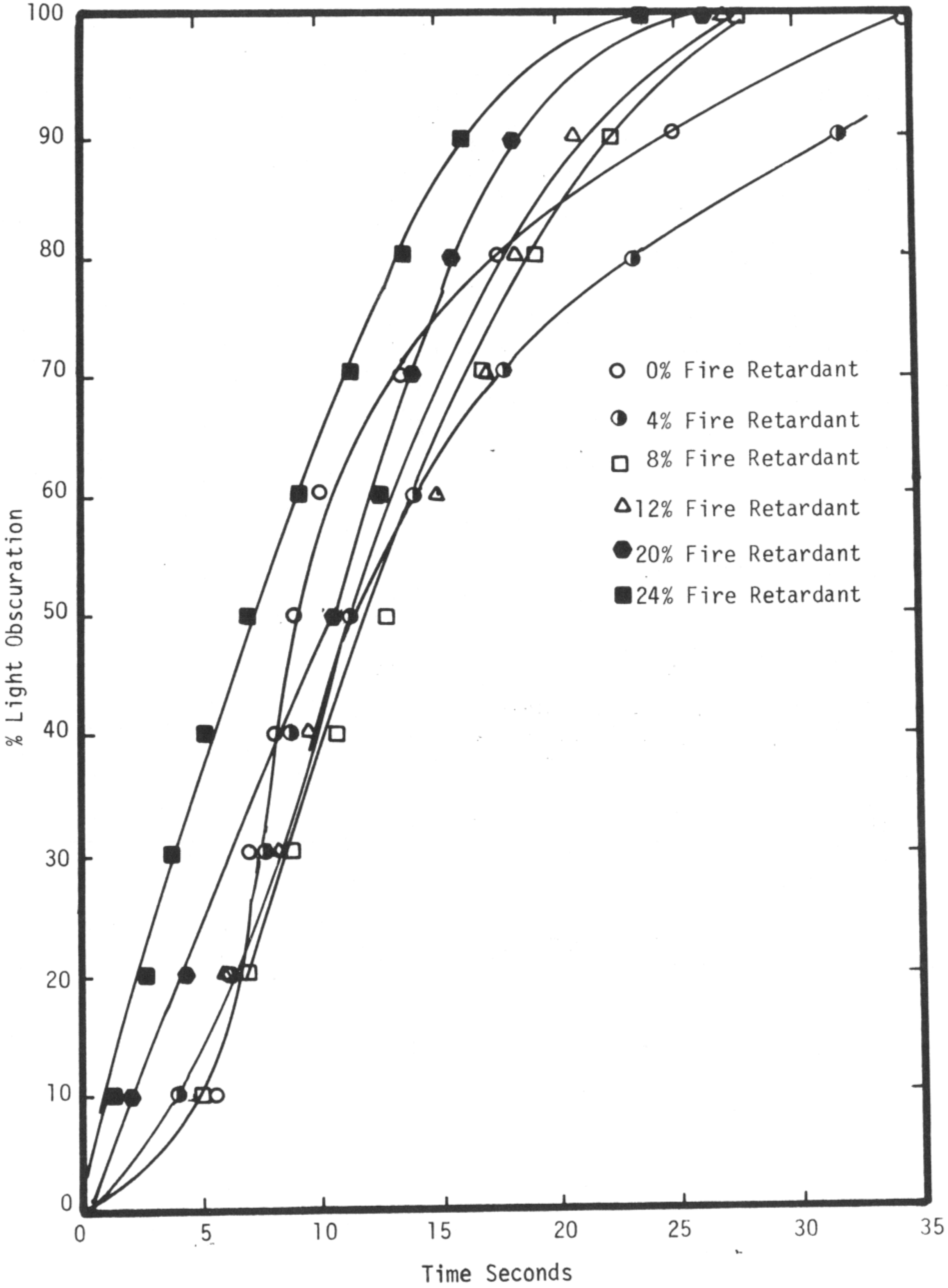


FIG. 17. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE IN TMP-312 TDI 2,4 FOAMS

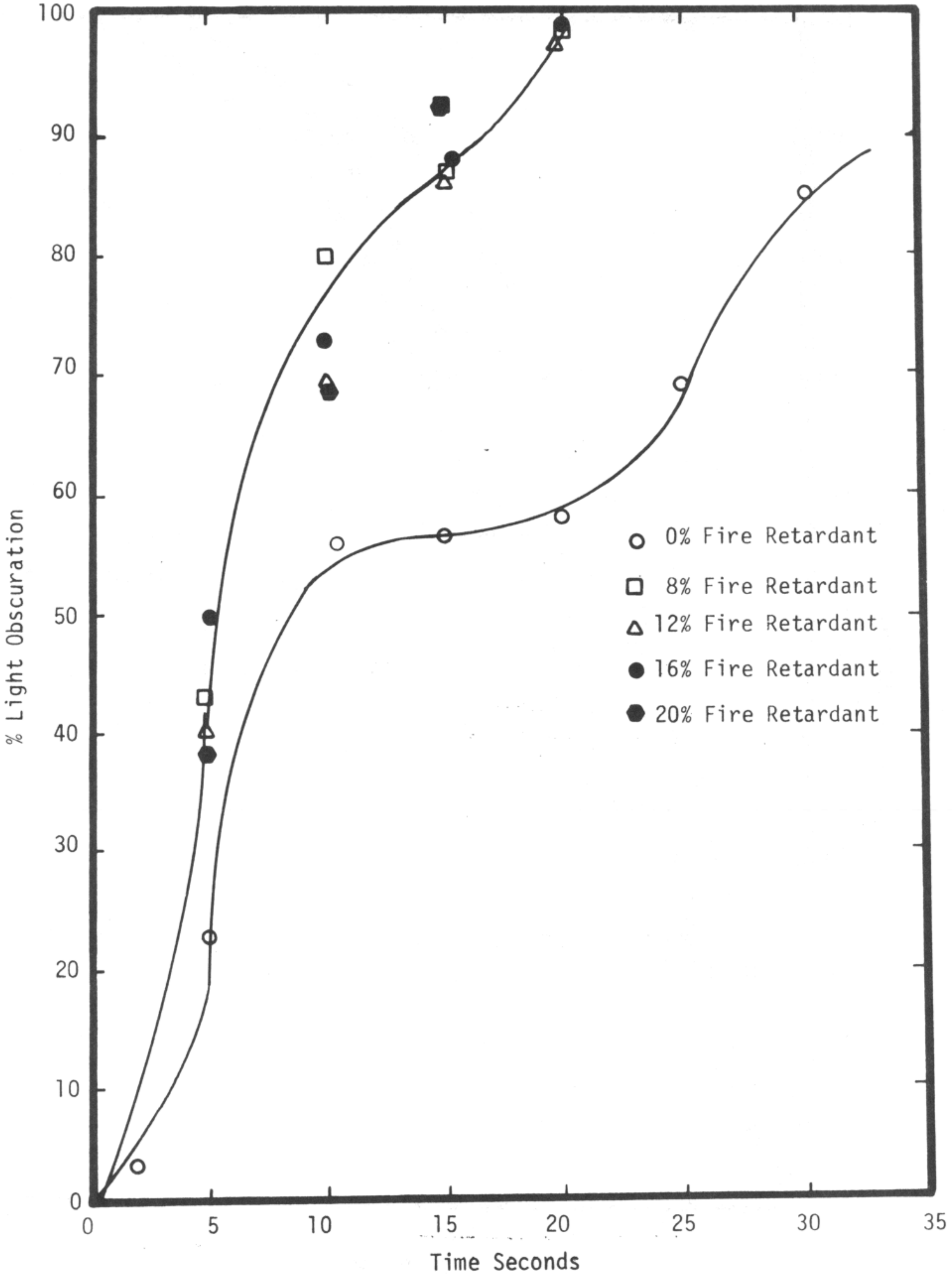


FIG. 18. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE IN TMP-312 TDI 65/35 FOAMS

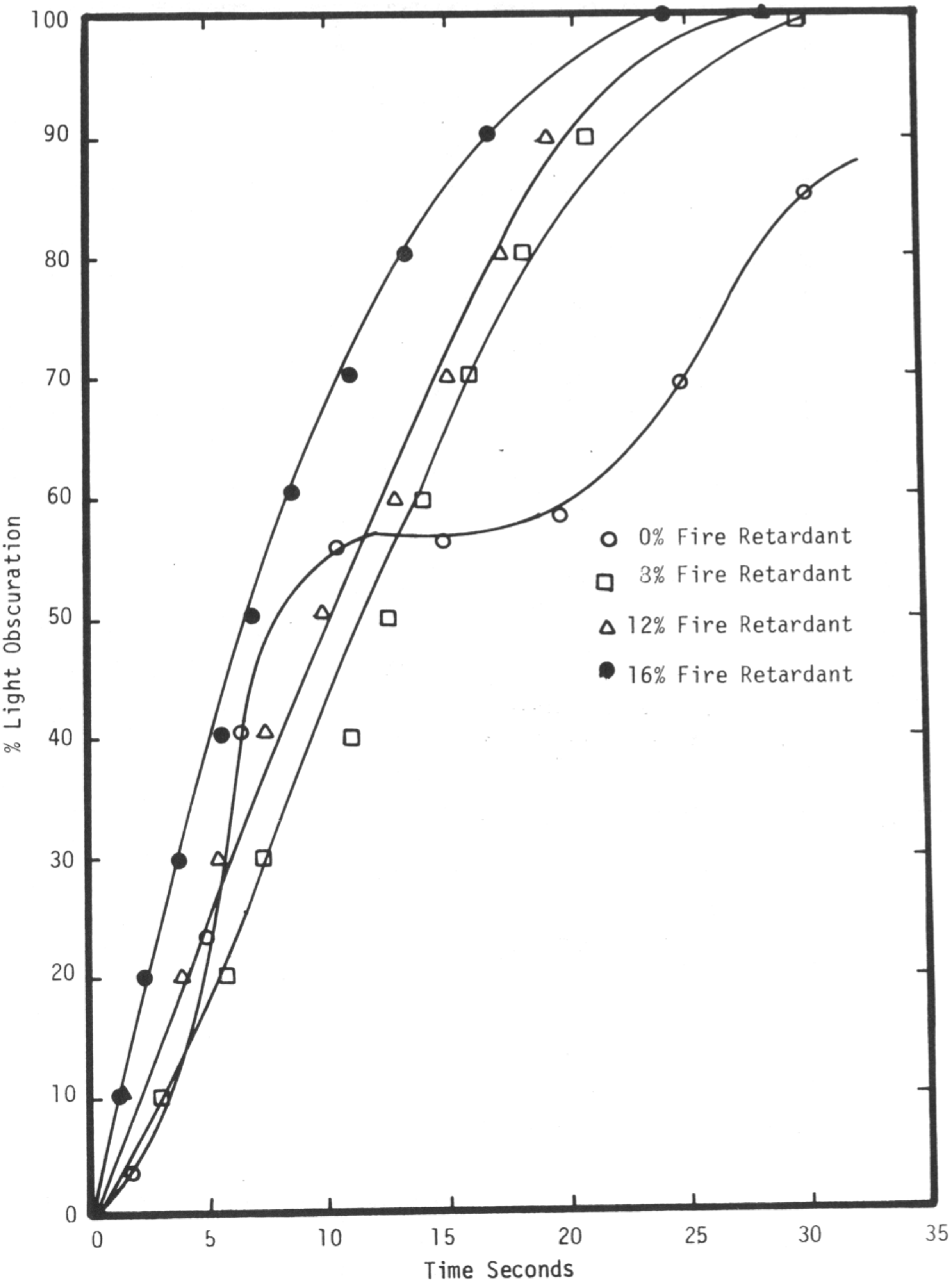


FIG. 19. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DIBROMOPROPYL PHOSPHATE IN TMP-312 TDI 65/35 FOAMS

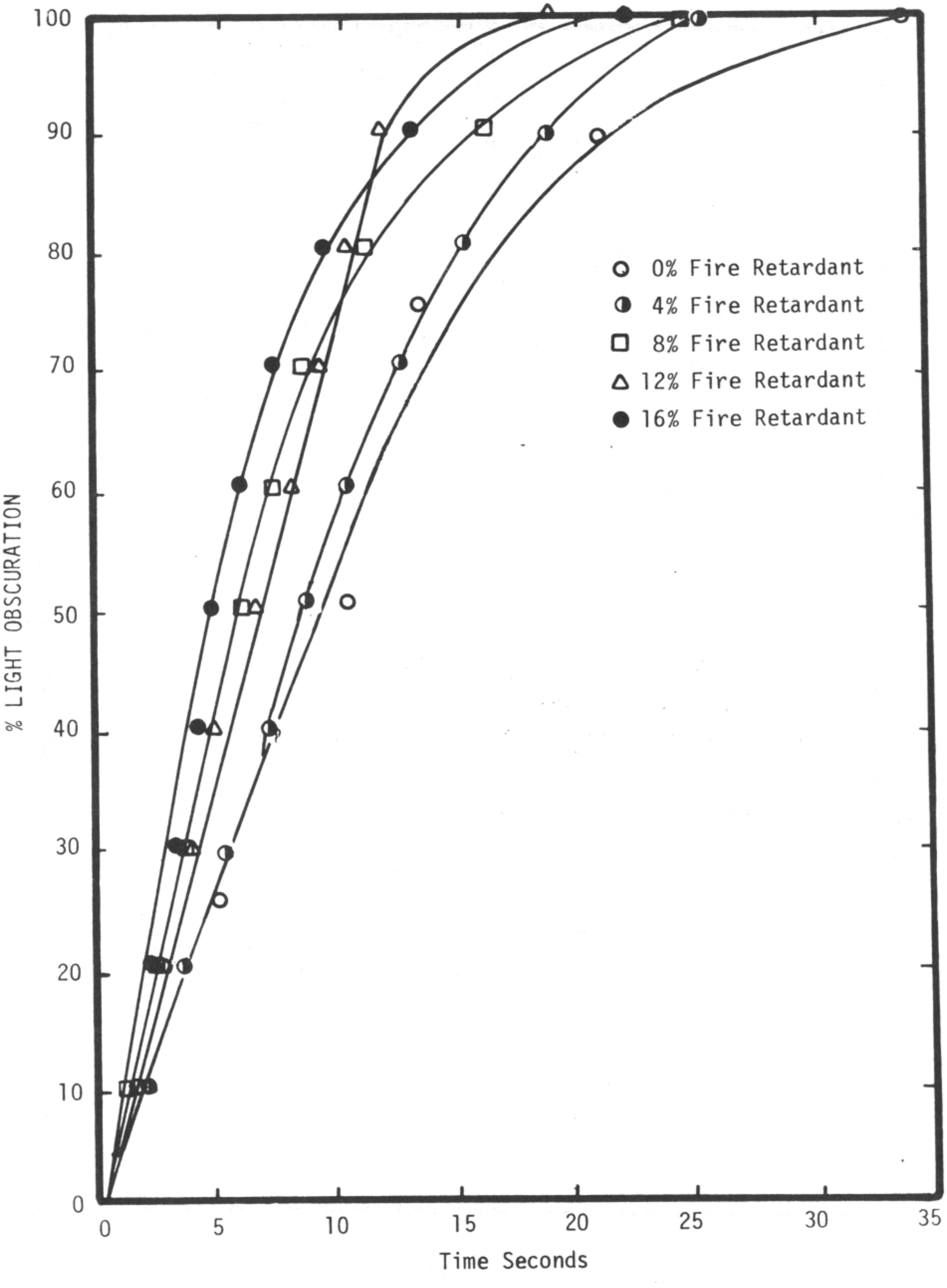


FIG. 20. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE IN TMP-425 PAPI FOAMS

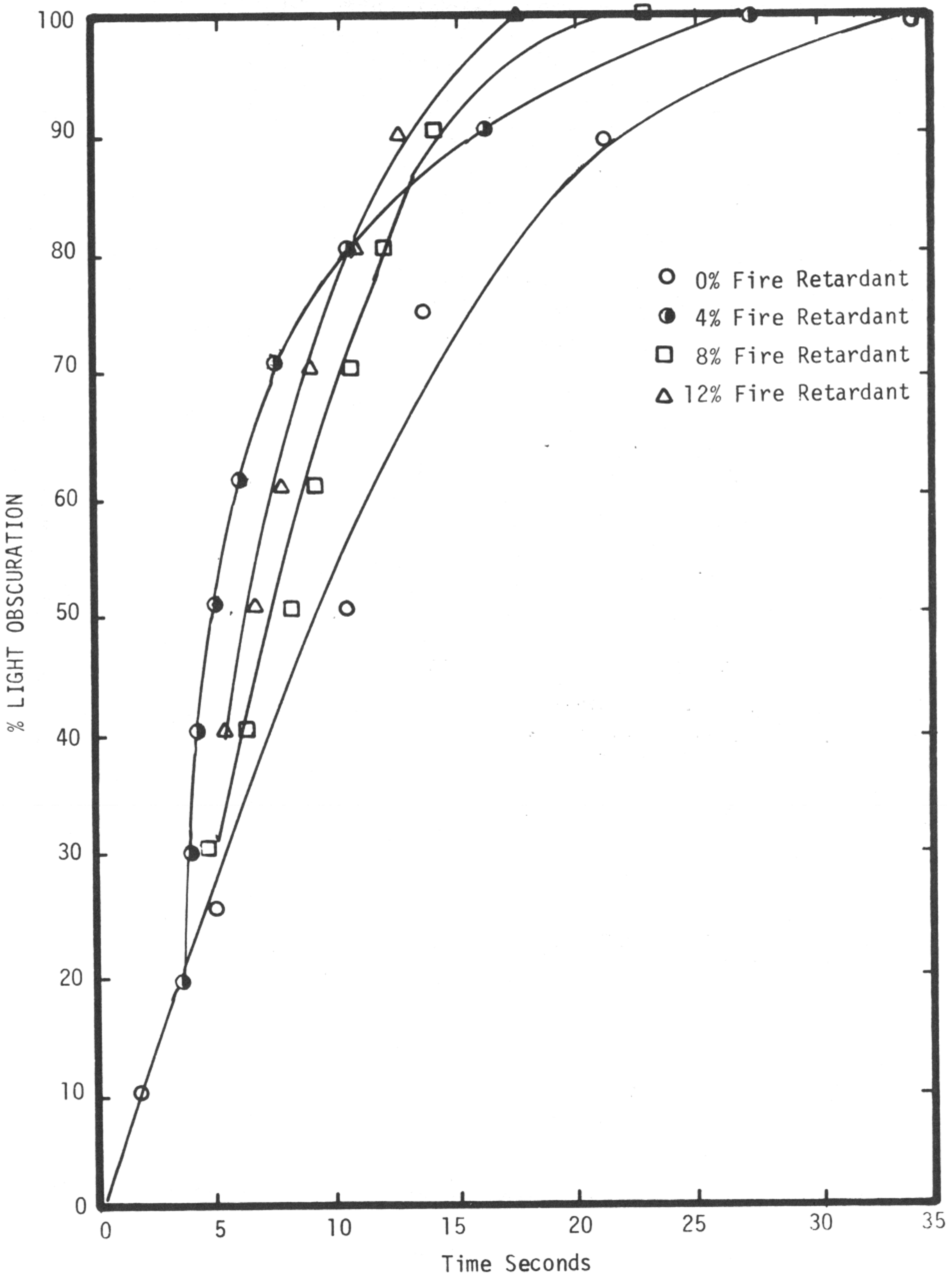


FIG. 21. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DIBROMOPROPYL PHOSPHATE IN TMP-425 PAPI FOAMS

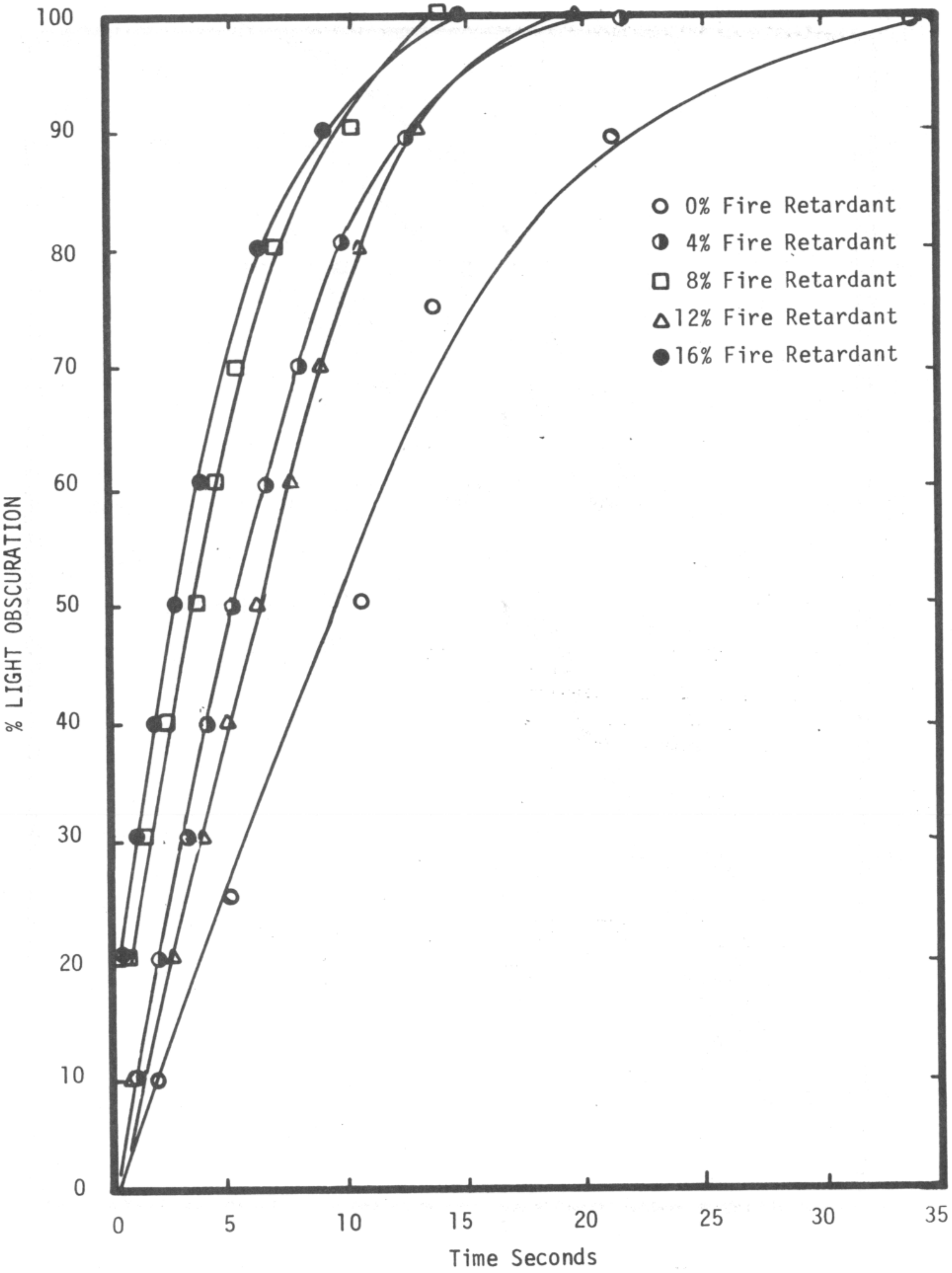


FIG. 22. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF O,O'-DIETHYL-N,N'-BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN TMP-425 PAPI FOAMS

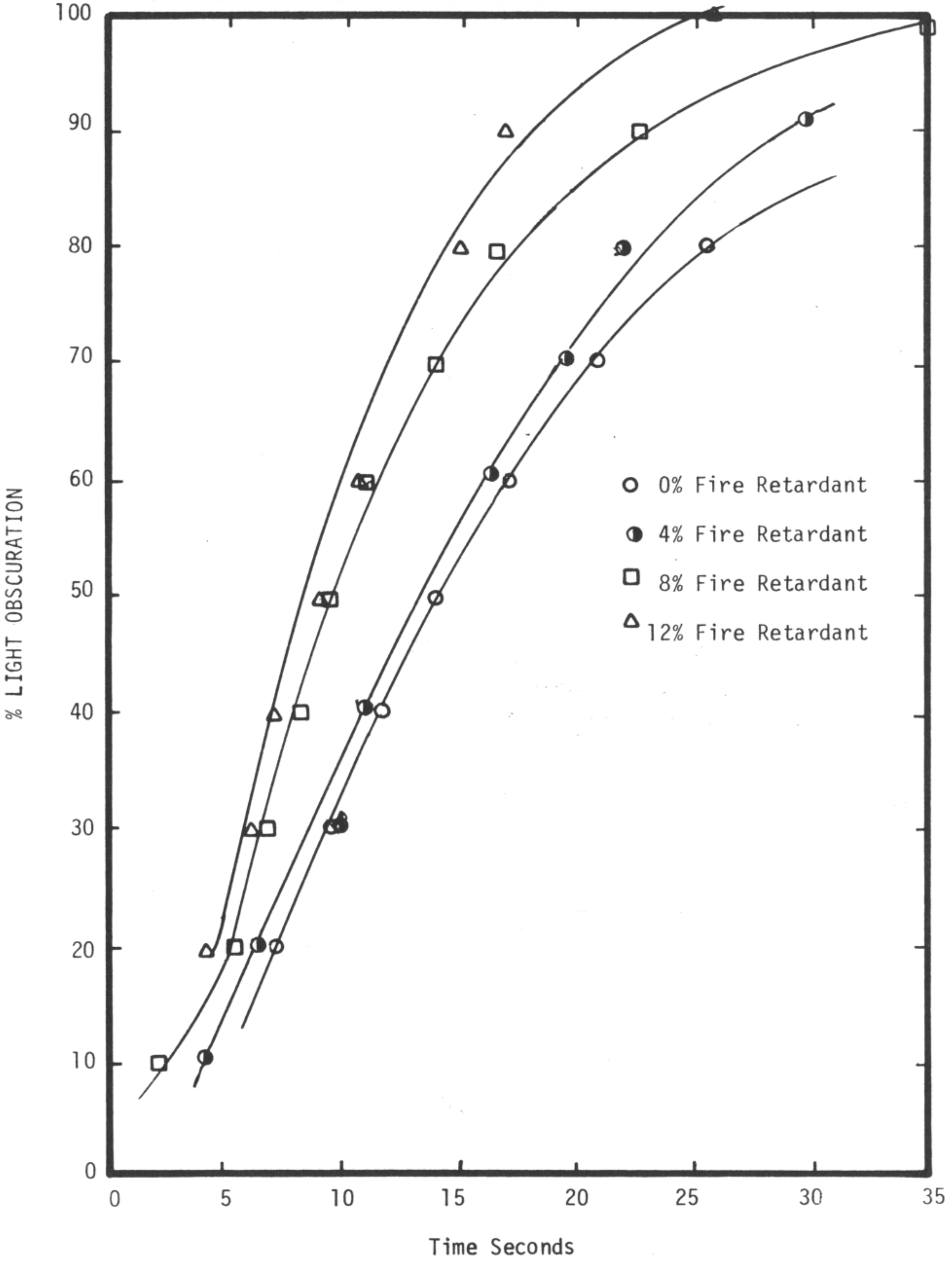


FIG. 23. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF TRIS 2,3 DIBROMOPROPYL PHOSPHATE IN TMP-425 TDI 65/35 FOAMS

TABLE XXIII

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) PAPI-BASED FOAMS (MODIFIED 45°)

Sample*	Fire Retardant	Weight Percent Fire Retardant	Density gm/cm³	Time (Sec.) Flame Travel To:						Percent Weight Loss
				1"	2"	3"	4"	5"	6"	
Foam 13	Tris 2,3 dichloropropyl phosphate	0	0.0362	4	7	10	13	16	22	81
Foam 14	Tris 2,3 dichloropropyl phosphate	4	0.0397	5	9	11	20	23	32	67
Foam 15	Tris 2,3 dichloropropyl phosphate	8	0.0360	5	10	16	24	27	SE	50
Foam 16	Tris 2,3 dichloropropyl phosphate	12	0.0470	6	11	19	30	SE**	SE	26
Foam 17	Tris 2,3 dichloropropyl phosphate	16	0.0504	9	16	32	SE	SE	SE	18
Foam 18	Tris 2,3 dichloropropyl phosphate	20	0.0555	15	20	40	SE	SE	SE	14
Foam 19	Tris 2,3 dibromopropyl phosphate	4	0.0398	5	7	14	16	22	30	45
Foam 21	Tris 2,3 dibromopropyl phosphate	12	0.0486	10	18	40	SE	SE	SE	12
Foam 22	Tris 2,3 dibromopropyl phosphate	16	0.0505	11	39	SE	SE	SE	SE	10
Foam 24	Tris 2,3 dibromopropyl phosphate	20	0.0525	16	47	SE	SE	SE	SE	7
Foam 25	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4	0.0387	6	10	15	23	30	38	59
Foam 26	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	8	0.0445	7	11	23	38	SE	SE	22
Foam 27	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	12	0.0391	7	11	24	42	SE	SE	25

*Formulations for all test specimens are presented in Appendix C, Tables C-I, C-II, and C-III.
**SE - Self Extinguishing Classification
(Sample Size 6"x2"x0.5")

Examination of data presented in Table XXIII indicates that all of the foam specimens based on the polymeric isocyanate (PAPI) can be flame retarded to the self-extinguishing classification as specified by this small-scale laboratory test procedure if a sufficient quantity of fire retardant is incorporated into the formulation. Caution should be exercised in the interpretation of these results in that this test procedure is used as a relative screening method and does not correspond to actual use conditions under a greater flame source. In addition, it must be noted that as the length of flame travel is reduced by the incorporation of additional fire retardant, the smoking tendency increases and many physical properties decrease.

Table XXIV presents data obtained for foams based on the 312-molecular-weight propoxylated adduct of trimethylolpropane and 4,4' diphenylmethane diisocyanate retarded with the tris 2,3-dichloropropyl phosphate and the tris 2,3 dibromopropyl phosphate non-reactive fire retardants.

Table XXV presents data obtained for foams based on the 312-molecular-weight propoxylated adduct of trimethylolpropane and the 100 per cent 2,4 isomer of tolylene diisocyanate and the 65:35 mixture of 2,4: 2.6 isomers of tolylene diisocyanate fire retarded with the chlorinated and brominated non-reactive (dihalopropyl phosphate) fire retardants.

A comparison of the information presented in Tables XXIII, XXIV, and XXV clearly indicates the effectiveness of decreasing flame travel is dependent upon isocyanate structure as well as the nature and concentration of fire retardant incorporated into the foam formulation. The polymethylene polyphenyl isocyanate, even in the absence of fire retardant, enhances the development of a protecting char structure and thus retains approximately 20 per cent of its original weight during flame contact. Foams based on isocyanates possessing a lesser degree of aromaticity (4,4' diphenylmethane diisocyanate, and tolylene diisocyanate) do not develop appreciable char structure and are completely destroyed during flame contact. Incorporation of the fire retardants greatly improves the resistance to flame travel in foams based on the highly aromatic isocyanate while affording little improvement in the reduction of flame travel in foam systems based on isocyanates of lesser aromaticity.

In order to determine the effect of molecular weight per cross-link density ($\overline{Mc}$), a similar series of rigid-urethane foams were prepared using the 425-molecular-weight propoxylated adduct of trimethylolpropane and polymethylene polyphenyl isocyanate (Table XXVI) and the 65:35 isomer mixture of 2,4: 2,6 tolylene diisocyanate (Table XXVII). The three fire retardants employed previously were used to protect the samples based on polymethylene polyphenyl isocyanate. The two non-reactive halogenated fire retardants were used in conjunction with the foams based on the tolylene diisocyanate.

TABLE XXIV

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) MDI-BASED FOAMS

(Modified 45°)

Sample*	Fire Retardant	Weight Percent Fire Retardant	Density gm/cm^3	Time (Sec.) Flame Travel To:						Percent Weight Loss
				1"	2"	3"	4"	5"	6"	
Foam 28	Tris 2,3 dichloropropyl phosphate	0	0.0307	3	5	6	10	12	16	100
Foam 29	Tris 2,3 dichloropropyl phosphate	8	0.0475	7	10	15	10	24	31	100
Foam 30	Tris 2,3 dichloropropyl phosphate	16	0.0672	10	17	25	39	54	70	100
Foam 31	Tris 2,3 dibromopropyl phosphate	8	0.0495	8	13	20	29	36	41	100
Foam 32	Tris 2,3 dibromopropyl phosphate	16	0.0574	11	20	36	48	SE**	SE**	38

*Formulations for all test specimens are presented in Appendix C, Table C-IV.
**SE - Self Extinguishing Classification

TABLE XXV

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) TDI-BASED FOAMS

(Modified 45°)

Sample*	Fire Retardant	Weight Percent Fire Retardant	Density gm/cm^3	Time (Sec.) Flame Travel To:						Percent Weight Loss
				1"	2"	3"	4"	5"	6"	
Foam 33	Tris 2,3 dichloropropyl phosphate	0	0.0300	3	4	--	8	9	10	100
Foam 34	Tris 2,3 dichloropropyl phosphate	4	0.0357	5	8	11	14	16	19	100
Foam 35	Tris 2,3 dichloropropyl phosphate	8	0.0445	6	11	15	20	23	29	100
Foam 36	Tris 2,3 dichloropropyl phosphate	12	0.0445	7	13	18	24	27	34	100
Foam 37	Tris 2,3 dichloropropyl phosphate	16	0.0505	9	16	23	28	31	38	100
Foam 38	Tris 2,3 dichloropropyl phosphate	20	0.0465	9	16	24	33	39	49	100
Foam 39	Tris 2,3 dichloropropyl phosphate	24	0.0545	12	16	24	34	47	SE**	58
Foam 40	Tris 2,3 dichloropropyl phosphate	0	0.0298	2	4	--	--	8	9	100
Foam 42	Tris 2,3 dichloropropyl phosphate	8	0.0457	5	7	12	15	16	23	100
Foam 43	Tris 2,3 dichloropropyl phosphate	12	0.0465	8	12	18	24	28	39	100
Foam 44	Tris 2,3 dichloropropyl phosphate	16	0.0525	10	17	25	30	46	59	100
Foam 45	Tris 2,3 dichloropropyl phosphate	20	0.0603	10	19	30	37	51	70	100
Foam 46	Tris 2,3 dichloropropyl phosphate	24	0.0600	10	17	29	--	45	50	100
Foam 47	Tris 2,3 dichloropropyl phosphate	28	0.0585	10	19	29	45	50	SE**	100
Foam 48	Tris 2,3 dibromopropyl phosphate	8	0.0474	7	9	14	17	21	26	100
Foam 49	Tris 2,3 dibromopropyl phosphate	12	0.0445	7	9	16	18	22	31	100

*Formulations for all test specimens are presented in Appendix C, Tables C-V and C-VI.

**SE - Self Extinguishing Classification.

TABLE XXVI

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) POLYMERIC ISOCYANATE - TMP 425

(Modified 45°)

Sample*	Fire Retardant	Weight Percent Fire Retardant	Density gm/cm3	Time (sec.) Flame Travel To:						Percent Weight Loss
				1"	2"	3"	4"	5"	6"	
Foam 50	Tris 2,3 dichloropropyl phosphate	0	0.0417	5	7	10	12	16	21	83
Foam 55	Tris 2,3 dichloropropyl phosphate	4	0.0433	7	13	18	20	25	31	72
Foam 56	Tris 2,3 dichloropropyl phosphate	8	0.0467	7	11	18	24	26	32	70
Foam 57	Tris 2,3 dichloropropyl phosphate	12	0.0535	10	16	23	32	39	SE **	35
Foam 58	Tris 2,3 dichloropropyl phosphate	16	0.0545	8	17	26	45	SE **	SE **	36
Foam 59	Tris 2,3 dibromopropyl phosphate	4	0.0525	6	10	13	16	22	28	70
Foam 60	Tris 2,3 dibromopropyl phosphate	8	0.0456	6	10	14	19	27	37	74
Foam 61	Tris 2,3 dibromopropyl phosphate	12	0.0555	7	11	20	28	40	SE **	17
Foam 62	Tris 2,3 dibromopropyl phosphate	16	0.0520	9	20	38	SE **	SE **	SE **	12
Foam 51	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4	0.0530	5	11	12	16	21	25	77
Foam 52	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	8	0.0450	8	--	15	--	--	28	77
Foam 53	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	12	0.0485	7	15	20	24	35	47	67

*Formulation for all test specimens are presented in Appendix C, Table C-VII.

**SE - Self Extinguishing Classification

TABLE XXVII

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) TOLYLENE DIISOCYANATE 65/35 AND TMP-440

(Modified 45°)

Sample*	Fire Retardant	Weight % Fire Retardant	Density gm/cm^3	Time (sec.) Flame Travel To:						% Weight Loss
				1"	2"	3"	4"	5"	6"	
Foam 63	Tris 2,3 dichloropropyl phosphate	0	0.0382	2	4	7	--	10	14	100
Foam 64	Tris 2,3 dichloropropyl phosphate	4	0.0447	5	7	11	15	16	20	100
Foam 65	Tris 2,3 dichloropropyl phosphate	8	0.0505	6	10	15	20	24	30	100
Foam 66	Tris 2,3 dichloropropyl phosphate	12	0.0610	10	17	23	26	30	35	100
Foam 67	Tris 2,3 dibromopropyl phosphate	4	0.0485	4	9	12	16	19	23	100
Foam 68	Tris 2,3 dibromopropyl phosphate	8	0.0515	7	14	19	23	27	34	100
Foam 69	Tris 2,3 dibromopropyl phosphate	12	0.0515	9	16	23	29	32	38	100

*Formulations for all test specimens are presented in Appendix C, Table C-VIII.

Figures 24 and 25 compare the rates of flame propagation of foam samples based on the most effective and least effective isocyanates, the 312- and 425-molecular-weight propoxylated adducts of trimethylolpropane fire retarded with varying concentrations of the non-reactive chlorinated fire retardant. Examination of the results presented in Tables XXIII through XXVII and Figures 24 and 25 clearly indicate that optimization of ignition and flame propagation characteristics may be obtained using the polymeric isocyanate polymethylene polyphenyl isocyanate, the 312-molecular-weight adduct of trimethylolpropane and the brominated non-reactive fire retardant tris, 2,3 dibromopropylphosphate. The reactive fire retardant o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate imparts a greater degree of protection than did the chlorinated non-reactive fire retardant.

Flame Penetration Test - Bureau of Mines Test (Modified)

This flame penetration test used previously to measure the fire endurance characteristics of non-fire-retarded foam systems was also employed in the evaluation of fire-retarded systems. Table XXVIII presents the data obtained during the evaluation of fire endurance of rigid foams.

Evaluation of the data presented in Table XXVIII indicates that the polymeric isocyanate, polymethylene polyphenyl isocyanate, afforded a greater degree of protection to the direct impingement of an oxidizing flame source than did the other isocyanates evaluated. The 312-molecular-weight polyol was slightly superior to its 425-molecular-weight homologue. There was little difference observed during this evaluation between the 3 classes of fire retardants employed. The brominated non-reactive fire retardant was very slightly better than its chlorinated homologue.

Comparison of flame penetration characteristics (Table XXVIII) with the smoke-development characteristics (Figures 12, 13, 14, 19, 20, 21, 22, and 23) clearly indicates that as the fire-endurance characteristics of the cellular plastic is improved, there is a subsequent reduction in the time for 100 per cent smoke obscuration.

Limiting Oxygen Index

The "Limiting Oxygen Index" procedure, as described previously, was used to evaluate the effect of polymer structure, fire-retardant type, and fire-retardant concentration on the combustion of rigid-urethane foams. Figures 26 and 27 illustrate, respectively, the effect of chlorinated and brominated non-reactive fire retardants used in systems based on the 312-molecular-weight adduct of trimethylolpropane and various isocyanates.

The brominated fire retardants are more effective in raising the concentration of oxygen required to sustain burning than are the chlorinated homologues. The oxygen-index values clearly indicate that the degree of aromaticity in the isocyanate moiety, for a given polyol,

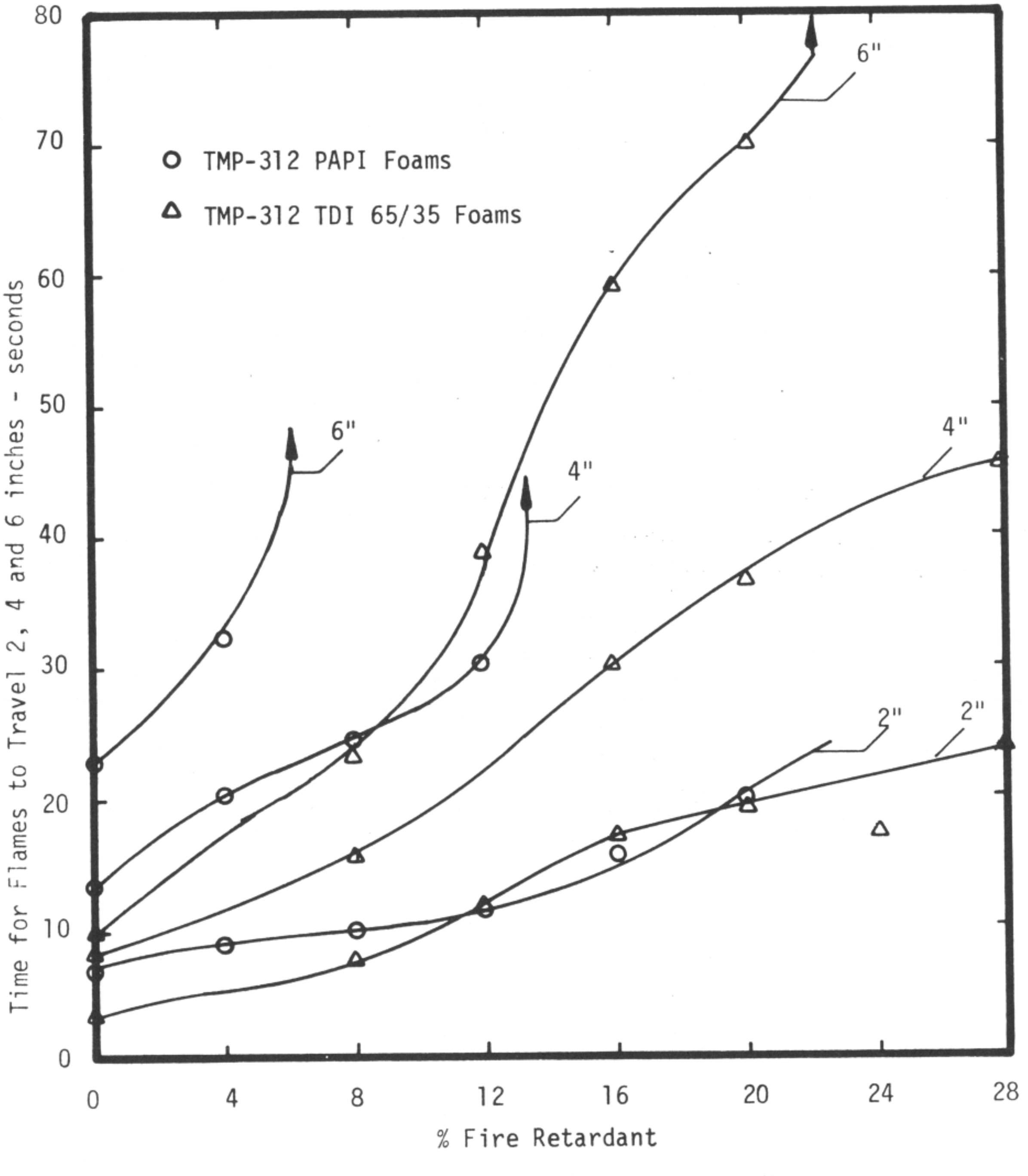


FIG. 24. EFFECT OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE ON FLAME TRAVEL TIME OF TMP-312 BASED FOAMS WITH VARIOUS ISOCYANATES

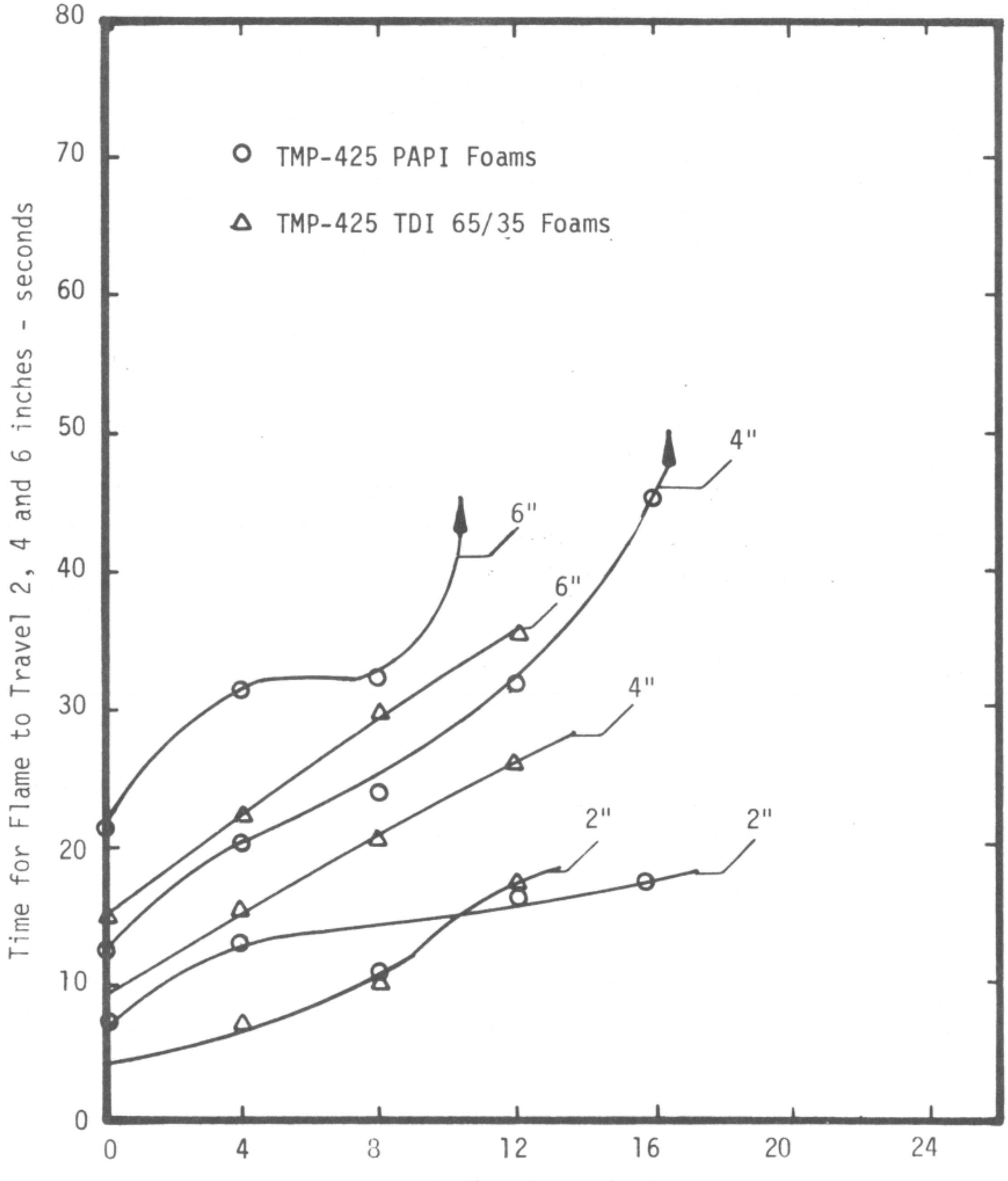


FIG. 25. EFFECT OF TRIS 2,3 DICHLOROPROPYL PHOSPHATE ON FLAME TRAVEL TIME OF TMP-425 BASED FOAMS WITH VARIOUS ISOCYANATES

TABLE XXVIII

FIRE ENDURANCE CHARACTERISTICS OF FIRE-RETARDED RIGID-URETHANE FOAMS

Sample*	Isocyanate	Polyol	Fire Retardant	Weight Percent Fire Retardant	Burn Through Time, (Seconds)	Percent Weight Loss
Foam 13	PAPI	TMP-312	Tris 2,3 dichloropropyl phosphate	0	15.3	33
Foam 14	PAPI	TMP-312	Tris 2,3 dichloropropyl phosphate	4	16.0	17
Foam 15	PAPI	TMP-312	Tris 2,3 dichloropropyl phosphate	8	16.0	22
Foam 16	PAPI	TMP-312	Tris 2,3 dichloropropyl phosphate	12	16.5	18
Foam 17	PAPI	TMP-312	Tris 2,3 dicholorpropyl phosphate	16	16.8	10
Foam 18	PAPI	TMP-312	Tris 2,3 dicholorpropyl phosphate	20	18.0	13
Foam 19	PAPI	TMP-312	Tris 2,3 dibromopropyl phosphate	4	15.8	20
Foam 21	PAPI	TMP-312	Tris 2,3 dibromopropyl phosphate	12	16.2	16
Foam 22	PAPI	TMP-312	Tris 2,3 dibromopropyl phosphate	16	16.3	20
Foam 24	PAPI	TMP-312	Tris 2,3 dibromopropyl phosphate	20	17.7	11
Foam 25	PAPI	TMP-312	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4	12.5	24
Foam 26	PAPI	TMP-312	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	8	15.0	12
Foam 27	PAPI	TMP-312	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	12	13.2	20
Foam 28	MDI	TMP-312	Tris 2,3 dichloropropyl phosphate	0	11.0	100
Foam 29	MDI	TMP-312	Tris 2,3 dichloropropyl phosphate	8	12.2	100
Foam 30	MDI	TMP-312	Tris 2,3 dichloropropyl phosphate	16	14.8	15
Foam 31	MDI	TMP-312	Tris 2,3 dibromopropyl phosphate	8	14.9	22
Foam 32	MDI	TMP-312	Tris 2,3 dibromopropyl phosphate	16	16.2	19
Foam 33	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	0	8.1	100
Foam 34	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	4	11.3	100
Foam 35	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	8	15.0	100
Foam 36	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	12	15.5	100
Foam 37	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	16	15.5	100
Foam 38	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	20	15.8	15
Foam 39	TDI 2,4	TMP-312	Tris 2,3 dichloropropyl phosphate	24	17.2	14
Foam 40	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	0	8.7	100
Foam 42	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	8	12.2	100
Foam 43	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	12	13.2	100
Foam 44	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	16	14.6	100
Foam 45	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	20	17.3	16
Foam 46	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	24	18.6	15
Foam 47	TDI 65:35	TMP-312	Tris 2,3 dichloropropyl phosphate	28	22.2	18
Foam 48	TDI 65:35	TMP-312	Tris 2,3 dibromopropyl phosphate	8	12.1	100
Foam 49	TDI 65:35	TMP-312	Tris 2,3 dibromopropyl phosphate	12	13.2	100
Foam 50	PAPI	TMP-425	Tris 2,3 dichloropropyl phosphate	0	13.1	63
Foam 55	PAPI	TMP-425	Tris 2,3 dichloropropyl phosphate	4	17.0	36
Foam 56	PAPI	TMP-425	Tris 2,3 dichloropropyl phosphate	8	17.0	23
Foam 57	PAPI	TMP-425	Tris 2,3 dichloropropyl phosphate	12	18.2	17
Foam 58	PAPI	TMP-425	Tris 2,3 dichloropropyl phosphate	16	18.1	23
Foam 59	PAPI	TMP-425	Tris 2,3 dibromopropyl phosphate	4	16.6	27
Foam 60	PAPI	TMP-425	Tris 2,3 dibromopropyl phosphate	8	17.5	25
Foam 61	PAPI	TMP-425	Tris 2,3 dibromopropyl phosphate	12	17.5	16
Foam 62	PAPI	TMP-425	Tris 2,3 dibromopropyl phosphate	16	18.0	20
Foam 51	PAPI	TMP-425	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4	11.0	38
Foam 52	PAPI	TMP-425	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	8	18.5	20
Foam 53	PAPI	TMP-425	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	12	19.4	20
Foam 63	TDI 65:35	TMP-425	Tris 2,3 dichloropropyl phosphate	0	10.5	100
Foam 64	TDI 65:35	TMP-425	Tris 2,3 dichloropropyl phosphate	4	16.5	100
Foam 65	TDI 65:35	TMP-425	Tris 2,3 dichloropropyl phosphate	8	16.9	100
Foam 66	TDI 65.35	TMP-425	Tris 2,3 dichloropropyl phosphate	12	17.6	100
Foam 67	TDI 65:35	TMP-425	Tris 2,3 dibromopropyl phosphate	4	13.2	100
Foam 68	TDI 65:35	TMP-425	Tris 2,3 dibromopropyl phosphate	8	18.7	100
Foam 69	TDI 65:35	TMP-425	Tris 2,3 dibromopropyl phosphate	12	19.0	100

*Formulations for all test specimens are presented in Appendix C, Tables C-I through C-VIII.
(Sample Size 6"x6"x1")

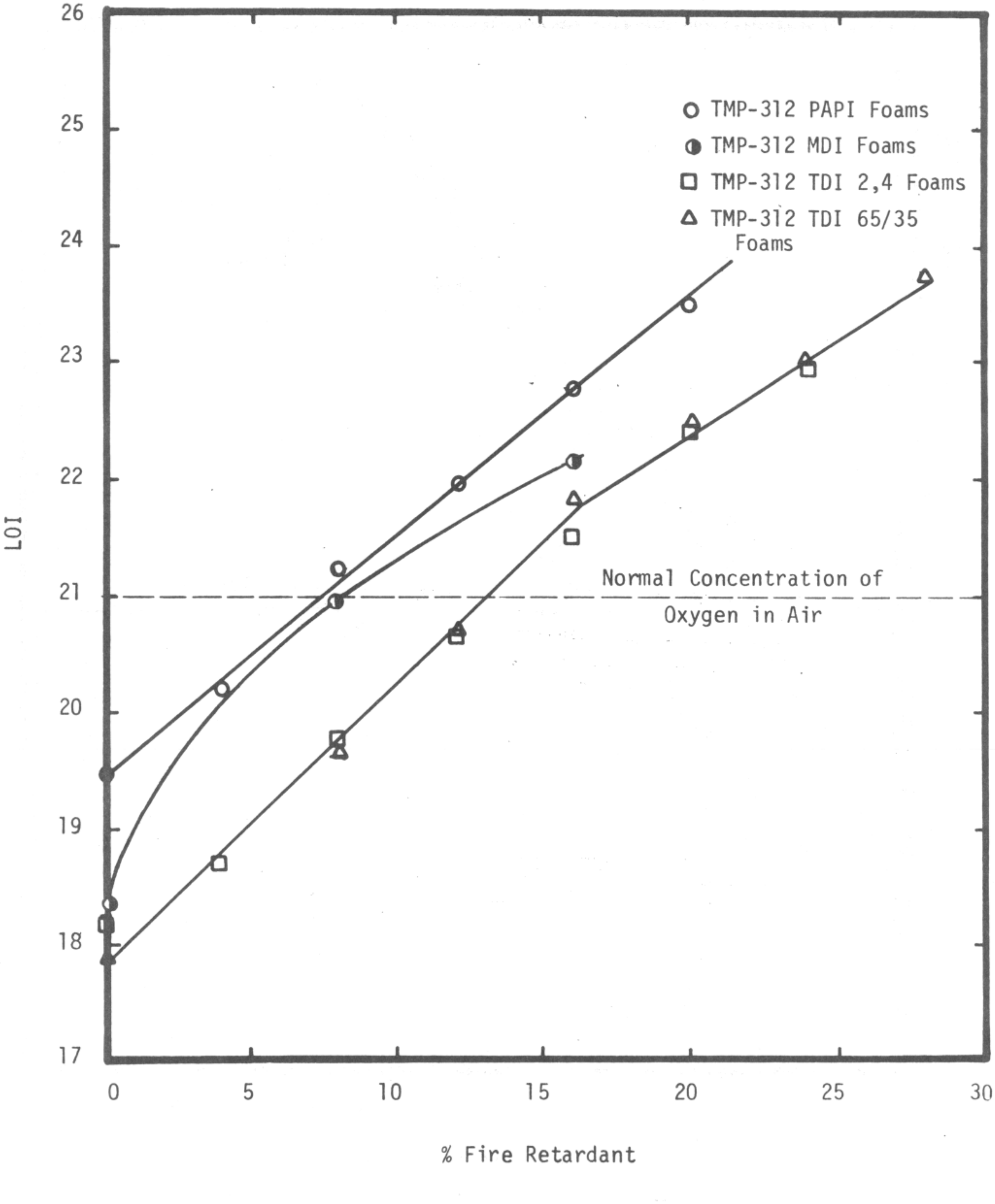


FIG. 26. EFFECT OF CHLORINATED FIRE RETARDANT ON LOI OF TMP-312 BASED FOAMS WITH VARIOUS ISOCYANATES (LOI = Least oxygen percent in air to maintain flaming combustion.)

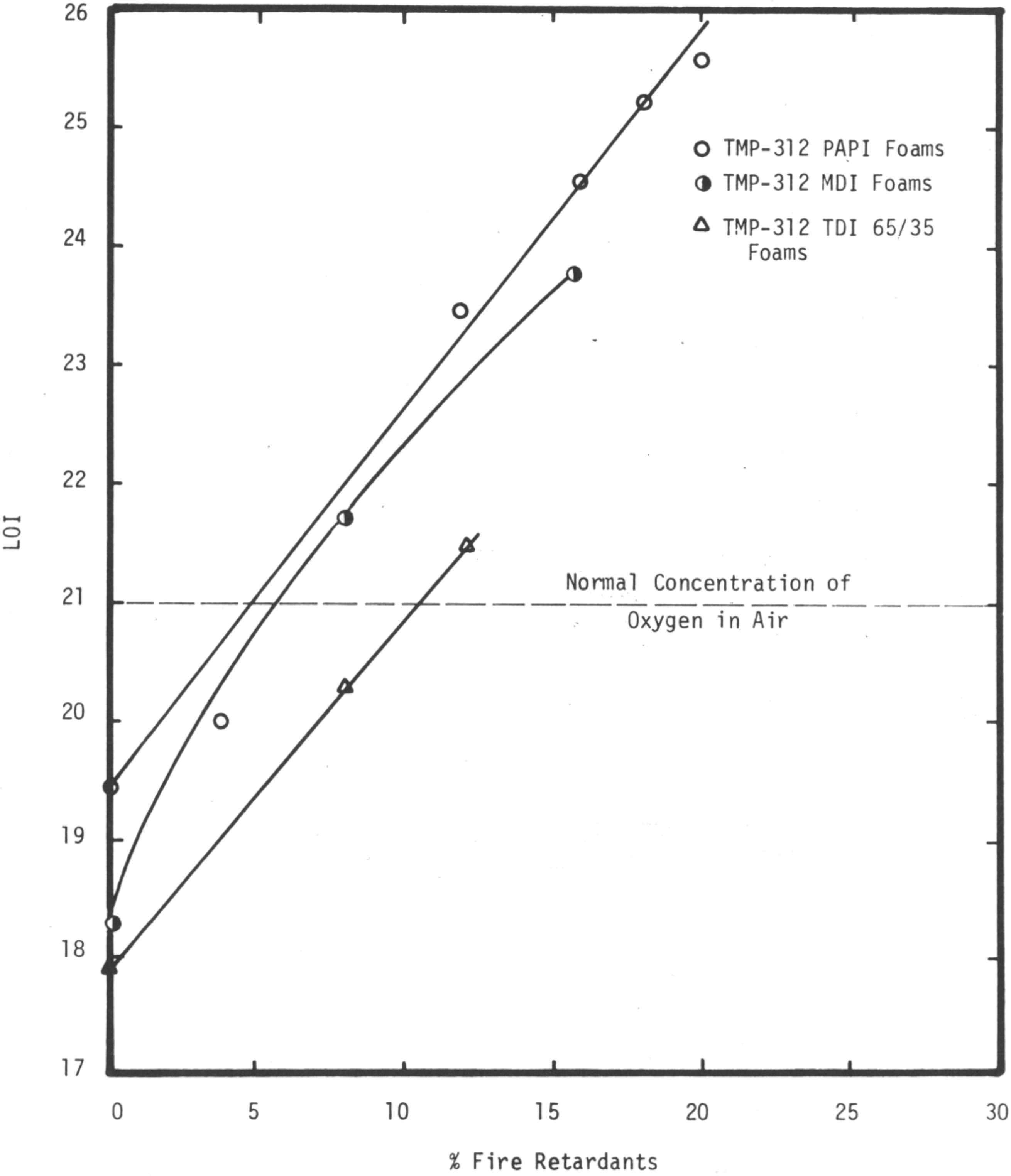


FIG. 27. EFFECT OF BROMINATED FIRE RETARDANT ON LOI OF TMP-312 BASED FOAMS WITH VARIOUS ISOCYANATES

influences the oxygen requirement necessary to support combustion. The effectiveness of the structure is PAPI>MDI>TDI.

Similar relationships are shown in Figures 28 and 29 for foams having a reduced cross-linked density (based on TMP-425 M.W.).

Figures 30 and 31 compare the effect of the 3 fire-retardant systems investigated on the Limiting Oxygen Index for foam systems based on polymethylene polyphenyl isocyanate and the 312-molecular-weight and 425-molecular-weight adducts of trimethylolpropane. Analysis of the data presented in these figures shows the effectiveness of fire retardants are rated brominated non-reactive retardant>non-halogenated reactive retardant> chlorinated non-reactive retardant.

Similar analyses were carried out using only the halogenated non-reactive retardants in systems utilizing other isocyanates. Figures 32 and 33 also show the brominated fire retardant to be more effective in raising the Limiting Oxygen Index than its chlorinated homologue.

The effects of chemical structure, fire-retardant type and concentration were evaluated using isocyanate foams prepared in the laboratory. The general trends clearly indicated that more functional polyols were required to substantially improve the flammability characteristics of rigid-urethane foams.

Optimized Rigid-Urethane Foams

Several rigid-urethane foam systems were prepared using a hepta-functional amine-containing Mannich adduct and the hexafunctional propyleneoxide adduct of sorbitol. The aromatic isocyanates, polymethylene polyphenyl isocyanate and 4,4' diphenylmethane diisocyanate were used in this evaluation. The technique reported by Einhorn, et al.,[37] for matching fire retardants with the polymer system were utilized in designing the optimun formulations. (See Appendix D for foam formulations.)

Analysis of the flammability characteristics of the optimized rigid-foam systems were determined using the procedures described earlier.

Smoke Development - ASTM D-2843T

The light obscuration characteristics of the optimized rigid-urethane foams were determined using the XP-2 Smoke Density Chamber, as described previously. Figures 34, 35, 36, and 37 present the values determined for foams based on polymethylene polyphenyl isocyanates and the Mannich adduct. Figure 38 illustrates similar results obtained during the combustion of the foams based on 4,4' diphenylmethane diisocyanate and the Mannich adduct.

Figures 39 and 40 present light-obscuration values obtained during the combustion of foam based on polymethylene polyphenyl isocyanate and 4,4' diphenylmethane diisocyanate and the propoxylated sorbitol polyols.

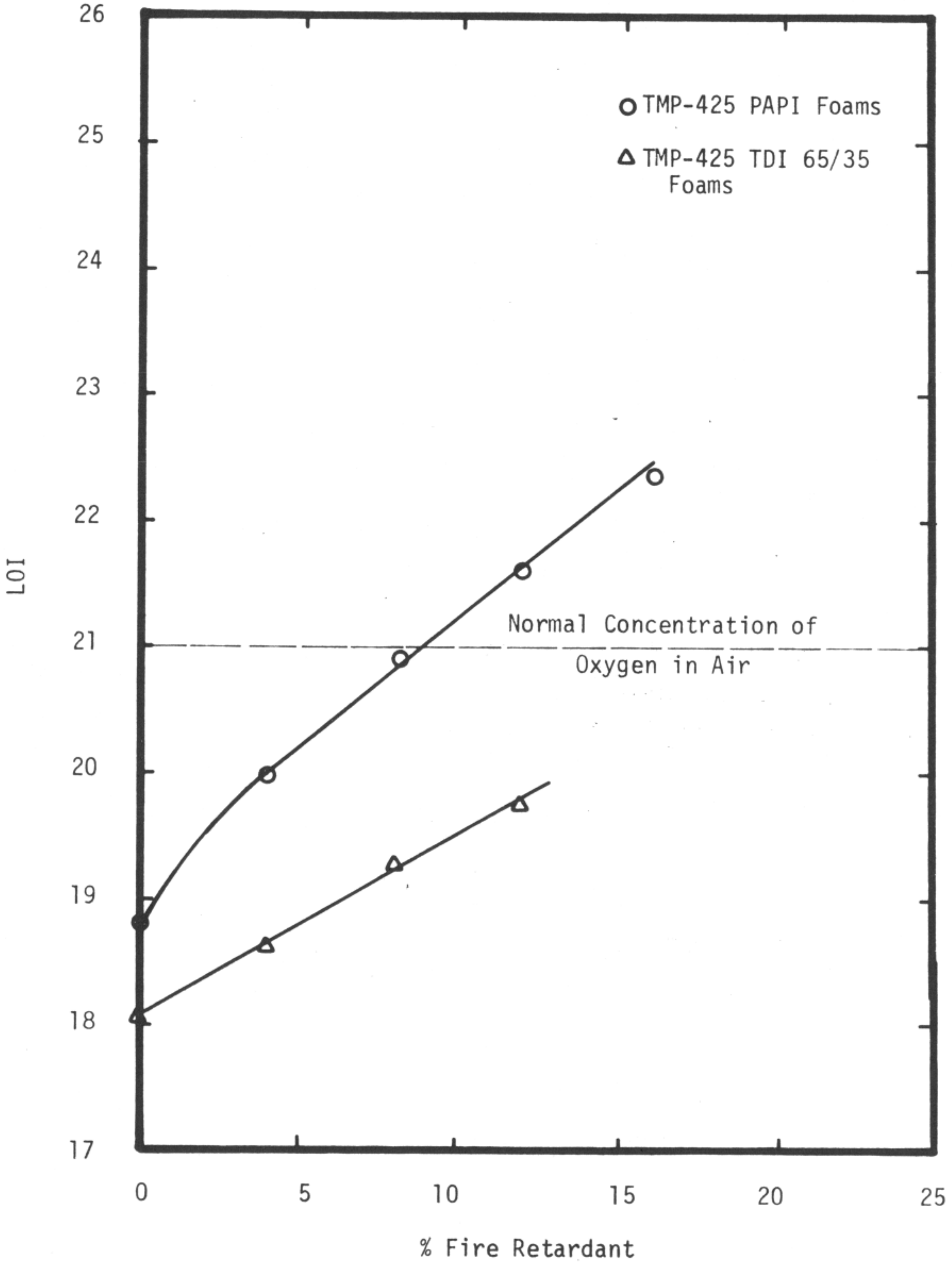


FIG. 28. EFFECT OF CHLORINATED FIRE RETARDANT ON LOI OF TMP-425 BASED FOAMS WITH VARIOUS ISOCYANATES (LOI = Least oxygen percent in air to maintain flaming combustion.)

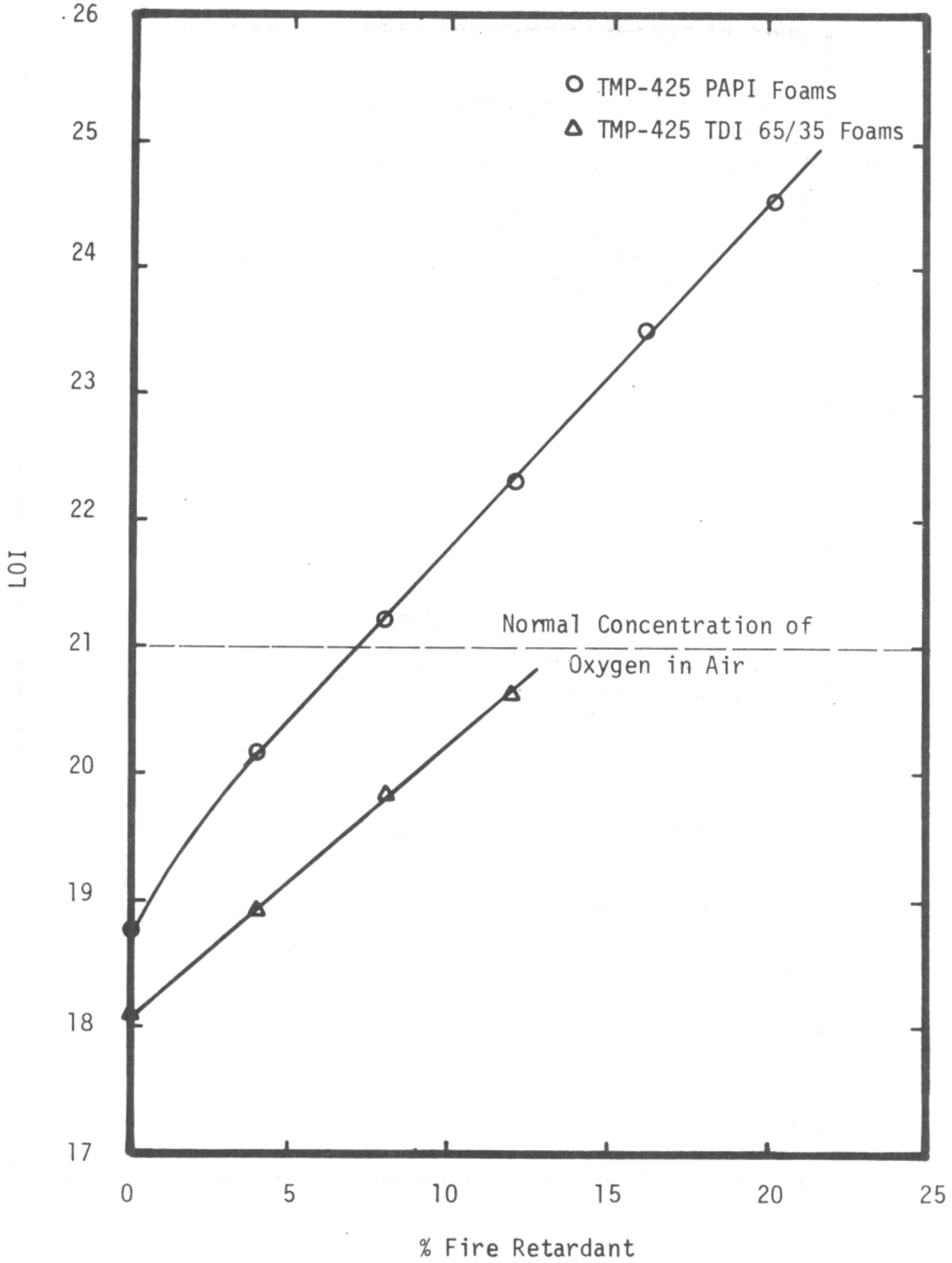


FIG. 29. EFFECT OF BROMINATED FIRE RETARDANT ON LOI OF TMP-425 BASED FOAMS WITH VARIOUS ISOCYANATES

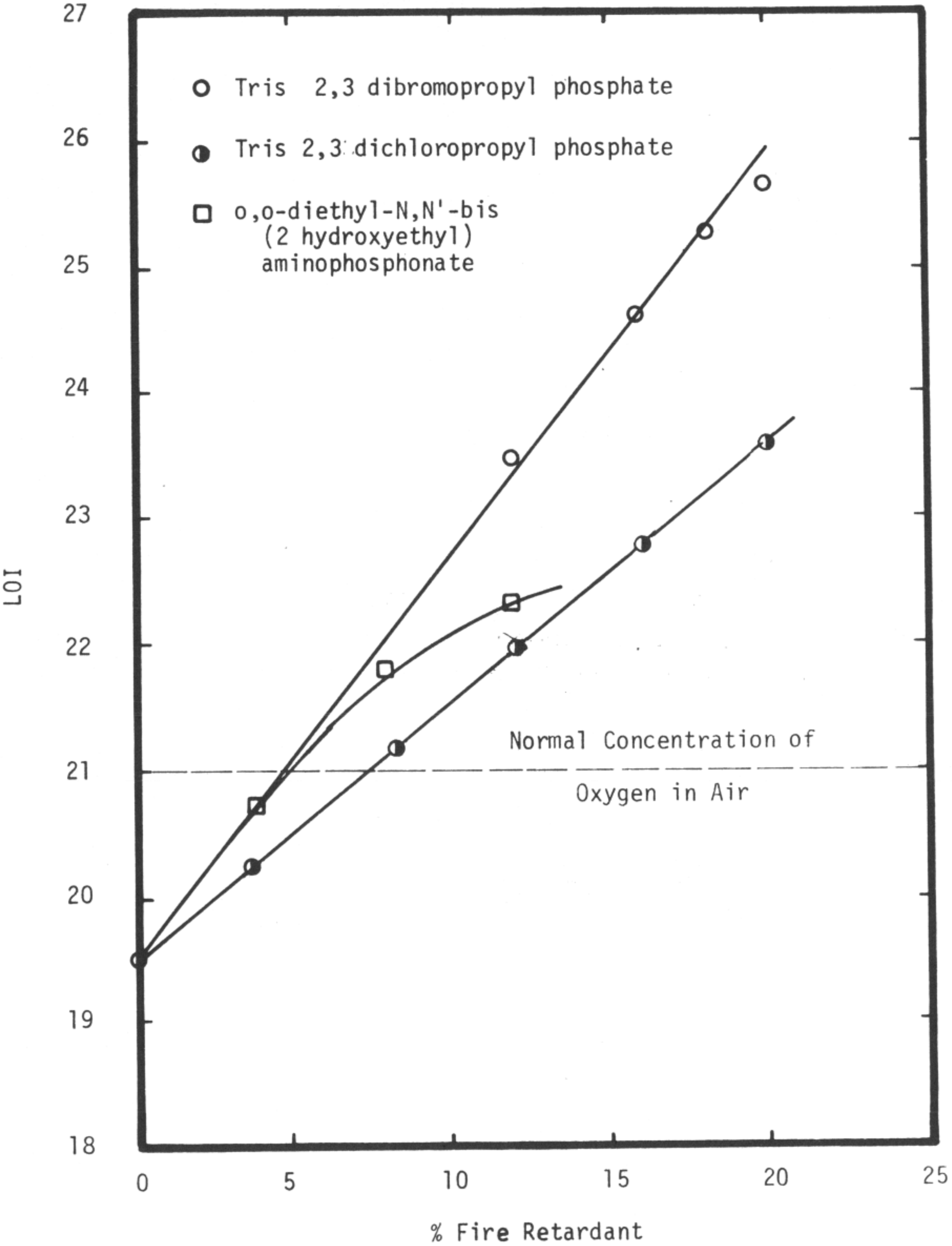


FIG. 30. OXYGEN INDEX FOR VARIOUS FIRE RETARDANTS IN TMP-312 PAPI FOAMS

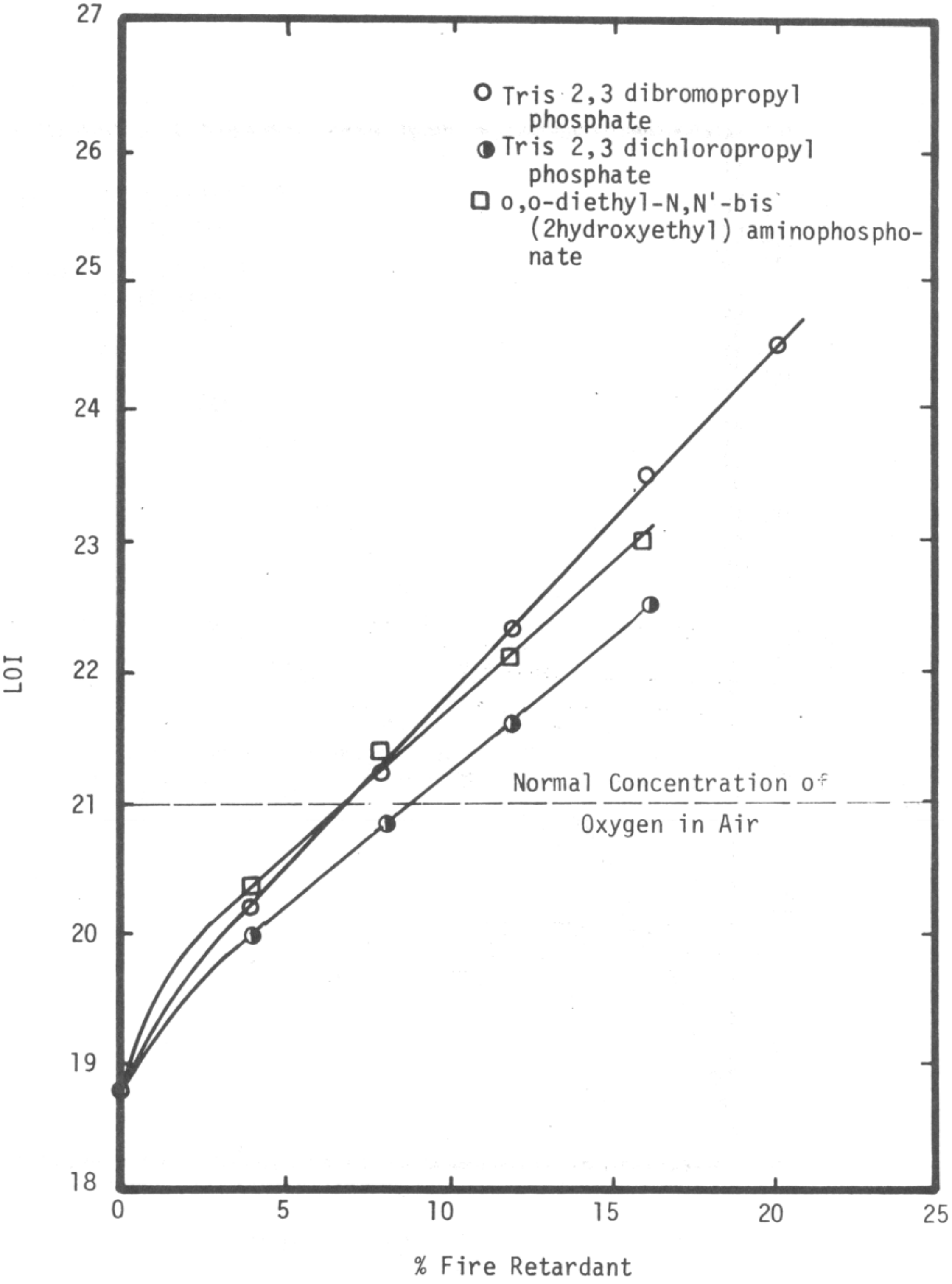


FIG. 31. OXYGEN INDEX FOR VARIOUS FIRE RETARDANTS IN TMP-425 PAPI FOAMS

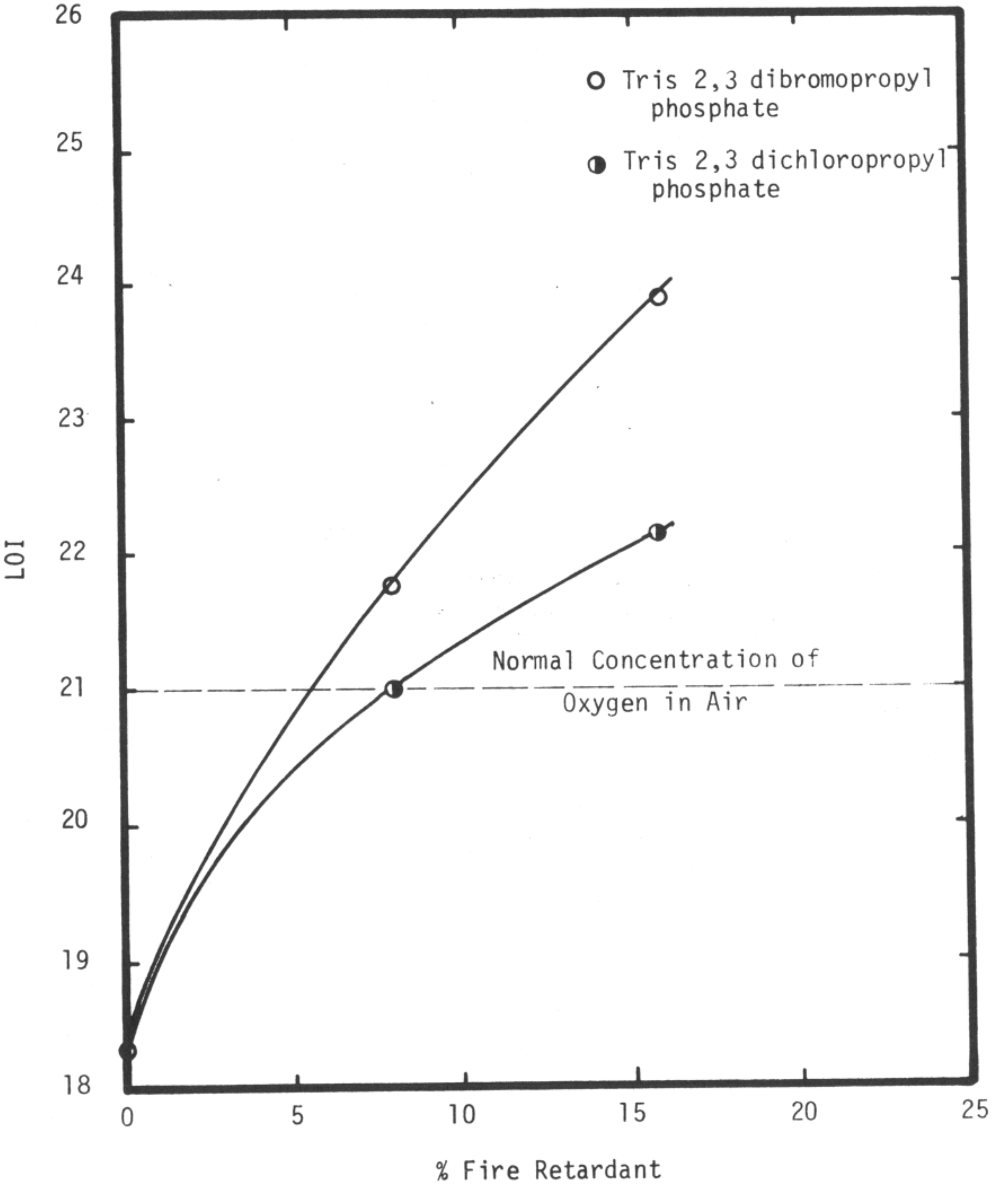


FIG. 32. OXYGEN INDEX FOR VARIOUS FIRE RETARDANTS IN TMP-312 MDI FOAMS

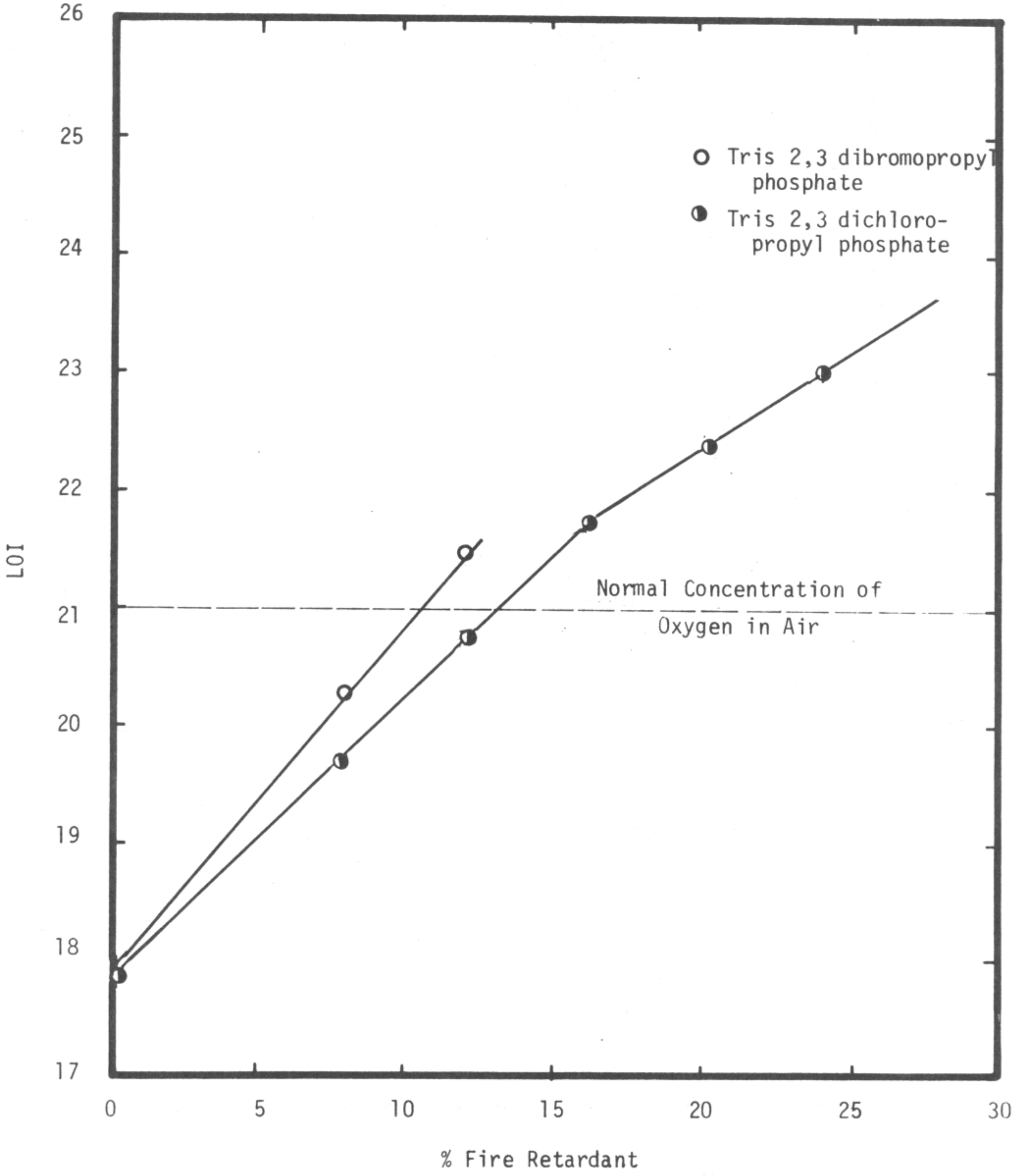


FIG. 33. OXYGEN INDEX FOR VARIOUS FIRE RETARDANTS IN TMP-312 TDI 65/35 FOAMS

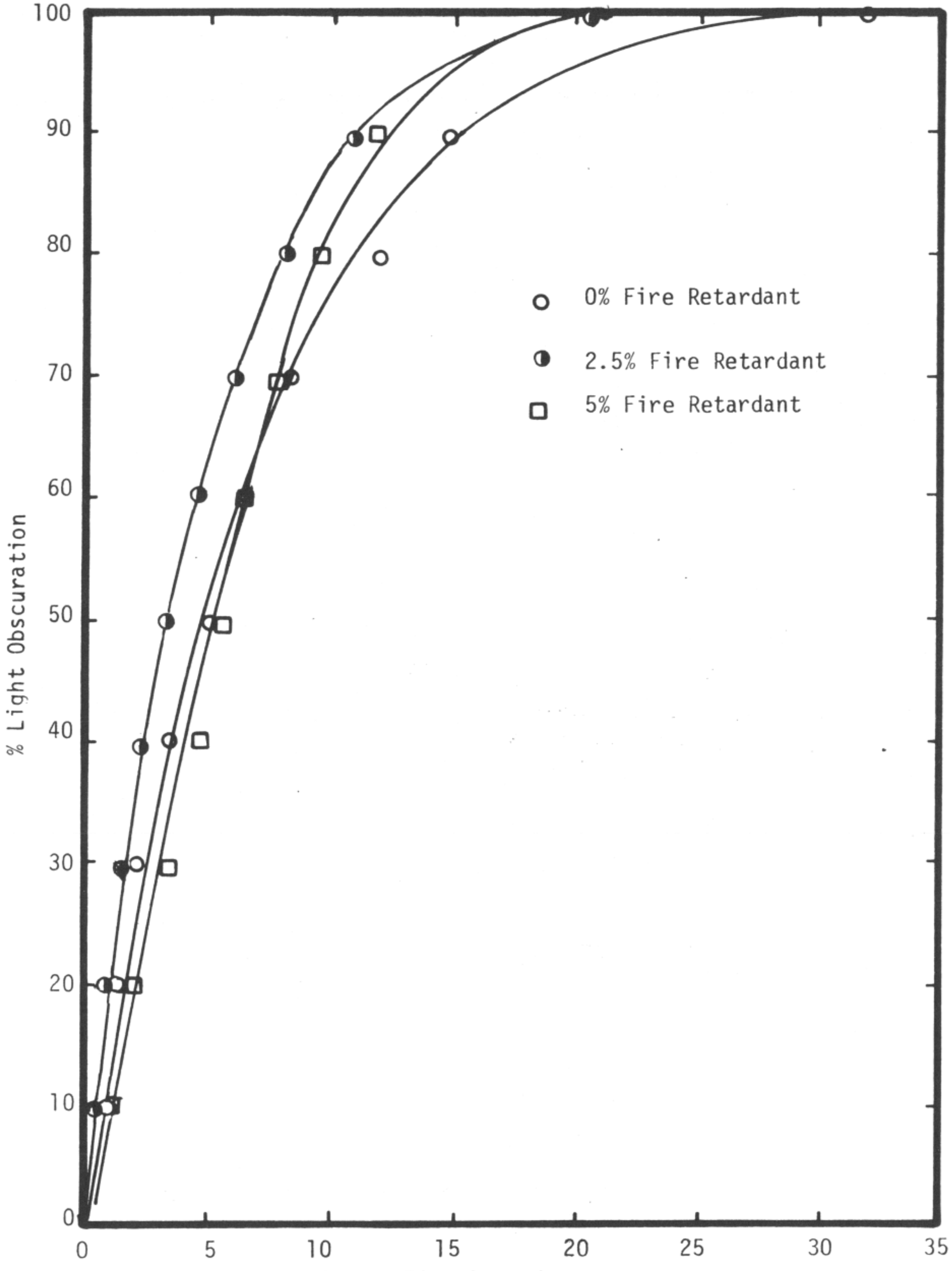


FIG. 34. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF O,O'-DIETHYL-N,N'-BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN MANNICH ADDUCT (MW 741) - PAPI FOAMS

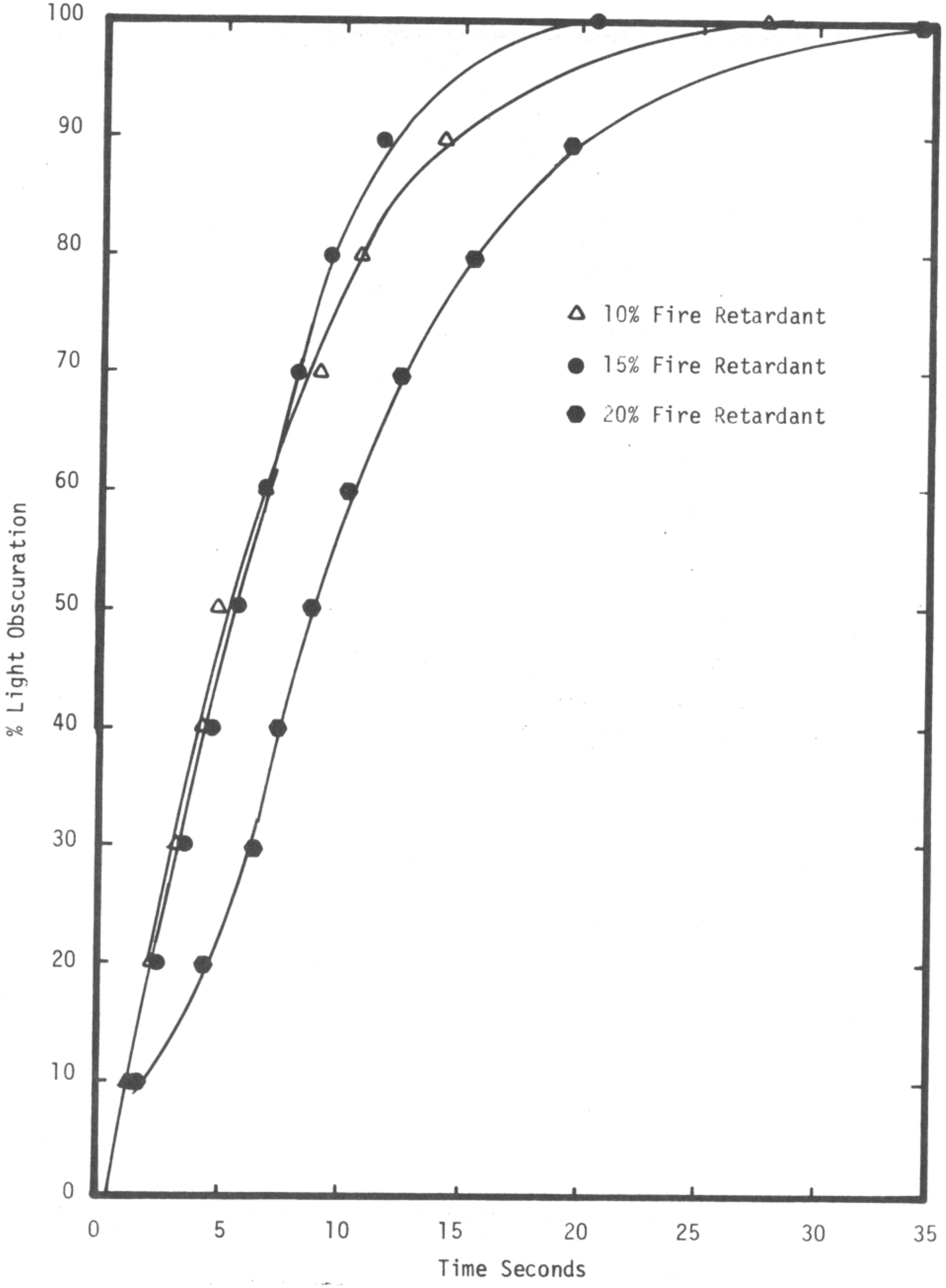


FIG. 35.. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF O,O'-DIETHYL-N,N'BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN MANNICH ADDUCT (MW 741) - PAPI FOAMS

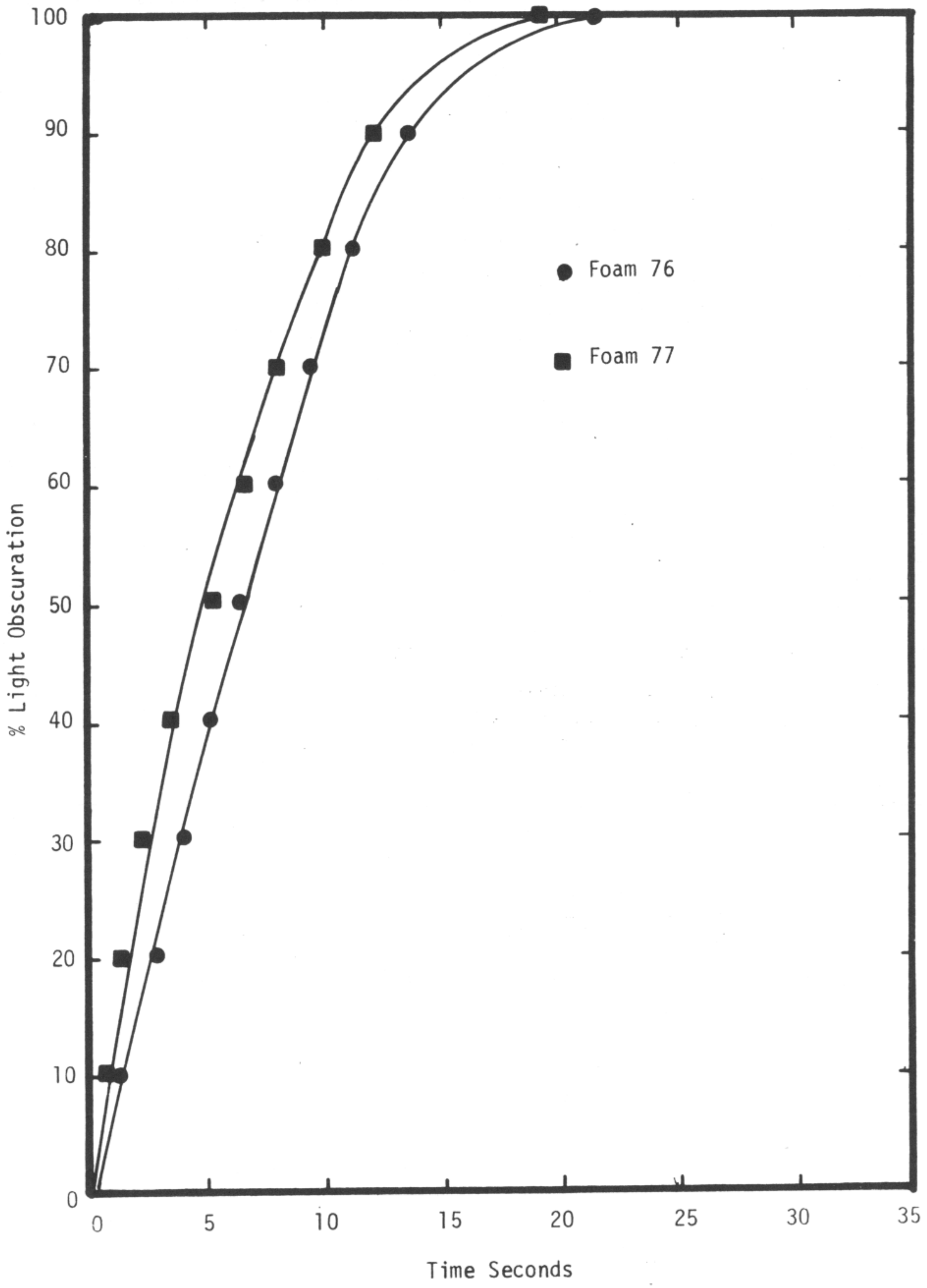


FIG. 36. LIGHT OBSCURATION FOR FOAMS 76 and 77

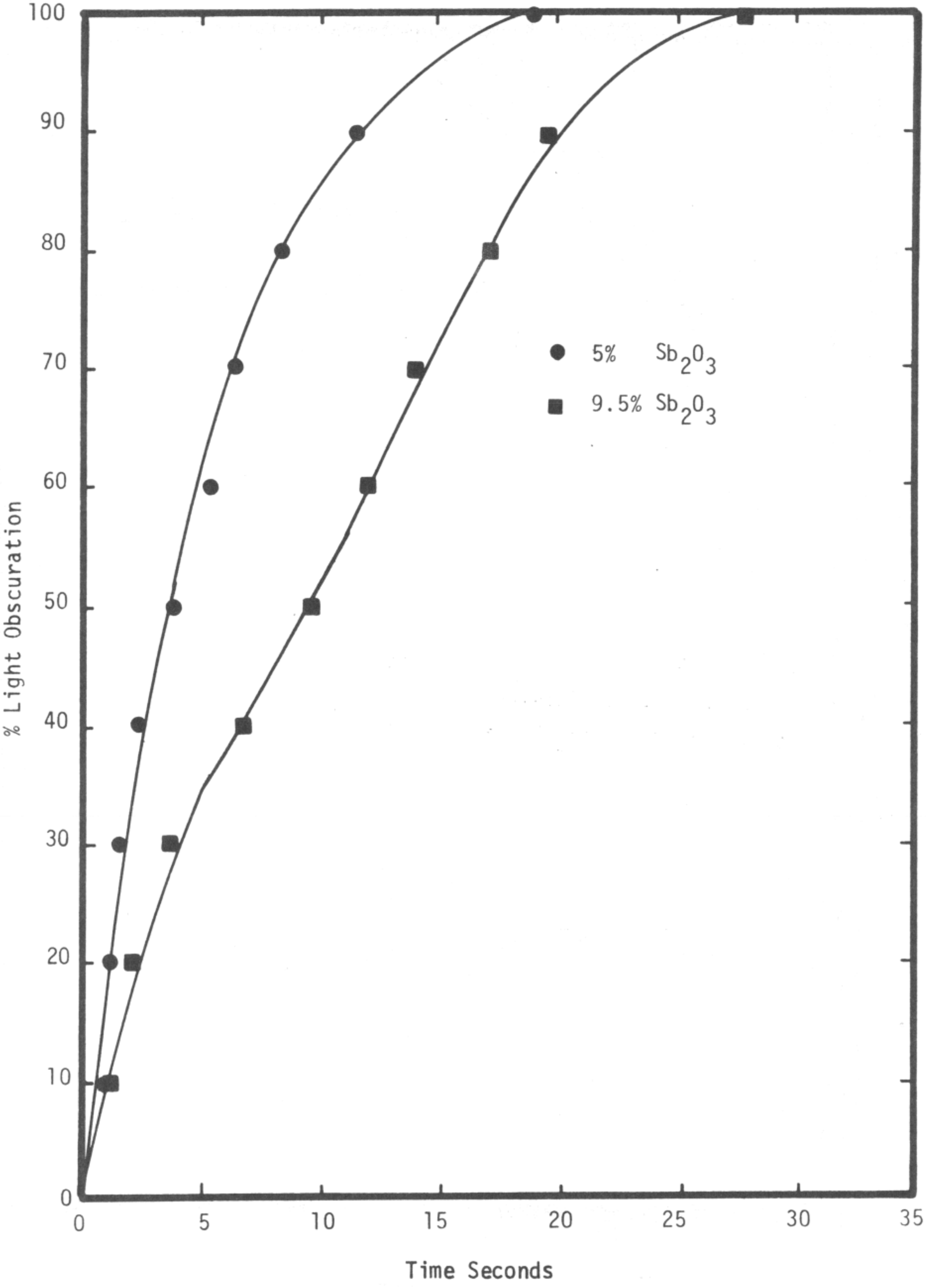


FIG. 37. EFFECT OF ANTIMONY OXIDE ON LIGHT OBSCURATION FOR MANNICH ADDUCT (MW 741) PAPI FOAMS

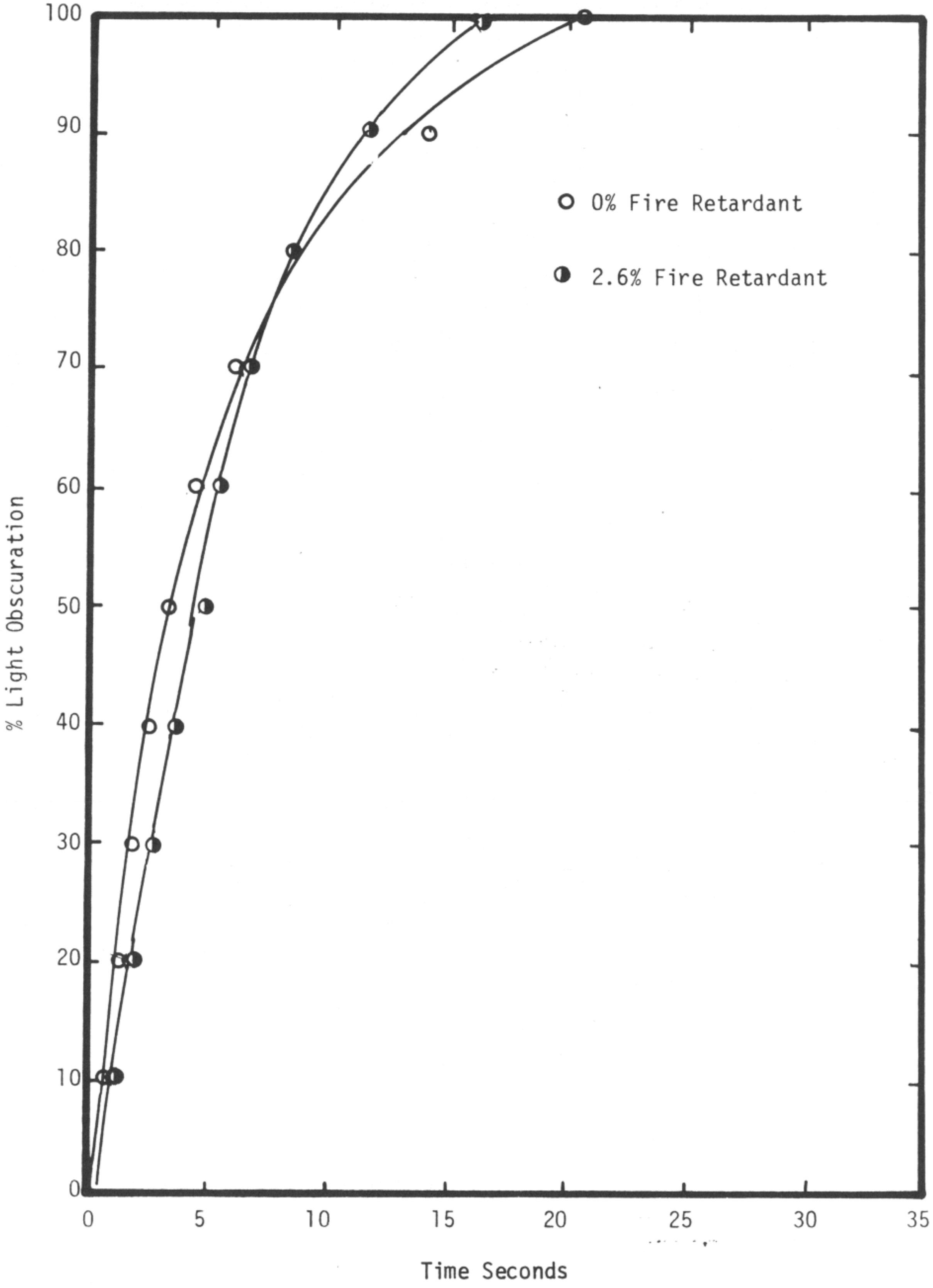


FIG. 38. LIGHT OBSCURATION IN MANNICH ADDUCT (MW 741) MDI FOAMS

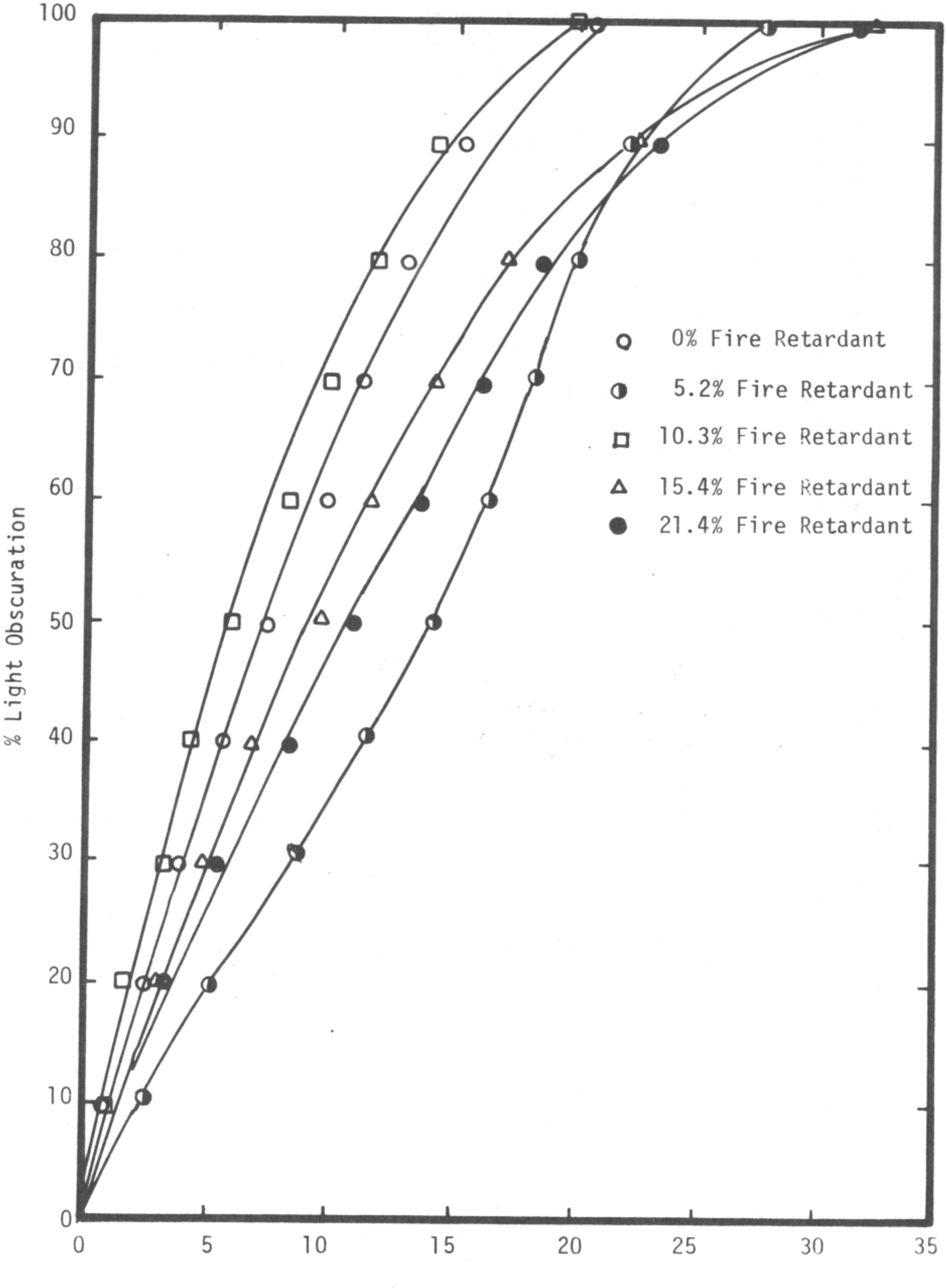


FIG. 39. LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF O,O'-DIETHYL-N,N'-BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN PROPOXYLATED ADDUCT OF SORBITOL (MW 686) - PAPI FOAMS

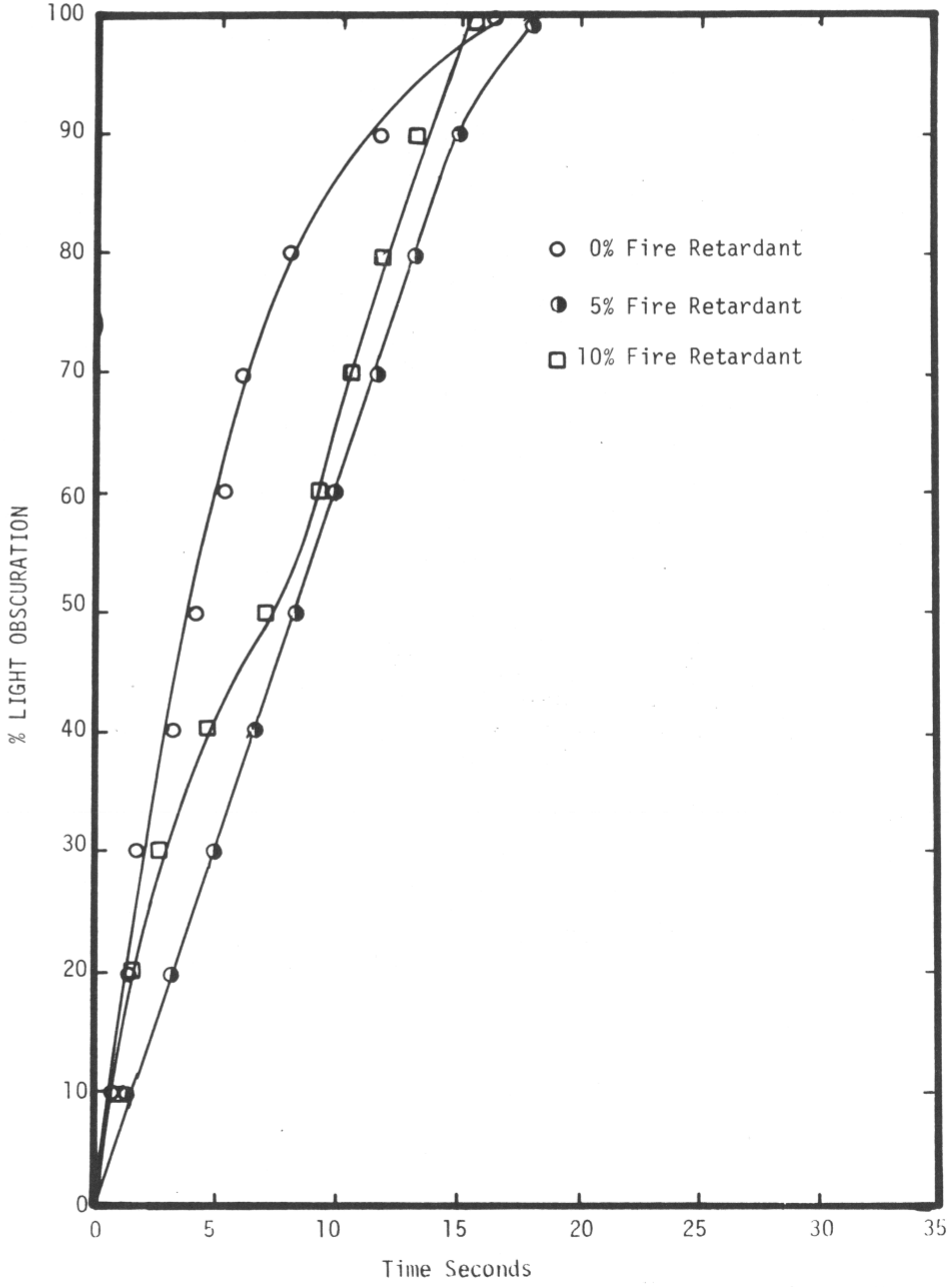


FIG. 40 LIGHT OBSCURATION FOR VARIOUS CONCENTRATIONS OF O,O'-DIETHYL-N,N'-BIS (2 HYDROXYETHYL) AMINOPHOSPHONATE IN PROPOXYLATED ADDUCT OF SORBITOL (MW 686) - PAPI FOAMS

It should be noted that although substantial improvement in the ignition, propagation, and endurance characteristics were achieved by optimizing the foam formulations on a structural basis, the light-obscuration characteristics remained similar to the fire-retarded foams studied previously.

Ignition and Flame Propagation - ASTM D-1692

The ignition and flame propagation characteristics of the optimized rigid-urethane foam systems were determined by ASTM D-1692, as described previously.

Foams based on polymethylene polyphenyl isocyanate and the propylene oxide adduct of sorbitol exhibited superior resistance to ignition and flame propagation compared to any rigid-urethane foams studied within the scope of this investigation. See Table XXIX.

Flame Penetration Test - Bureau of Mines Test (Modified)

The fire-endurance characteristics of the optimized rigid-urethane foams exhibited markedly improved burn-through resistance. Foams based on polymethylene polyphenyl isocyanate, the Mannich adduct, and reactive fire retardant had fire-endurance times ranging from 1.5 minutes to 9.3 minutes. (See Table XXX.)

Limiting Oxygen Index

Table XXXI and Figure 41 summarize the limiting oxygen indices obtained during the combustion of the optimized foam systems. Essentially, the values obtained were in the same general range as exhibited by the previous fire-retarded foam systems.

TABLE XXIX

IGNITION AND FLAME PROPAGATION (ASTM D-1692 TEST) OPTIMIZED RIGID-URETHANE FOAMS (MODIFIED 45°)

Sample*	Fire Retardant System	Weight % Reactive Fire Retardant	Density gm/cm^3	Time (Sec.) Flame Travel To: 1"	2"	3"	4"	5"	6"	% Weight Loss
Foam 70	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	0.0393	4	8	11	14	20	SE**	31
Foam 71	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.5	0.0455	4	7	15	28	40	SE**	12
Foam 72	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.0	0.0435	7	20	30	35	SE**	SE**	16
Foam 73	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.0	0.0415	7	15	25	SE**	SE**	SE**	20
Foam 74	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.2	0.0376	7	16	26	SE**	SE**	SE**	9
Foam 75	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	20.3	0.0357	10	20	38	SE**	SE**	SE**	25
Foam 76	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	9.2	0.0450	5	10	30	SE**	SE**	SE**	20
Foam 77	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.8	0.0455	5	13	30	SE**	SE**	SE**	14
Foam 78	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.0	0.0510	4	11	20	SE**	SE**	SE**	27
Foam 79	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	7.6	0.0535	5	13	30	SE**	SE**	SE**	21
Foam 80	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	0.0423	2	5	7	--	11	17	100
Foam 81	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.6	0.0324	4	6	9	--	15	19	100
Foam 82	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	0.0410	3	6	8	12	16	22	67
Foam 83	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.2	0.0380	7	13	SE**	SE**	SE**	SE**	22
Foam 84	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.3	0.0338	10	29	SE**	SE**	SE**	SE**	9
Foam 85	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.4	0.0315	11	30	SE**	SE**	SE**	SE**	9
Foam 86	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	21.4	0.0320	17	SE	SE**	SE**	SE**	SE**	8
Foam 87	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	0.0327	3	5	--	8	11	19	100
Foam 88	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4.8	0.0358	5	7	10	17	21	23	100
Foam 89	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	9.5	0.0341	7	10	16	20	23	25	100

*Formulation for all test specimens are presented in Appendix D, Tables D-I and D-II.
**SE - Self Extinguishing Classification
(Sample size 6"x2"x5")

TABLE XXX

FIRE ENDURANCE CHARACTERISTICS OF OPTIMIZED RIGID-URETHANE FOAMS

Sample*	Isocyanate	Polyol	Fire Retardant	Weight % Reactive Fire Retardant	Burn Through Time (Sec.)	% Weight Loss
Foam 70	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	97	35
Foam 71	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.5	247	41
Foam 72	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.0	270	40
Foam 73	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.0	280	50
Foam 74	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.2	292	40
Foam 75	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	20.3	560	21
Foam 76	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	9.2	123	36
Foam 77	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.8	164	35
Foam 78	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.0	239	32
Foam 79	PAPI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	7.6	53	21
Foam 80	MDI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	15	100
Foam 81	MDI	Mannich adduct	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.6	12	100
Foam 82	PAPI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	20	26
Foam 83	PAPI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.2	25	20
Foam 84	PAPI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.3	51	33
Foam 85	PAPI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.4	60	37
Foam 86	PAPI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	21.4	79	34
Foam 87	MDI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	10	100
Foam 83	MDI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4.8	11	100
Foam 89	MDI	Propoxylated sorbitol	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	9.5	8	100

*Formulations for all test specimens are presented in Appendix D, Tables D-I and D-II.

TABLE XXXI

LIMITING OXYGEN INDEX - OPTIMIZED RIGID-URETHANE FOAMS

Sample*	Fire Retardant System	Weight % Reactive Fire Retardant	LOI
Foam 70	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	21.02
Foam 71	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.5	22.45
Foam 72	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.0	23.18
Foam 73	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.0	23.18
Foam 74	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.2	24.00
Foam 75	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	20.3	24.58
Foam 76	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	9.2	24.90
Foam 77	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.8	24.58
Foam 78	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	8.0	25.80
Foam 79	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate + auxiliary F.R.	7.6	26.12
Foam 80	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	20.35
Foam 81	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	2.6	20.35
Foam 82	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	20.00
Foam 83	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	5.2	21.82
Foam 84	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	10.3	22.46
Foam 85	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	15.4	22.80
Foam 86	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	21.4	24.00
Foam 87	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	0.0	18.60
Foam 88	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	4.8	20.35
Foam 89	o,o'-diethyl-N,N'-bis (2 hydroxyethyl) aminophosphonate	9.5	21.40

*Formulations for all test specimens are presented in Appendix D, Tables D-I and D-II.

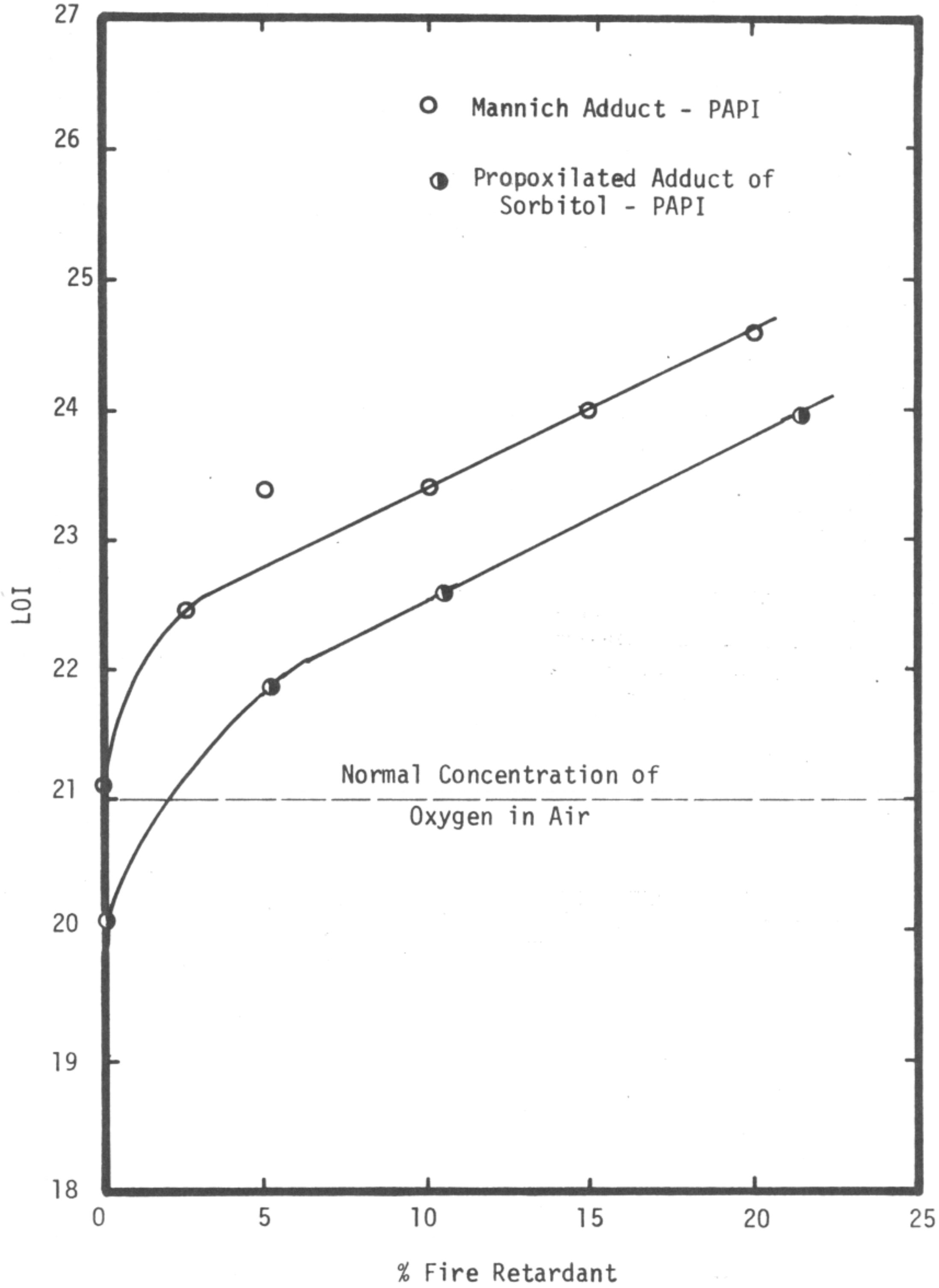


FIG. 41. EFFECT OF REACTIVE FIRE RETARDANT ON LOI OF PAPI-BASED FOAMS WITH MANNICH ADDUCT AND PROPOXYLATED ADDUCT OF SORBITOL

Flexible-Urethane Foams

General Background

The early flexible-urethane foams produced in the United States were classified as polyester foams. These cellular plastics were based on tolylene diisocyanate, a slightly branched adipate polyester, tertiary amine catalysts, ionic emulsifiers and used water as the blowing agent. These polyester-based flexible urethane foams possessed good mechanical properties but lacked the desired load-deflection and rebound characteristics necessary for use in the comfort-cushioning industry. A second detriment to acceptance in the cushioning industry was the poor humid aging characteristics of the early commercial flexible polyester foams.

In the late 1950's polyesters based on linoleic acid (dimer acid) were introduced.[38] These dimer-acid based flexible foams possessed excellent resistance to hydrolysis and had load-deflection characteristics resembling rubber latex foams.

Numerous references relating to flexible-urethane foams based on polyether polyols derived from adducts of ethylene oxide and propylene oxide appeared in the late 1950's and early 1960's.[39,40,41,42,43] Most of the early polyether foams were prepared using prepolymers based on polypropylene glycols either alone or in combination with tri- or tetra-functional polyols and tolylene diisocyanate. The development of the "one-shot" process by Houdry,[44] using Dabco as a catalyst, and by Mobay,[45] and Union Carbide[46] using organotin catalyst eliminated the intermediate and more costly prepolymer process.

Raw Materials

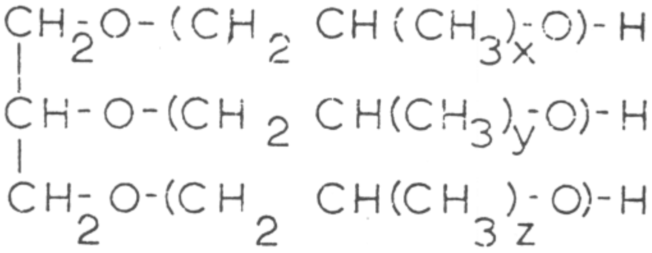
The raw materials employed in the commercial preparation of flexible foams are quite similar to those described previously for the preparation of rigid-urethane foams.

Isocyanates

Flexible foams have been prepared from a variety of aliphatic, cycloaliphatic, and aromatic diisocyanates. To this date, however, tolylene diisocyanate has maintained a preponderant position in the flexible foam industry. The 80/20 mixture of the 2,4 and 2,6 isomers of tolylene diisocyanate is preferred in the United States. The 65/35 ratio of isomers of TDI is frequently used in Europe.

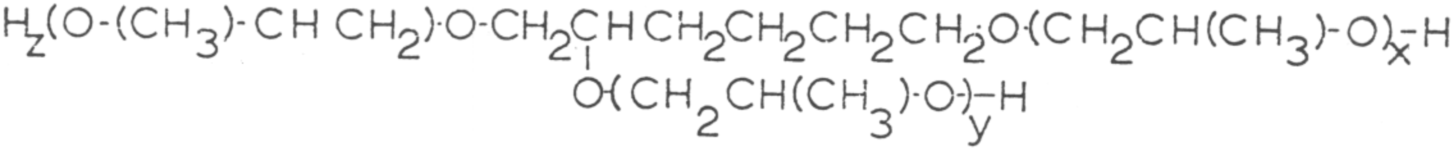
Polyols

The polyesters and dimer acids have been largely replaced by polyethers in most major flexible-urethane foam markets in the United States, thus the polyols used in this study were selected as typical representatives of those materials used in commercial production. Figure 42 illustrates the chemical structure of typical polyols used in flexible foam production.



$$\begin{array}{l} CH_2\text{-}O\text{-}(CH_2\,CH(CH_3)_x\text{-}O)\text{-}H \\ | \\ CH\text{-}O\text{-}(CH_2\,CH(CH_3)_y\text{-}O)\text{-}H \\ | \\ CH_2\text{-}O\text{-}(CH_2\,CH(CH_3)_z\text{-}O)\text{-}H \end{array}$$

Propylene Oxide Adduct of Glycerol

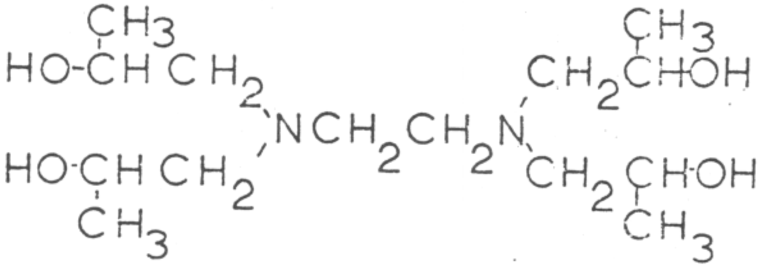


$$\begin{array}{l} H_z(O\text{-}(CH_3)\text{-}CH\,CH_2)\text{-}O\text{-}CH_2\underset{|}{C}H\,CH_2CH_2CH_2CH_2\text{-}O(CH_2CH(CH_3)\text{-}O)_x\text{-}H \\ \qquad\qquad\qquad\qquad\quad O(CH_2CH(CH_3)\text{-}O)_y\text{-}H \end{array}$$

Propylene Oxide Adduct of 1,2,6 Hexanetriol

$HO(CH_2CH_2O\text{-})_x\text{-}(CH_2CH\text{-}(CH_3)O\text{-})_y\text{-}(CH_2CH_2O)_z\text{-}H$

Block Copolymer of Ethylene Oxide and Propylene Oxide



N,N,N',N',- Tetrakis(2 - hydroxypropyl) ethylenediamine

FIG. 42. STRUCTURES OF POLYETHER POLYOLS USED IN THE PRODUCTION OF FLEXIBLE-URETHANE FOAMS

Table XXXII presents the properties of representative polyether polyols.

TABLE XXXII

TYPICAL POLYETHER POLYOLS USED IN THE PRODUCTION OF FLEXIBLE-URETHANE FOAMS

Chemical Identification	Type of Polyol	M.W. Range
Poly(oxypropylene) glycols	Diols	400-4000
Poly(oxypropylene)-poly(oxyethylene) glycols (block copolymers)	Diols	1000-2800
Poly(oxypropylene) adducts of glycerin	Triols	400-5000
Poly(oxypropylene) adducts of trimethylolpropane	Triols	300-4000
Poly(oxypropylene) adducts of 1,2,6-hexanetriols	Triols	700-4400
Poly(oxypropylene) adducts of pentaerythritol	Tetrols	400- 600
Poly(oxypropylene) poly(oxyethylene) adducts of ethylenediamine (block copolymers)	Tetrols	1000-5000
Poly(oxypropylene) adducts of sorbitol	Hexols	700

Flexible Foam Surfactants

Many different types of surfactants have been employed for flexible foams, but organic nonionic and anionic surfactants and silicones are generally used. The choice of surfactant depends on the choice of processing method employed (prepolymer, quasi-prepolymer, or "one-shot" method), the desired cell size, and the desired porosity. The most commonly employed surfactants for polyether-based foams are silicones such as the polyalkylsiloxane-polyoxyalkylene copolymers. Conventional polydimethylsiloxanes of relatively low viscosity have been used for polyether systems prepared and foamed as prepolymers. In the prepolymer process the primary role of the silicone surfactant is to lower surface tension and to provide film (cell wall) resilience. Resilient cell walls prevent collapse during the expansion process and thus stabilize the foam until it is self-supporting.

Flexible Foam Catalysts

The reaction between an isocyanate and the labile hydrogen in a polyol will take place without a catalyst, but at too slow a rate to be useful in the preparation of a flexible foam. The urethane reaction can be catalyzed by basic compounds. Tertiary amines such as triethylenediamine, tetramethylenebutane diamine, diethylaminoethanol, and triethylamine have been widely used as catalysts for flexible foams.

The choice of catalysts for the preparation of flexible foams is governed by the type of polyol used. In polyether-based systems, where low resin viscosity and reactivity must be overcome, more active catalysts are required. For such systems the stannous salts of dicarboxylic acid, such as stannous octoate, are preferred.

Flexible Foam Blowing Agents

Carbon dioxide, produced in situ by the reaction of water with the isocyanate, is the chief blowing agent for all commercially-produced flexible-urethane foams.

In addition to water, auxiliary blowing agents may be included in the foam formulation to further control foam density. These agents may be included in the foam formulation to further reduce the foam density. Methylene chloride and trichlorofluromethane are commonly used auxiliary blowing agents for flexible urethane foams.

Non-Fire-Retarded Flexible-Urethane Foams

General Background

The study of the parameters necessary for optimization of the flammability characteristics of cellular plastics are compared in Table XXXIII.

TABLE XXXIII

PARAMETERS REQUIRED FOR OPTIMIZATION
OF FLAMMABILITY CHARACTERISTICS OF URETHANE FOAMS

Parameter Desired	Present in Rigid Foams	Present in Flexible Foams
Highly Aromatic Isocyanate	Highly Aromatic Isocyanate	Slightly Aromatic Isocyanate
Highly Functional Polyols (F=3 to F=7)	Highly Functional Polyols (F=3 to F=7)	Low Functionality Polyols (F=2 to F=4)
Cross-link Density <500	Cross-link Density <500	Cross-link Density >1500
High Thermal Decomposition Temperature	Decomposition Temperatures (240°C--380°C)	Decomposition Temperatures (180°C--240°C)
Closed cells	90-95 per cent Closed Cells	<20 per cent Closed Cells

Examination of Table XXXIII clearly indicates the difficulties which are encountered when trying to impart a desirable degree of flame retardancy to flexible-urethane foam systems. Figures 5, 6, and 7 and Tables XII, XIII, and XIV show that it is not possible to develop the needed char strength necessary to provide adequate flame retardancy with the isocyanates and polyols available for the preparation of flexible-urethane foams.

Preparation and Analysis of Non-Fire-Retarded Flexible-Urethane Foams

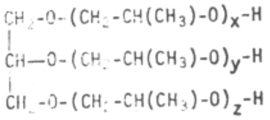
Three non-fire-retarded flexible-urethane foams were prepared using laboratory equipment to emphasize the fact that flexible foams comparable to commercial systems have inherently poor flammability characteristics. Foam 90 was prepared by reacting a propylene oxide adduct of glycerine (M.W. 3000) with the 80:20 isomer of tolylene diisocyanate. Table XXXIV summarizes the properties of the polyol, the foam formulation used, and the properties of this flexible foam.

TABLE XXXIV

FLEXIBLE NON-FIRE-RETARDED URETHANE FOAM, CHEMISTRY AND PROPERTIES (FOAM 90)

Propylene Oxide Adduct of Glycerine

Chemical Structure



$$\begin{array}{l} CH_2\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_x\text{-}H \\ | \\ CH\text{—}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_y\text{-}H \\ | \\ CH_2\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_z\text{-}H \end{array}$$

where $x,y,z \cong 16$

Approximate Molecular Weight	3000	
Acid number, mg KOH/g	0.2	maximum
Ash, weight per cent	0.005	maximum
Hydroxyl number, mg KOH/g	55.0	
Potassium, ppm	5	maximum
Total unsaturation, meq/g	0.04	maximum
Water, per cent (K.F.)	0.01	maximum

Flexible Foam Formulation

Ingredient	Parts By Weight
Polyol 3000 M.W.	100.0
TDI (80:20 isomer ratio)	46.0
Water	3.7
Stannous Octoate	0.3
Triethylenediamine	0.07
N-ethylmorpholine	0.2
Silicone oil	1.3
NCO/OH	1.04

Flexible Foam Properties

Density, pcf	1.6
ILD, 4-inch	
25% deflection	32
65% deflection	52
ILD loss (static), per cent	17
Tensile strength, p.s.i.	19
Elongation, per cent	285
Compression set. 70°C, 50% RH, 22 hrs.	20%
ASTM D-1692 Test, 45°	Burning rate 27 inches/min.

Foams 91 and 92 were prepared via the prepolymer process using as the basic polyol a 2000 molecular weight polyoxypropylene glycol. Two different urethane branched prepolymers were synthesized and modified by the addition of a triol and tetrol to provide greater stability during the foaming process. Prepolymer 1 was modified using 1,2,6 hexane triol, which prepolymer 2 was stabilized by the addition of N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine. Table XXXV summarizes the properties of the polyol, prepolymer, the foam formulation, and foam properties for the 2 non-fire-retarded flexible urethane foams.

TABLE XXXV

FLEXIBLE NON-FIRE-RETARDED URETHANE FOAMS, CHEMISTRY AND PROPERTIES (FOAMS 91 AND 92)

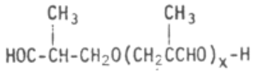
Polyoxypropylene Glycol (Diol)		
Chemical Structure		
 $HOC\text{-}\overset{CH_3}{C}H\text{-}CH_2O(CH_2\overset{CH_3}{C}CHO)_x\text{-}H$	where $x \geqq 34$	
Approximate Molecular Weight	2000	
Acid number, mq KOH/g	0.1 maximum	
Ash, weight per cent	0.005 maximum	
Hydroxyl number, mq KOH/g	55.0	
Potassium, ppm	5 maximum	
Total unsaturation, meq/g	0.04 maximum	
Water, per cent (K.F.)	0.01 maximum	
Urethane Branched Prepolymers		
	Prepolymer 1	Prepolymer 2
Polyoxypropylene glycol M.W. 2000	100.0	100.0
Triol (1,2,6 hexane triol) M.W. 134	3.0	---
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine M.W. 294	---	0.5
Water	0.15	0.15
TDI (80/20 isomer mix) NCO/OH	1.05/1.0	1.05/1.0
Prepolymer Properties		
Viscosity @ 86°F CPS	18,000	6,300
-NCO, per cent	9.5	9.5
Foam Formulation		
Ingredients	Parts By Weight	
Prepolymer (9.5% NCO)	100.0	
Silicone Oil - 50 cths	0.5	
N-methyl morpholine	1.0	
Triethyl amine	0.3	
Water 110% of theory	2.25	
Foam Properties		
	Prepolymer 1	Prepolymer 2
Density, p.c.f.	2.1	2.3
Tensile strength, p.s.i.	12	19
Elongation, per cent	200	450
Compression - deflection, p.s.i.		
25% deflection	0.53	0.44
50% deflection	0.68	0.56
Compression set, 70°C, 50% RH, 22 hrs.	5%	6%
ASTM D-1692 Burning rate	29 inches/min.	21 inches/min.

Figure 43 indicates the effect of temperature on the thermal decomposition of the 3 flexible foams.

The complete flammability characteristics of these 3 flexible foams are presented in Table XXXVI.

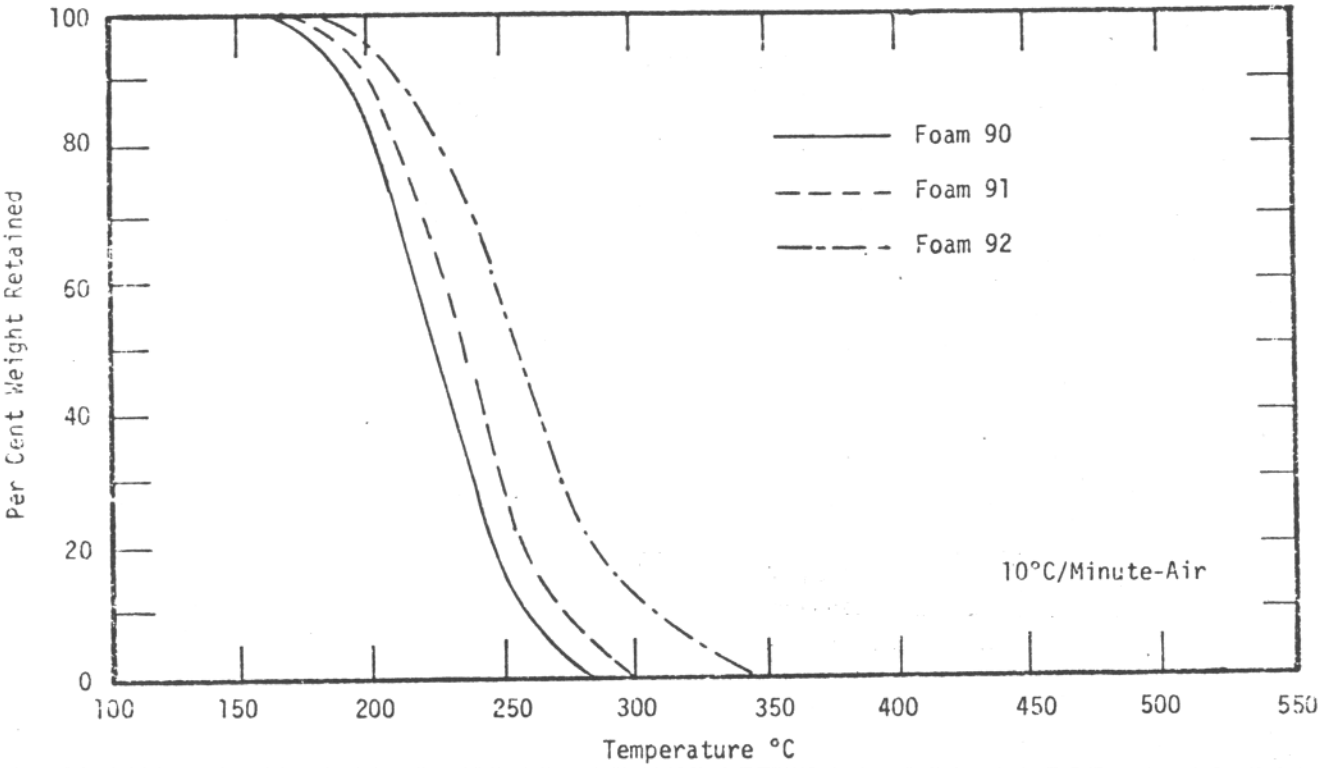


FIG. 43. EFFECT OF POLYOL STRUCTURE ON THERMAL DECOMPOSITION

TABLE XXXVI

FLAMMABILITY AND SMOKE CHARACTERISTICS OF NON-FIRE-RETARDED FLEXIBLE URETHANE FOAMS

Flammability Test	Foam 90	Foam 91	Foam 92
Smoke Development (ASTM D-2843T)			
Time Seconds To: 10% L.O.	4.0	3.5	3.1
Time Seconds To: 20% L.O.	7.8	6.1	5.2
Time Seconds To: 30% L.O.	16.2	14.0	13.0
Time Seconds To: 40% L.O.	----	17.5	15.0
Ignition and Propagation (ASTM D-1692)			
Self-Extinguishing	----	----	----
Burning Rate, Inches/Minute	27.0	29.0	21.0
Flame Penetration Test (Modified Bureau of Mines Test)			
Burn-Through Time, Seconds	5.0	4.0	5.5
Limiting Oxygen Index Test			
$\left[\frac{n_{O_2}}{n_{O_2} + n_{N_2}}\right]$	0.185	0.176	0.186

Analysis of the information presented in Table XXXVI clearly indicates that all of the formulations evaluated representing flexible-urethane foams must be rated as highly combustible.

Modified Flexible-Urethane Foams

A series of flexible-polyether foams based on a propylene oxide adduct of glycerine (approximately 3000 M.W.) and tolylene diisocyanate were prepared via the "one-shot" technique. Expansion was accomplished by the addition of water leading to the generation of carbon dioxide during processing. The idealized structure representing this foam is illustrated in Figure 44.

The basic formulation used to produce this series of foam samples is given in Table XXXVII.

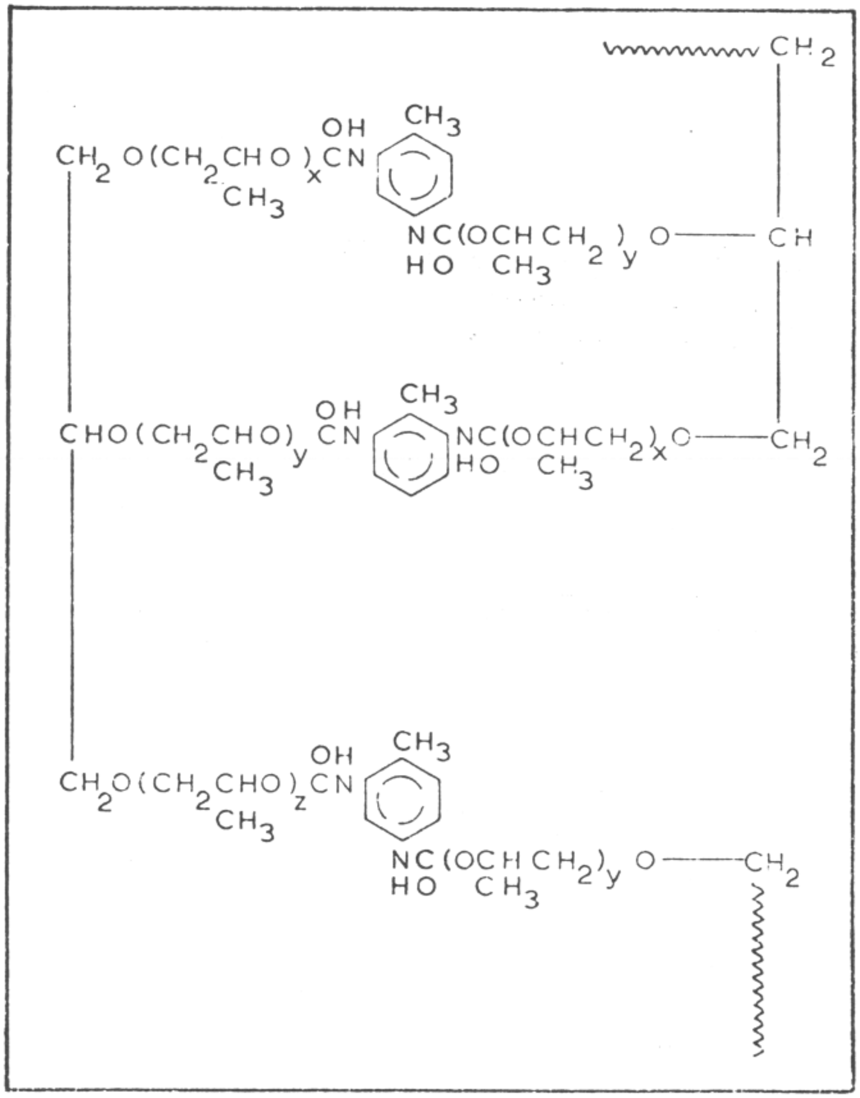


FIG. 44. IDEALIZED STRUCTURE FOR A FLEXIBLE-URETHANE FOAM

TABLE XXXVII

FLEXIBLE FOAM FORMULATIONS AND PROPERTIES

Raw Materials	Parts By Weight
Propylene oxide adduct of glycerine (3000 M.W.	100.0
Tolylene diisocyanate (80/20 isomer ratio)	46.0
Water	3.7
Stannous octoate	0.3
Triethylenediamine	0.7
N-ethylmorpholine	0.1
Silicone oil	1.3
NCO/OH Index	1.04
Physical Properties	
Density, p.c.f.	1.6
Tensile strength, p.s.i.	19
Elongation, per cent	285
Compression set, 20°C, 50% RH, (22 hours)	2.0%

This basic formulation was modified to produce samples of a flexible foam extended (5 per cent by weight) with a purified, finely-ground form of the barium sulfate minera, baryte. A fire-retardant flexible-urethane foam was prepared by adding the reactive phosphorous containing polyol o,o-diethyl-n,n-bis (2-hydroxyethyl) aminomethylphosphonate:

$$(C_2H_5O)_2P(O)\text{-}CH_2N\text{-}(C_2H_4\text{-}OH)_2$$

The basic formulation was modified in order to maintain the desired stochiometry when the fire retardant was added to produce a phosphorous level of 1.4 per cent by weight.

Samples of the three flexible foams prepared from the formulations described previously were burned in the XP-2 smoke chamber according to procedures outlined in ASTM D-2843T. A summary of the observations made during the burning tests is presented in Table XXXVIII.

TABLE XXXVIII

FLAMMABILITY AND SMOKE CHARACTERISTICS OF MODIFIED FLEXIBLE-URETHANE FOAMS

Sample Description		Density (p.c.f.)	Maximum % Light Obscuration	Time-Total Consumption	Remarks
Basic Formulation	(Foam 92)	1.6	33	20 seconds	Heavy drips
Barytes Extended Foam	(Foam 93)	2.1	15	55 seconds	No drips
Fire Retarded Foam	(Foam 94)	2.0	65	40 seconds	Moderate drips

The measured smoke obscuration rates obtained during the burning tests are summarized in Figure 45. The samples of foam prepared from the basic formulation burned readily and were consumed in 20 seconds. A small quantity of smoke was developed during the burning tests. Microscopic examination of collected particulate matter indicated that a rather uniform distribution of finely divided particles was deposited on sample plates suspended within the test chamber. Severe dripping occurred during combustion igniting cotton waste placed under the sample support.

Incorporation of an inert, non-reactive extender substantially reduced the burning rate, led to the reduction of smoke development during combustion, and minimized dripping.

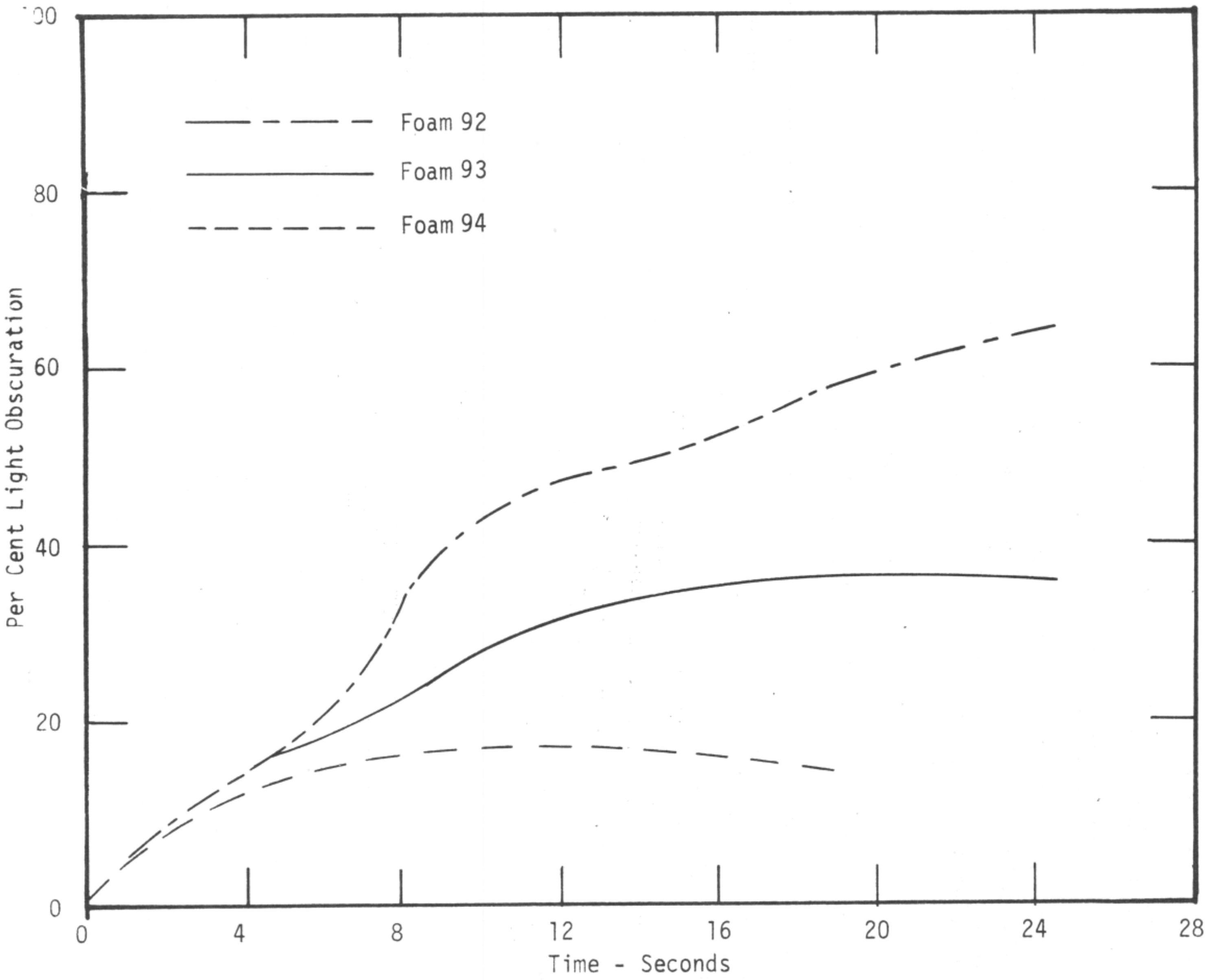


FIG. 45. SMOKE DEVELOPMENT IN FLEXIBLE-URETHANE FOAMS

The addition of phosphorous (1.4 per cent by weight) in the form of a reactive phosphonate fire retardant reduced the flame propagation rate as compared to the basic formulation. This addition of fire retardant led to an incomplete combustion process resulting in the doubling of the light obscuration rate.

Fire-Retarded Flexible Urethane Foams - Series 1

Sample Preparation

A series of fire-retarded flexible urethane foams were prepared in the laboratory using the three component Martin Sweets Company foam metering system. The first series of foams prepared utilized the general foam formulation listed in Table XXXIX.

TABLE XXXIX

FIRE-RETARDED FLEXIBLE URETHANE FOAMS (SERIES 1)

	Foam 95 (Control)	Foam 96	Foam 97	Foam 98
Ingredients	Parts By Weight			
Oxypropylated Glycerol (M.W. 3000)	100.00	100.00	100.00	100.00
Tris (2-chlorethyl) phosphate	0.00	5.00	10.00	15.00
Stannous Octoate	0.50	0.50	0.50	0.50
Triethylene Dianine	0.15	0.15	0.15	0.15
Water	3.50	3.50	3.50	3.50
Silicone-oxyalkylene copolymers	1.00	1.00	1.00	1.00
TDI (80/20 isomer mixture)	45.40	45.40	45.40	45.40

All foams were crushed immediately after preparation to ensure a high percentage of open cells and to prevent shrinkage. The samples were then postcured in an air convection oven for one hour at 200°F. Following the postcure the samples were held at 70°F, 50 per cent relative humidity prior to testing.

The flexible foams were subjected to flammability tests described previously. Table XXXX lists the results of these tests.

TABLE XXXX

FLAMMABILITY AND SMOKE CHARACTERISTICS OF FIRE-RETARDED FLEXIBLE URETHANE FOAMS

Flammability Test	Foam 95	Foam 96	Foam 97	Foam 98
Smoke Development (ASTM D-2843T)				
Time Seconds To: 10 LO	4.1	3.8	3.4	2.8
Time Seconds To: 20% LO	7.6	6.5	5.8	4.3
Time Seconds To: 30% LO	14.5	11.8	10.4	9.6
Time Seconds To: 40% LO	---	15.5	14.5	11.2
Time Seconds To: 50% LO	---	---	16.4	14.3
Time Seconds To: 60% LO	---	---	18.1	16.7
Time Seconds To: 70% LO	---	---	---	20.2
Ignition and Propagation (ASTM D-1692) 45°				
Self-Extinguishing	---	---	---	---
Burning Rate, inches/minute*	26.5	24.3	20.7	17.4
Flame Penetration Test (Modified Bureau of Mines Test)				
Burn-through Time, Seconds	5.0	6.1	7.2	8.6
Limiting Oxygen Index Test				
$\left[\dfrac{n_{O_2}}{n_{O_2} + n_{N_2}}\right]$	0.188	0.191	0.206	0.215

*All samples were completely consumed during testing.

Analysis of the information presented in Table XXXX clearly indicates that all of the formulations evaluated in this series of tests (both the control foam and the three fire-retarded foams), although slightly better than the non-fire-retarded foams summarized in Table XXXVI, must still be rated as highly combustible.

Fire-Retarded Flexible Urethane Foams - Series 2

A review of the studies by Pitts, et al.,[48] shows that the addition of antimony oxychloride, $S_bO\,Cl$, and antimony trioxide, Sb_2O_3, while retarding the burning rate of flexible urethane foams, as measured by the small-scale laboratory test, ASTM D-1692, did not substantially improve the overall flammability characteristics of these materials necessary to pass more stringent large-scale tests. The flexible foam system utilized by Pitts, et al., is presented in Table XXXXI.

TABLE XXXXI

BASIC FLEXIBLE FOAM SYSTEM USED IN STUDY OF ANTIMONY COMPOUNDS

Ingredients	Parts By Weight
Oxypropylated Glycerol (3000 M.W.)	100.0
TDI (80/20 Isomer Mixture)	50.0
Water (Distilled)	4.0
Silicone Surfactant - DC-190*	1.5
Amine Catalyst - 33LV**	0.3
Stannous Octoate	0.4

* Dow Corning Corporation
**Houdry Chemical Company

The concentrations of antimony trioxide and antimony oxychloride were varied from 0 to 60 and 0 to 40 parts by weight respectively. The results of this study are summarized in Table XXXXII.

TABLE XXXXII

ANTIMONY MODIFIED FLEXIBLE URETHANE FOAMS (ASTM D-1692-67T Flammability Tests)

Parts By Weight		Average Extent of Burn (Inches)	Average Rate of Burn (Inches/Minute)	Rating
SbO Cl	Sb_2O_3			
0	0	5.0*	7.0	Burning
10	0	5.0*	4.7	Burning
20	0	5.0*	3.4	Burning
30	0	3.7	2.2	Self-Extinguishing
40	0	2.8	2.1	Self-Extinguishing
0	10	5.0*	7.1	Burning
0	20	5.0*	7.1	Burning
0	40	5.0*	7.0	Burning
0	60	5.0*	5.7	Burning

*Sample consumed.

A final series of fire-retarded flexible urethane foams were prepared using Sb_2O_3 and tris (2,3 dibromopropyl) phosphate or tris (2,3 dichloropropyl) phosphate. Table XXXXIII presents the formulations used for this series of foams.

Foams 94 through 104 were subjected to analysis of their flammability characteristics by test procedures described earlier in the report. A summary of their flammability characteristics is presented in Table XXXXIV.

Analysis of the data presented in Table XXXXIV indicates that it is not possible to develop satisfactory flammability characteristics in flexible-urethane foams by the methods undertaken in this study. Considerable further research and development is required to raise the level of resistance during fire exposure to permit safe utilization of flexible-urethane foam products in commercial applications.

TABLE XXXXIII

FIRE-RETARDED FLEXIBLE-URETHANE FOAMS (CO-SYNERGISTIC RETARDANTS)

Ingredients	Foam 95 (Control)	Foam 99	Foam 100	Foam 101	Foam 102	Foam 103	Foam 104
				Parts By Weight			
Oxypropylated Glycerol (M.W. 3000)	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Stannous Octoate	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Triethylene Diamine	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Water	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Siloxane - oxyalkylene copolymer	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TDI (80/20 isomer mixture)	45.40	45.40	45.40	45.40	45.40	45.40	45.40
Tris (2,3 dibromopropyl) phosphate	----	8	16	20	----	----	----
Tris (2,3 dichloropropyl) phosphate	----	----	----	----	8	16	20
Sb_2O_3	----	10	10	10	10	10	10

TABLE XXXXIV

FLAMMABILITY AND SMOKE CHARACTERISTICS OF FIRE-RETARDED FLEXIBLE FOAMS (SYNERGISTIC RETARDANTS)

Flammability Test	Foam 95 (Control)	Foam 99	Foam 100	Foam 101	Foam 102	Foam 103	Foam 104
Smoke Development (ASTM D-2843T)							
Time Seconds To: 10% LO	4.1	3.8	2.5	2.1	3.9	3.0	2.7
Time Seconds To: 20% LO	7.6	5.4	4.8	4.1	6.3	5.8	5.4
Time Seconds To: 30% LO	14.5	9.2	8.7	7.2	11.4	10.8	10.2
Time Seconds To: 40% LO	---	12.7	12.1	11.4	14.6	13.8	13.2
Time Seconds To: 50% LO	---	17.0	16.2	15.9	20.2	19.8	18.6
Time Seconds To: 60% LO	---	27.0	24.2	23.8	31.1	28.9	27.8
Time Seconds To: 70% LO	---	34.0	32.1	31.7	42.0	41.4	40.4
Time Seconds To: 80% LO	---	44.6	40.8	34.7	48.2	47.1	46.2
Ignition and Propagation (ASTM D-1692) 45°							
Self-Extinguishing	---	---	---	---	---	---	---
Burning Rate, inches/minute	26.5*	18.4*	17.1*	14.2*	24.0*	21.2*	20.3*
Flame Penetration Test (Modified Bureau of Mines Test)							
Burn-Through Time, seconds	5.0	6.4	7.2	8.4	6.1	6.4	6.8
Limiting Oxygen Index Test							
$n_{O_2} / (n_{O_2} + n_{N_2})$	0.188	0.205	0.212	0.224	0.194	0.201	0.207

*Samples completely consumed during testing.

SUMMARY

An extensive survey of worldwide and United States markets and applications for rigid- and flexible-cellular plastics was carried out. Special emphasis was directed toward the development and utilization of urethane foam systems.

A review of the development and utilization of flame retardants for plastics is presented as background information.

The chemical literature pertaining to smoke development in polymeric materials was reviewed and served as a basis for experimental design utilized within the scope of this study.

A series of model urethane polymers, representative of systems used in commercial applications, were prepared under controlled conditions in the laboratory. The chemical and physical properties of these model systems were determined and their flammability characteristics evaluated. Parameters pertaining to the nature of the chemical reactants, the effects of cross-link density, and the functionality of the isocyanate and polyol moieties were related to temperature and the mode of thermal decomposition as well as the major flammability characteristics of ignition, flame propagation, fuel contribution and fire endurance.

A detailed study of factors contributing to smoke development was undertaken. Attempts were made to prepare cellular plastics possessing optimum flammability characteristics and minimize smoke development tendency. Three typical classes of fire retardants were incorporated into the rigid foam formulations, in a wide variety of concentrations, to determine their effect on flammability characteristics and smoke development during fire exposure.

It may be generally concluded that major improvements in the desirable flammability characteristics of rigid foams may be accomplished by modification of chemical structure and formulation. However, as the general flammability characteristics improve, the degree of smoke produced also increases.

The flexible foam systems evaluated within the scope of this study, did not possess the necessary chemical prerequisites (degree of cross-linking, aromaticity, etc.) to permit the formulation of truely flame-resistant systems. Numerous flexible-urethane foam systems have been evaluated by personnel of the Flammability Research Center after the completion of the research phase of this program. Many of these commercial systems possess improved flammability characteristics as measured by small-scale laboratory test procedures. It is the opinion of this investigator that these improved foam systems, although possessing improved properties, do not have sufficient resistance to flame in a severe fire exposure.

CONCLUSIONS

Based on an analysis of the results contained herein, it was determined that:

1. Flexible, semi-rigid, and rigid urethane cellular plastics ignite, support flame propagation, and have a strong tendency to produce smoke during the combustion process.

2. Chemical additives (halogen- and phosphorus-containing compounds) effective in reducing the flammability characteristics of flexible, semi-rigid, and rigid foams increase smoke emission during fire exposure.

3. Present test procedures used to evaluate the smoking tendency of cellular plastics provide a measure of the light-obscuring characteristics but are not capable of evaluating the physiological or toxicological aspects of combustion.

4. The development of a reliable hazard index pertaining to smoke produced during fires must incorporate a continuous weight-monitoring device, necessary to determine the amount of material required to reach a given smoke level.

5. Consideration must be given to the effect of lachrymatory agents on vision during the thermal degradation or combustion of materials.

6. Increased aromaticity of the isocyanates used in the formulation of rigid-urethane foams coupled with a cross-link density ($\overline{Mc}$) less than 350 results in a major decrease in ignition, flame propagation, and fire endurance.

7. The most effective fire retardants in reducing the flammability of optimized foam systems were compounds containing both phosphorus and bromine.

8. The optimum concentration of phosphorus in urethane foams is approximately 1.5 percent by weight.

9. Bromine-containing fire retardants are more effective than their chlorine-containing homologues in reducing the flammability of urethane foams.

10. Increasing the percent concentration of fire retardants above the optimum determined for a given foam system actually decreases resistance to flames.

11. The structure present in flexible urethane foams, necessary to obtain the required resiliency, does not enhance fire retardation.

12. Significant reduction of smoke in cellular plastics requires new types of polymers similar in flammability characteristics to polyimide foams.

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APPENDIX A

CELLULAR PLASTICS TECHNOLOGY

General Background

Commercially, cellular plastics can be produced in the form of slabs, blocks, boards, sheets, molded shapes, extruded insulation, and sprayed coatings. In addition, several types of expanded plastics can be "foamed-in-place" or "packed-in-place" in an existing cavity for potting of electrical components within a housing or for providing thermal insulation or structure strength.

A cellular plastic can be developed by several methods (not all of them applicable to all of the materials which will be considered within this survey):

1. Air or gas is whipped into a suspension or solution of the plastic, which is then hardened by heat or catalytic action or both.
2. A gas is dissolved in a resin and expands when pressure is reduced.
3. A liquid component of the mix is volatilized by heat.
4. Water produced in an exothermic chemical reaction is volatilized within the mass by the heat of reaction.
5. Carbon dioxide gas is produced within the mass by chemical reaction.
6. A gas, such as nitrogen, is liberated within the mass by thermal decomposition of a chemical blowing agent.
7. Tiny beads of thermoset resins, hollow or expandable by heat, are incorporated in a plastic mix.

Nine chemical types of cellular plastics are of commercial importance according to chemical composition as follows: cellulose acetate, epoxide, phenol-formaldehyde, polyethylene, polystyrene, silicone, urea-formaldehyde, urethane, and vinyl. Within the scope of this study emphasis was placed on urethane polymers.

History of Urethane Cellular Plastics

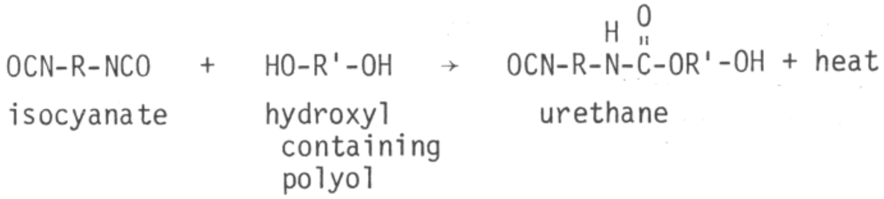
Introduction

Urethane technology was well developed in Germany by the mid 1930's. Bayer and co-workers produced urethane foams by reacting polyisocyanates with difunctional or higher hydroxyl-containing compounds in the presence of water. American survey teams sent to Germany shortly after the war reviewed the progress made by the Germans; this led to the licensing of German-owned patents to the American aircraft industry. Stimulated research resulted in the development of practicable production techniques, improvements in equipment design and reliability, and formulations based on materials other than alkyd-type polyester resins. A review of the American patent literature revealed that duPont, in a series of patents applied for in 1939 and 1940, and granted in the early 1940's, had done much work along these lines. Their patents covered the reaction products of polyisocyanates with the various glycols, alkyd resins, polyamides, polyesters, diamines, polyester amides, etc.

Chemistry

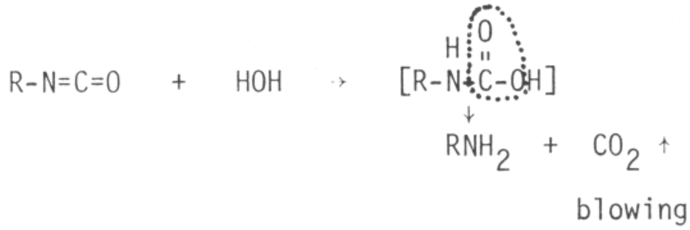
The reactive ingredients of a urethane foam system usually include an isocyanate and a hydroxyl-terminated resin. Blowing agents, either flurocarbons or materials which decompose to yield CO_2 or N_2, are necessary to induce the foaming process. Surfactants, usually silicones or stearates, are used to control surface tension of the evolving gas bubbles thus controlling cell size and porosity. Catalysts, usually amines, are employed to control the different phases of polymerization. Additives, such as fire retardants, colorants, light-stabilizers, and anti-oxidants, may be employed to vary specific foam characteristics or properties.

Several reactions found in foam production are summarized below:



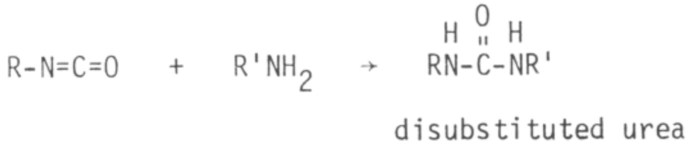
$$\underset{\text{isocyanate}}{OCN\text{-}R\text{-}NCO} \quad + \quad \underset{\substack{\text{hydroxyl}\\ \text{containing}\\ \text{polyol}}}{HO\text{-}R'\text{-}OH} \quad \rightarrow \quad \underset{\text{urethane}}{OCN\text{-}R\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}OR'\text{-}OH} + \text{heat} \qquad (1)$$

Water may be used to react with the isocyanate to produce an unstable carbamic acid which will subsequently break down to produce CO_2 gas (blowing agent) and an amide.



$$R\text{-}N{=}C{=}O \quad + \quad HOH \quad \rightarrow \quad \begin{array}{c} [R\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}OH] \\ \downarrow \\ RNH_2 \quad + \quad \underset{\text{blowing agent}}{CO_2 \uparrow} \end{array} \qquad (2)$$

The residual amine will react quickly to produce a disubstituted urea.



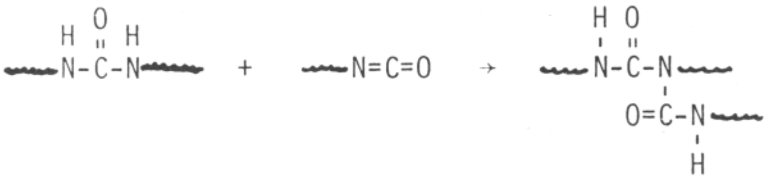
$$R\text{-}N{=}C{=}O \quad + \quad R'NH_2 \quad \rightarrow \quad \underset{\text{disubstituted urea}}{R\overset{H}{N}\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}\overset{H}{N}R'} \qquad (3)$$

Thus, the amount of water added to a urethane polymer controls the density by regulating the amount of CO_2 evolved and further varies the chemical structure of the resulting polymer by increasing the concentration of disubstituted urea groups.

The isocyanate may also react with the urea and with the urethane groups to yield undesirable relatively unstable biuret and allophonate structures.

Biuret formation takes place when the hydrogen or the nitrogen atoms in the urea structure (Equation 4) react with isocyanate groups to cause cross-linking.

The reaction proceeds as follows:

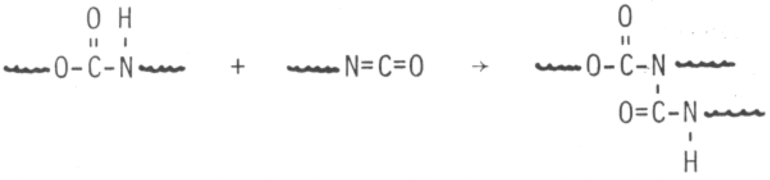


(4)

biuret

Allophanate linkages are formed when the biuret hydrogen or the nitrogen atom in the urethane group reacts with an isocyanate group.

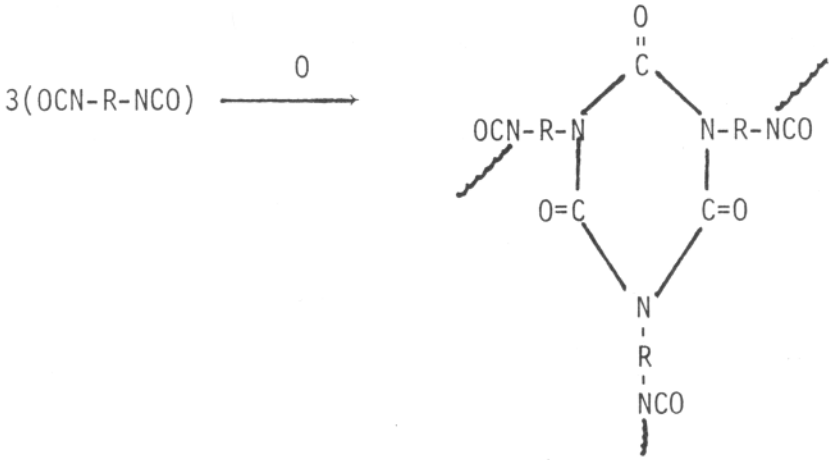
This reaction proceeds as follows:



(5)

allophanate

Another cross-linking reaction involves the formation of trimers, which may be considered trisubstituted isocyanurates. This reaction usually occurs at temperatures in excess of 100°C and may be preferentially increased by the use of various catalysts.



(6)

isocyanurate

The isocyanurate trimers are very resistant to both heat and hydrolysis. Another reaction of isocyanates, which occurs at high temperatures, is the formation of heat-resistant carbodiimides.

$$2(\mathrm{OCN\text{-}R\text{-}NCO}) \xrightarrow{\Delta} \underbrace{\mathrm{OCN\text{-}R\text{-}N{=}C{=}N\text{-}R\text{-}NCO}}_{\text{carbodiimide}} + \mathrm{CO_2}\uparrow \qquad (7)$$

Carbodiimides have been isolated from the thermal degradation of urethanes. Catalysts used to induce carbodiimide formation include phospholines and tributyl- and triphenyl-phosphine oxides. These compounds improve thermal stability and flammability characteristics of urethane polymers.

Processing of Foams

Urethane foams may be prepared via three processes:

Prepolymer process,
"One-Shot" process,
Quasi-Prepolymer process.

Prepolymer Process. In this process, used mostly for flexible or semi-rigid foams, the hydroxyl-containing polyol is reacted with an excess of isocyanate (NCO/OH ratio of approximately 2:1) to form an isocyanate-terminated prepolymer. When CO_2 is used as the blowing agent, the prepolymer is further reacted with water to yield the foamed polymer which contains substituted urea groups in addition to urethane groups. The formation of a urethane-foamed polymer is shown schematically in Figure 1 for the case of a trifunctional resin.

The concentration of water used to cross-link prepolymer systems is very critical because of the preferential reactivity of water with isocyanate groups. When water is added to a urethane prepolymer in the presence of an amine catalyst, it reacts with prepolymer terminal isocyanate groups, resulting in polymer growth and cross-linking and with free isocyanate monomers to liberate the CO_2 blowing agent.

The prepolymer process offers the possibility of a more controlled chemical reaction favoring higher foaming due to reduced exotherm. Since the polymerization reaction is partially completed with the use of a prepolymer, less heat is generated during foam formation than in the quasi-prepolymer or "one-shot" process. This is important in the preparation of high-density foams.

"One-Shot" Foaming Process. In the "one-shot" method, all of the reactants (polyol, isocyanate, surfactant, catalyst, blowing agents, and other additives), are combined at one time to form a foam, thus the reaction is completed in "one-shot." A highly exothermic reaction is encountered during the foam process utilizing the "one-shot" technique. This high exotherm reduces the possibility of good process control because of possible scorching. The greater heat buildup increases the rate of foam production and this increases the hazards due to volatilization of the relatively toxic isocyanates and amine catalysts.

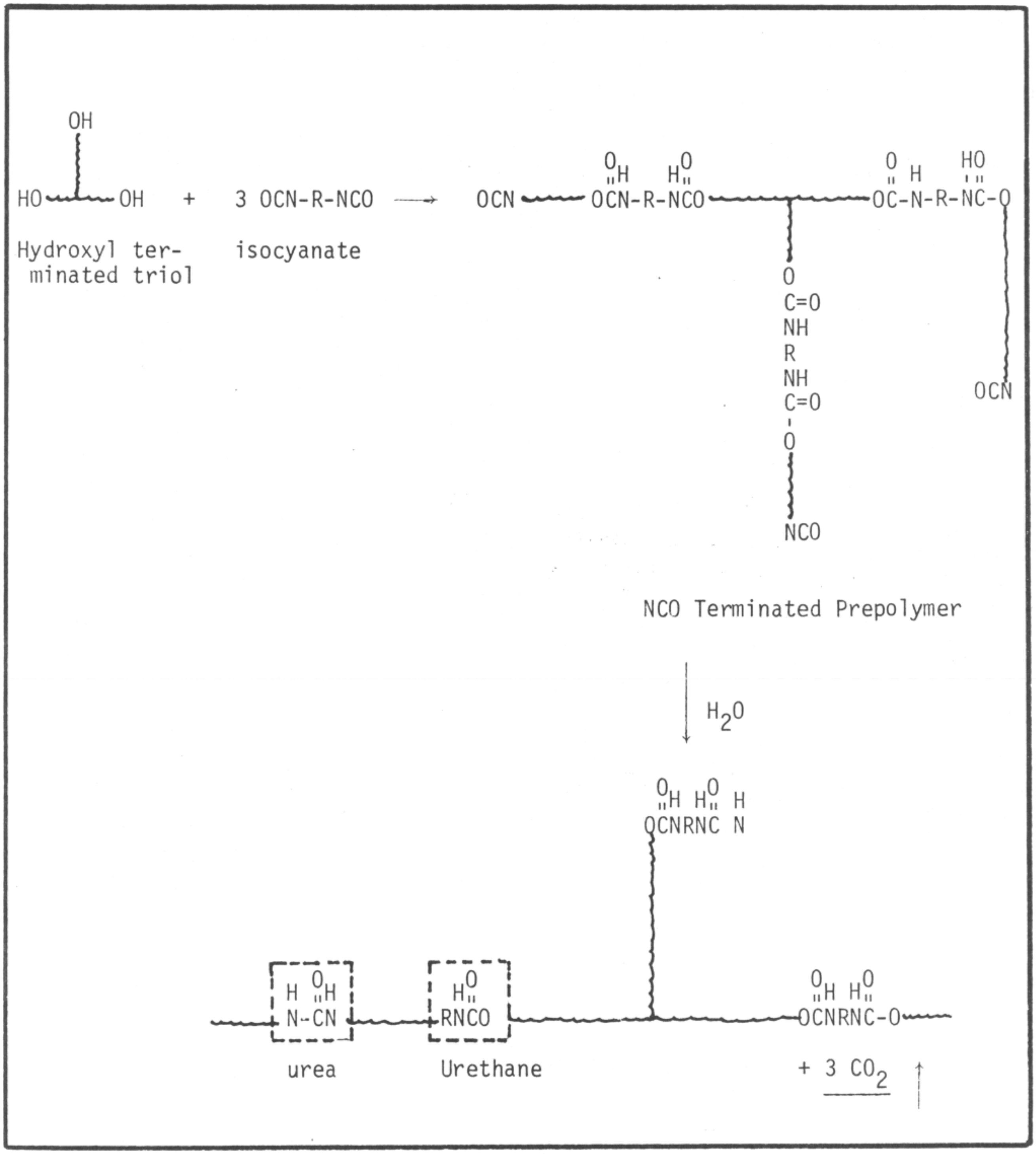


FIG. A-1. SCHEMATIC REPRESENTATION OF URETHANE FORMATION VIA PREPOLYMER PROCESS

The "one-shot" process has been widely used in the production of flexible foam buns and within the past few years has been adapted for the production of rigid-foam slabstock.

Quasi-Prepolymer Process. The quasi-prepolymer, or semi-prepolymer, process is a combination of the prepolymer and "one-shot" techniques. The polyol moiety is pre-reacted with the isocyanate to form one component. Water, catalyst, and other additives are mixed with additional polyol to form the second component. The two components are mixed in nearly equal quantities at the time of foaming. This method is widely used in the manufacture of rigid and semi-rigid foams.

In this process only part of the polyol is reacted with all of the isocyanate (usually in an NCO/OH ratio of about 4:1) to yield a low-viscosity prepolymer dissolved in excess isocyanate. In the foaming step the quasi-prepolymer is then reacted with the remainder of the polyol to which catalysts, surfactant, and blowing agent has been added.

If a flurocarbon blowing agent is used in the absence of water, the resulting foamed polymer should be substantially free of linkages other than urethane. This is advantageous since biuret or allophanate linkages are susceptible to temperature and result in polymers with poor flammability characteristics.

Colloid Chemistry of Urethane-Foam Formation

The colloidal aspects of foam formation are of importance in understanding the basic phenomena occurring during the different stages of the foaming process. As the blowing agent is released, gas bubbles are formed in the polymerizing liquid system. The liquid phase undergoes rapid polymerization, increasing in viscosity to a gel phase which cures to a hard solid phase. The colloidal nature of the gas-liquid phase exists at least in the initial fluid stages of foam formation, which may persist for only a matter of seconds after the mixing of the foam components.

There are several distinct stages which occur during foam formation. In the first stage, the blowing agent dissolves in the liquid phase until saturation is reached. The liquid phase then becomes unsaturated. The gas then begins to migrate out of solution and forms bubbles by means of a nucleation process. The nucleation process may be aided by the incorporation of finely divided solids or air bubbles. A surfactant may be added to modify surface tension and drawings during the foaming process. An increase in surfactant concentration results in faster nucleation and produces a finer-celled foam.

Another important stage of urethane foam formation is the stabilization of bubbles to avoid foam collapse. Factors affecting bubble stability in soap-water systems are similar to those used in a urethane foam system. For the dispersion of a given volume of gas in a unit volume of liquid, the free energy of the system, ΔF, must increase as follows:

$$\Delta F = \gamma A \qquad (8)$$

where: γ is the surface tension
A is the total interfacial area.

Hence, a greater increase in free energy is required to produce finer cells than is necessary for the production of larger cells. In a liquid foam system there is always a tendency to reduce the interfacial area, thereby favoring coalescence of cells and foam collapse, from an energy point of view. Thus, rapid polymerization and high cross-link density will aid the formation of a stable polymer of high molecular weight and minimize cell collapse. The addition of a surfactant will reduce the free energy increase associated with the dispersion of the gas in the liquid because of reduced surface tension. The surfactant will also cause the production of smaller cells corresponding to a large value of A. Care must be exercised since too fine cells may lead to foam collapse.

Another major factor affecting bubble stability is the drainage of liquid in the bubble wall due to capillary action and gravity. An increase in the viscosity of the liquid due to the growing molecular weight of the polymer will reduce drainage and thus retard thinning of the cell membrane.

In flexible foams, cell rupture occurs to a large extent when the foam reaches the point of maximum expansion. At this point the cell membranes exhibit high viscosity but insufficient elasticity to expand and relieve the internal gas pressure. Thus, membrane rupture occurs.

In rigid-foam systems a balance is maintained so that cell membranes do not rupture at the point of maximum gas evolution. The cell membranes are of sufficiently high elasticity to permit stretching without rupture. The highly cross-linked structure permits the rigid foam to maintain cell geometry during cooling, thus minimizing shrinkage and collapse.

APPENDIX B

SOLUTION POLYMERIZATION AND SAMPLE PREPARATION

A method was developed which permitted the preparation of solid polymers using a polymerization technique that eliminated formation of undesirable biuret or allophonate groups and minimized the reaction between the isocyanates and water, thus controlling formation of disubstituted ureas.

The polymerization of model urethane polymers was carried out in a baffled four-neck reaction flask under a nitrogen atmosphere. A one-to-one mixture of dimethylsulfoxide (DMS) and methylisobutyl ketone (MIBK) was prepared from a freshly-distilled solvent supply. The degassed polyol was added to the reaction flask. The isocyanates were added slowly with external cooling, without catalyst, until an NCO/OH ratio of 1.05/1.0 was reached. External heat was then applied and the temperature of the reactants raised to 90°C. Aliquot samples were withdrawn every 15 minutes and the percent free - NCO determined by a dibutylamine-hydrochloric acid titration. The progress of the reaction was followed in this manner until the analysis procedure indicated the completion of the polymerization. The heating was then continued for an additional 30 minutes after which the polymers were rapidly cooled and stored under dry nitrogen. Infrared analysis was carried out using a Perkin-Elmer Model 237 Infrared Spectrophotometer to assure the disappearance of the strong - NCO group at 4.4mμ.

Polymers prepared from the reaction mixture solidified during the final phase of polymerization. The model polymers were ground in a blender, washed and filtered twice with acetone. The filtered polymers were then dried in a vacuum desiccator at 50°C. and 25 mm Hg until a constant weight was obtained. The temperature of the desiccator was then raised to 80°C. and the polymers then heated for an additional four hours to remove any remaining traces of solvent.

The polymers were then dissolved in dimethylformamide (20% solution), cast on polished glass plates using a calibrated doctor blade, and placed in the clean box. After the major portion of solvent evaporated, permitting the polymer to coalesce, the films were stripped and dried to constant weight in the vacuum desiccator. Figures B-1, B-2, B-3, and B-4 present the idealized structures for the urethane polymers prepared by the reaction of hexamethylene diisocyanate, tolylene diisocyanate, 4,4' diphenylmethane diisocyanate, and polymethylene polyphenyl isocyanate, and the propoxylated adduct of trimethylolpropane.

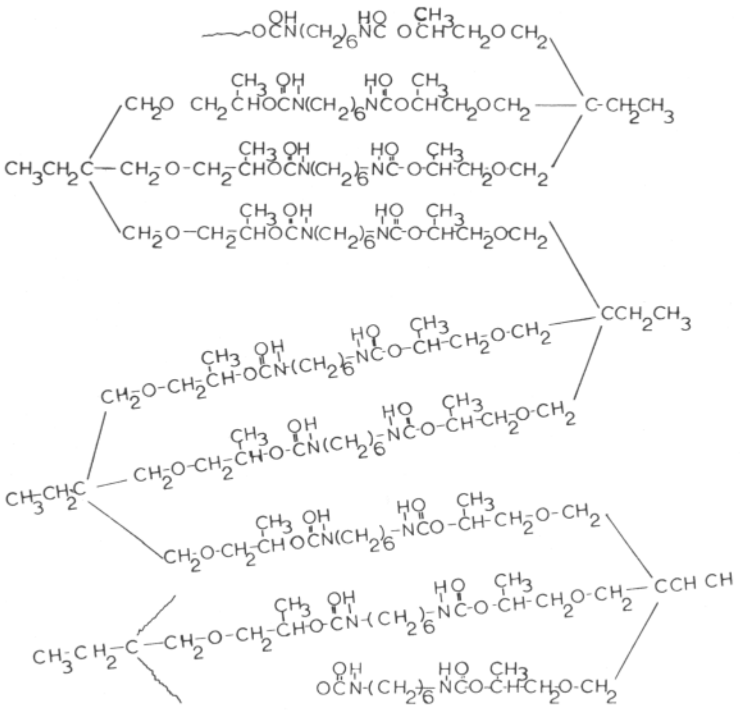


FIG. B-1. IDEALIZED STRUCTURE OF URETHANE POLYMER FORMED BY REACTION OF HDI AND PROPOXYLATED TRIOL

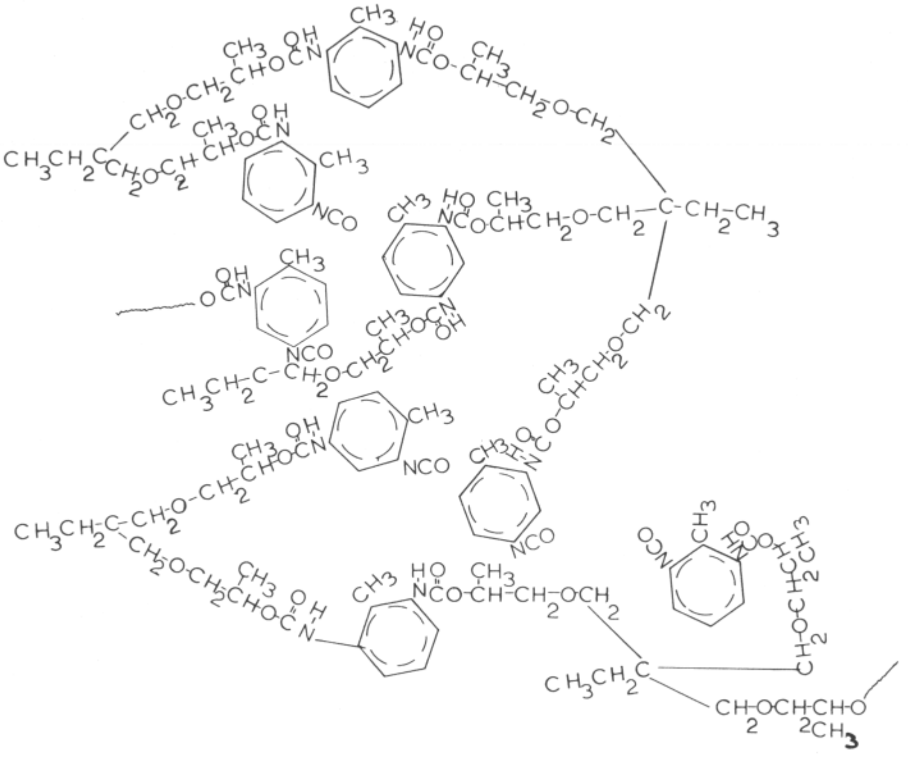


FIG. B-2. IDEALIZED STRUCTURE OF URETHANE POLYMER FORMED BY REACTION OF TDI AND PROPOXYLATED TRIOL

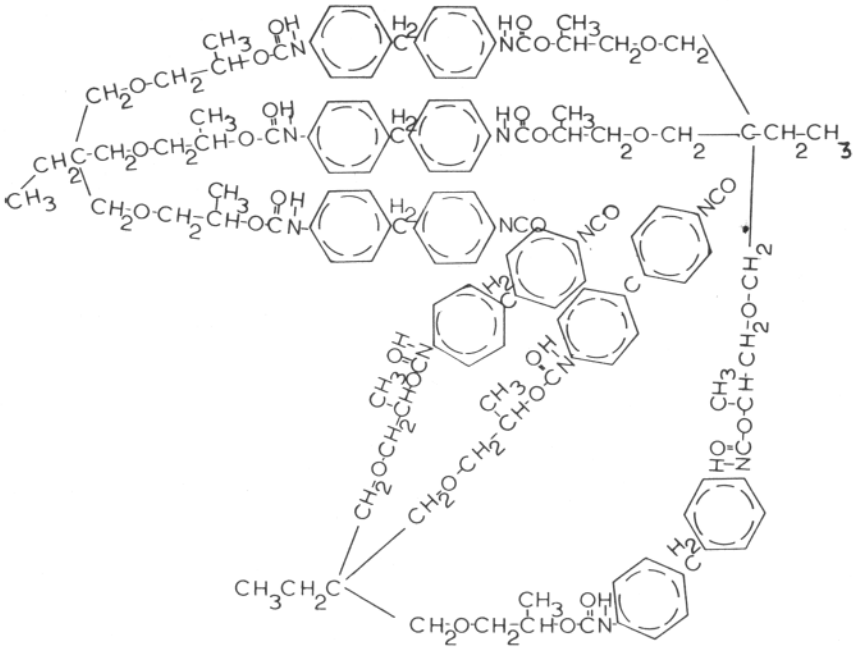


FIG. B-3. IDEALIZED STRUCTURE OF URETHANE POLYMER FORMED BY REACTION OF MDI AND PROPOXYLATED TRIOL

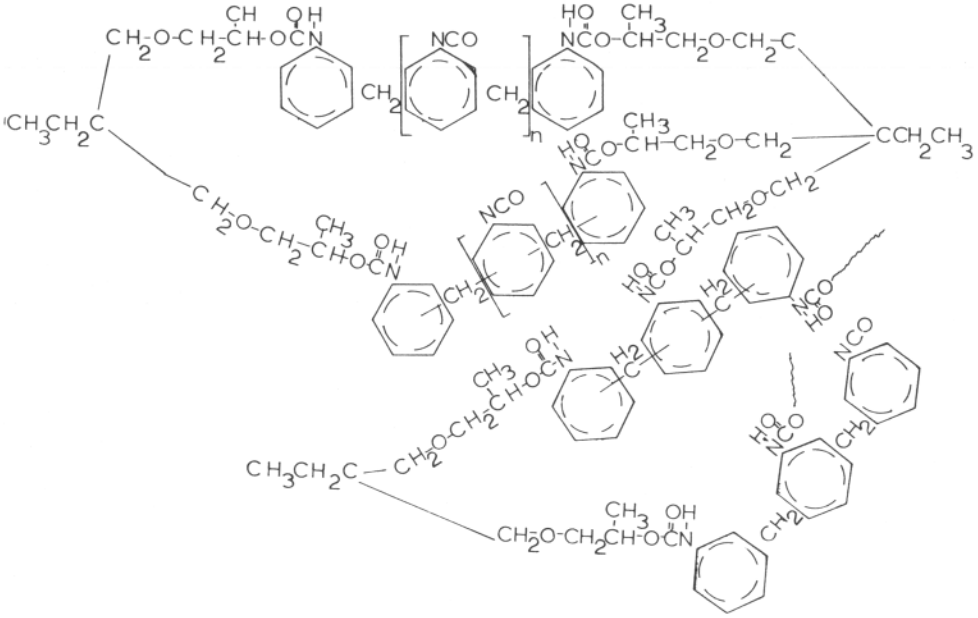


FIG. B-4. IDEALIZED STRUCTURE OF URETHANE POLYMER FORMED BY REACTION OF PAPI AND PROPOXYLATED TRIOL

APPENDIX C

TABLE C-I

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-312/PAPI SYSTEM) - NON-REACTIVE CHLORINATED FIRE RETARDANT

Raw Materials	Foam 13 (pbw)	Foam 14 (pbw)	Foam 15 (pbw)	Foam 16 (pbw)	Foam 17 (pbw)	Foam 18 (pbw)
Polymethylene polyphenyl isocyanate	134.7	134.7	134.7	134.7	134.7	134.7
Propoxylated adduct-trimethylol propane (mw 312)	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	3.53	3.53	3.53	3.53	3.53	3.53
Tris 2,3 dichloropropylphosphate	--	11.21	23.4	36.7	51.3	67.2
weight % fire retardant	--	4.0	8.0	12.0	16.0	20.0
% chlorine	0	1.98	3.96	5.94	7.92	9.90
% phosphorous	0	0.286	0.572	0.868	1.154	1.440

TABLE C-II

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-312/PAPI SYSTEM) - NON-REACTIVE BROMINATED FIRE RETARDANT

Raw Materials	Foam 19 (pbw)	Foam 20 (pbw)	Foam 21 (pbw)	Foam 22 (pbw)	Foam 23 (pbw)	Foam 24 (pbw)
Polymethylene polyphenyl isocyanate	134.7	134.7	134.7	134.7	134.7	134.7
Propoxylated adduct - trimethylolpropane (mw 312)	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	3.53	3.53	3.53	3.53	3.53	3.53
Tris 2,3 dibromopropylphosphate	11.21	23.4	36.7	51.3	59.0	67.2
% bromine	2.75	5.50	8.25	11.00	12.50	13.75
% phosphorous	0.178	0.356	0.534	0.712	0.803	0.890

TABLE C-III

FIRE-RETARDED RIGID-URETHANE FOAM FROMULATIONS

(TMP-312/PAPI SYSTEM)- REACTIVE NON-HALOGENATED FIRE RETARDANT

Raw Materials	Foam 25 (pbw)	Foam 26 (pbw)	Foam 27 (pbw)
Polymethylene polyphenyl isocyanate	134.7	134.7	134.7
Propoxylated adduct-trimethylolpropane (mw 312)	91.5	82.7	73.5
Silicone surfactant	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0
Triethylene diamine	3.53	3.53	3.53
0,0 -diethyl-N,N' -bis (2 hydroxyethyl) amino phosphonate	10.9	21.9	33.2
weight % fire retardant	4.0	8.0	12.0
% phosphorous	0.48	0.96	1.44

TABLE C-IV

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-312/MDI SYSTEM) - NON-REACTIVE HALOGENATED FIRE RETARDANTS

Raw Materials	Foam 28 (pbw)	Foam 29 (pbw)	Foam 30 (pbw)	Foam 31 (pbw)	Foam 32 (pbw)
4, 4' diphenylmethane diisocyanate	135.9	135.9	135.9	135.9	135.9
Propoxylated adduct trimethylolpropane (mw 312)	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	2.36	2.36	2.36	2.36	2.36
Tris 2-3 dichloropropylphosphate	--	23.5	51.4	--	--
Tris 2-3 dibromopropylphosphate	--	--	--	23.5	51.4
Weight % fire retardant	0	8.0	16.0	8.0	16.0
% chlorine	0	3.96	7.92	--	--
% bromine	0	--	--	5.50	11.0
% phosphorous	0	0.572	1.154	0.356	0.712

TABLE C-V

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-312/TDI/2,4 ISOMER) - NON-REACTIVE CHLORINATED FIRE RETARDANT

Raw Materials	Foam 33 (pbw)	Foam 34 (pbw)	Foam 35 (pbw)	Foam 36 (pbw)	Foam 37 (pbw)	Foam 38 (pbw)	Foam 39 (pbw)
Tolylene diisocyanate (2,4 isomer)	94.5	94.5	94.5	94.5	94.5	94.5	94.5
Propoxylated adduct - trimethylolpropane (mw 312)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	2.92	2.92	2.92	2.92	2.92	2.92	2.92
Tris 2,3 dichloropropylphosphate	--	9.5	19.8	31.1	43.5	57.2	72.0
weight % fire retardant	0	4.0	8.0	12.0	16.0	20.0	24.0
% chlorine	0	1.98	3.96	5.94	7.92	9.90	11.88
% phosphorous	0	0.286	0.572	0.868	1.154	1.440	1.726

TABLE C-VI

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-312/TDI 65:35 - 2,4:2,6 ISOMER MIXTURE) - NON-REACTIVE HALOGENATED FIRE RETARDANTS

Raw Materials	Foam 40 (pbw)	Foam 41 (pbw)	Foam 42 (pbw)	Foam 43 (pbw)	Foam 44 (pbw)	Foam 45 (pbw)	Foam 46 (pbw)	Foam 47 (pbw)	Foam 48 (pbw)	Foam 49 (pbw)
Tolylene diisocyanate (65:35 -2,4:2,6 isomer mixture)	94.5	94.5	94.5	94.5	94.5	94.5	94.5	94.5	94.5	94.5
Propoxylated adduct - trimethylolpropane (mw 312)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	2.92	2.92	2.92	2.92	2.92	2.92	2.92	2.92	2.92	2.92
Tris 2,3 dichloropropylphosphate	--	9.5	19.8	31.1	43.5	57.2	72.0	89.0	--	--
Tris 2,3 dibromopropylphosphate	--	--	--	--	--	--	--	--	19.8	31.1
weight % fire retardant	0	4.0	8.0	12.0	16.0	20.0	24.0	28.0	8.0	12.0
% chlorine	0	1.98	3.96	5.94	7.92	9.90	11.88	13.86	--	--
% bromine	0	--	--	--	--	--	--	--	5.50	8.25
% phosphorous	0	0.26	0.572	0.868	1.154	1.440	1.726	2.012	0.356	0.534

TABLE C-VII

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-425/PAPI SYSTEM) - REACTIVE AND NON-REACTIVE FIRE RETARDANTS

Raw Materials	Foam 50 (pbw)	Foam 51 (pbw)	Foam 52 (pbw)	Foam 53 (pbw)	Foam 54 (pbw)	Foam 55 (pbw)	Foam 56 (pbw)	Foam 57 (pbw)	Foam 58 (pbw)	Foam 59 (pbw)	Foam 60 (pbw)	Foam 61 (pbw)	Foam 62 (pbw)
Polymethylene polyphenyl isocyanate	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Propoxylated adduct - trimethylolpropane (mw 425)	100.0	89.8	79.6	70.6	57.3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
0,0 - diethyl -N,N' -bis (2 hydroxyethyl) amino phosponate	--	9.3	18.6	26.8	38.0	--	--	--	--	--	--	--	--
Tris 2,3 dichloropropyephosphate	--	--	--	--	--	9.8	20.4	30.9	44.5	--	--	--	--
Tris 2,3 dibromopropylphosphate	--	--	--	--	--	--	--	--	--	9.8	20.4	30.9	44.5
weight % fire retardant	0	4.0	8.0	12.0	16.0	4.0	8.0	12.0	16.0	4.0	8.0	12.0	16.0
% chlorine	0	0	0	0	0	1.98	3.96	5.94	7.92	0	0	0	0
% bromine	0	0	0	0	0	0	0	0	0	2.75	5.50	8.25	11.00
% phosphorous	0	0.48	0.96	1.44	1.92	0.286	0.572	0.868	1.154	0.178	0.356	0.534	0.712

TABLE C-VIII

FIRE-RETARDED RIGID-URETHANE FOAM FORMULATIONS

(TMP-425/TDI 65:35 ISOMER MIXTURE 2:4, 2:6 TDI) - HALOGENATED NON-REACTIVE FIRE RETARDANTS

Raw Materials	Foam 63 (pbw)	Foam 64 (pbw)	Foam 65 (pbw)	Foam 66 (pbw)	Foam 67 (pbw)	Foam 68 (pbw)	Foam 69 (pbw)
Tolylene diisocyanate (65:35 isomer mixture 2,4:2,6 isomers)	65.35	65.35	65.35	65.35	65.35	65.35	65.35
Propoxylated adduct - trimethylolpropane (mw 425)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Silicone surfactant	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Trichlorofluoromethane	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Triethylene diamine	2.48	2.48	2.48	2.48	2.48	2.48	2.48
Tris 2,3 dichloropropylphosphate	--	8,38	17.3	27.2	--	--	--
Tris 2,3 dibromopropylphosphate	--	--	--	--	8.38	17.3	27.2
weight % fire retardant	--	4.0	8.0	12.0	4.0	8.0	12.0
% chlorine	--	1.98	3.96	5.94	0	0	0
% bromine	--	0	0	0	2.75	5.50	8.25
% phosphorous	--	0.286	0.572	0.868	0.178	0.356	0.534

APPENDIX D

TABLE D-I

FIRE-RETARDED OPTIMIZED RIGID-URETHANE FOAM FORMULATIONS
MANNICH ADDITION ADDUCT (M.W. 741) AND AROMATIC POLYISOCYANATES

Raw Materials	Foam 70 (pbw)	Foam 71 (pbw)	Foam 72 (pbw)	Foam 73 (pbw)	Foam 74 (pbw)	Foam 75 (pbw)	Foam 76 (pbw)	Foam 77 (pbw)	Foam 78 (pbw)	Foam 79 (pbw)	Foam 80 (pbw)	Foam 81 (pbw)
Polymethylene polyphenyl isocyanate	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	--	--
4, 4' diphenylmethane diisocyanate	--	--	--	--	--	--	--	--	--	--	100.0	100.0
Mannich addition adduct propoxylated (mw 741)	73.5	69.5	65.5	55.0	44.5	34.0	55.0	55.0	55.0	55.0	78.0	73.6
Silicone surfactant	1.5	1.5	1.5	1.5	1.5	1.5	1.6	1.5	1.5	1.5	1.6	1.6
Trichlorofluoromethane	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	22.2	22.2
0,0 - diethyl - N, N' - bis (2 hydroxyethyl) aminophosphonate	--	5.0	10.0	20.0	30.0	40.0	20.0	20.0	20.0	20.0	--	5.3
Tris 2,3 dichloropropyl phosphate	--	--	--	--	--	--	--	--	10.0	10.0	--	--
Potassium fluoroborate	--	--	--	--	--	--	10.0	20.0	20.0	20.0	--	--
Vinyl chloride - vinyl acetate copolymer	--	--	--	--	--	--	10.0	--	--	--	--	--
Antimony oxide	--	--	--	--	--	--	--	--	12.0	24.0	--	--
weight % reactive fire retardant	0.0	2.5	5.0	10.0	15.2	20.3	9.2	8.8	8.0	7.7	0	2.6
weight % KBF_4	--	--	--	--	--	--	4.6	8.8	8.0	7.7	--	--
weight % Sb_2O_3	--	--	--	--	--	--	--	--	4.82	9.2	--	--

TABLE D-II

FIRE-RETARDED OPTIMIZED RIGID-URETHANE FOAM FORMULATIONS

SORBITOL ADDUCT (M.W. 686) AND AROMATIC ISOCYANATES

Raw Materials	Foam 82 (pbw)	Foam 83 (pbw)	Foam 84 (pbw)	Foam 85 (pbw)	Foam 86 (pbw)	Foam 87 (pbw)	Foam 88 (pbw)	Foam 89 (pbw)
Polymethylene polyphenyl isocyanate	100.0	100.0	100.0	100.0	100.0	--	--	--
4,4' diphenylmethane diisocyanate	--	--	--	--	--	100.0	100.0	100.0
Propylene oxide adduct of sorbitol (mw 686)	81.0	71.0	61.0	51.0	41.7	88.3	78.3	69.3
Silicone surfactant	1.5	1.5	1.5	1.5	1.5	1.1	1.1	1.1
Trichlorofluoromethane	28.0	28.0	28.0	28.0	28.0	28.0	28.0	28.0
Triethylene diamine	1.25	1.25	1.25	1.25	1.25	1.40	0.5	0.5
Stannous octoate	0.5	0.5	0.5	0.5	0.5	--	--	--
0,0 -diethyl -N,N' -bis (2 hydroxyethyl) amino phosphonate	--	11.0	22.0	33.0	44.0	--	10.6	21.2
weight % fire retardant	0.0	5.2	10.3	15.4	21.4	0.0	4.8	9.5
% phosphorous	0.0	0.63	1.25	1.88	2.51	0.0	0.58	1.16