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DEVELOPMENT AND FIELD PRODUCTION OF FOAMED-IN-PLACE, PLASTIC, ENERGY-ABSORBING MATERIALS

Contracts DA-19-129-QM-838 and DA-19-129-QM-1257

FILE

Final Report

December 31, 1956 to March 31, 1961

Submitted to

Commanding General
The Quartermaster Research and Engineering Command
U. S. Army
Natick, Massachusetts
Attention: Dr. George E. Murray
Project Officer

ATLANTIC RESEARCH
CORPORATION

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ALEXANDRIA, VIRGINIA

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N. D. Stewart
R. O. Thomas
S. V. Dubiel
J. J. Papajohn
R. C. Bryant
D. Mock
P. L. Garwig

Submitted to

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Attention: Dr. George E. Murray
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by

Atlantic Research Corporation
Shirley Highway at Edsall Road
Alexandria, Virginia

FOREWORD

This report summarizes the work performed by the Atlantic Research Corporation under two contracts:

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Atlantic Research personnel who contributed to the project were:

Chemical Investigators

W. D. Stewart, Head, Pioneering Research Group

R. O. Thomas, Chemist

S. V. Dubiel, Chemist

H. J. Papajohn, Chemist

Physical Testing

Royal C. Bryant, Director, Electromechanical Division

Dana Mock, Physicist

Dr. George E. Murray of the Chemicals and Plastics Division of the Quartermaster Research and Engineering Command administered the project and contributed significantly.

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I. SUMMARY

A. DEVELOPMENT OF FOAMS

1. Problem

Materials, methods, and equipment were investigated which would be suitable for the production in the field of foamed-in-place, plastic, energy-dissipating structures. These would later be assembled with aerial-drop containers. The resin system was to foam, cure, and develop the necessary energy-dissipating characteristics within 12 hours, without an accessory source of heat and under field conditions at ambient temperatures of 42° to 125°F. The energy-dissipating properties desired for the foams would be similar to those of foamed glass at comparable densities. Polyurethane systems were selected for the initial investigations.

Also to be investigated was the thermal balance of several highly exothermic foamed-in-place plastic systems, which might have application as energy absorbers and as flexible or rigid insulating materials. Exploratory trials to determine feasibility of foaming-in-place with some of these resin systems at arctic temperatures, -40 to -65°F, were to be carried out. It was necessary to devise, construct, and install an inexpensive but reliable instrument for measuring and comparing the energy-dissipating properties of the experimental foams.

2. Experimental

A process was developed for the production of highly exothermic, "one-shot" resin systems which could be foamed-in-place and cured under their own heat of reaction. These were modified castor oil-polyurethane systems. The cured, rigid foams had energy-dissipating properties equivalent to or better than foamed glass at comparable densities. It was found that the heat of condensation of mixtures of castor oil and other simple polyols with diisocyanates or isocyanate adducts, when properly catalyzed, would induce the formation of thermal radicals from added vinyl and related monomers. Subsequent copolymerization with castor oil resulted in rigid foams of high strength and good energy-dissipating properties. In the absence of the monomers, the castor oil-based foams were

semi-rigid and too resilient for this application. The monomers serve an additional purpose, since they may be admixed with aromatic diisocyanates or adducts, which are solid at temperatures below 20°C, to obtain the fluidity needed for storage, mixing, and foaming over the temperature range of 42 to 125°F. Diallyl phthalate and vinyl toluene were the best monomers for this use. Raw material costs were less than $0.60 per pound of foam.

A simple laboratory drop-tester was constructed. It was used to screen out experimental and commercial products which would not meet specifications and to select the better formulations for futher improvement in energy-absorbing properties. Aluminum honeycomb was found to have the most favorable ratio of density to energy absorption, and it showed no resilience. Glass foam also showed no resilience, and paper honeycomb almost none. Some of the commercial foams tested had favorable ratios of density to energy absorption but they were resilient. Several of the experimental rigid foams tested were equivalent to glass foam in energy-absorbing characteristics, but lighter. These foams developed most of their strength the first day, and increased in strength about 10 per cent between the first and thirteenth days.

The energy absorbed by foamed plastics over the density range tested, 2 to 8 lb/cu ft, appears to depend approximately on the square of the foam density. Cellular structure was not an important factor.

Thermal properties of the resin systems and foams pertaining to processing were studied and foam formulations adjusted to permit preparation under field conditions. Heat conductivity measurements on two of the experimental foams characterized by good energy-absorbing properties indicated that these foams were good insulating materials. Thermal conductivities ranged from 0.26 to 0.40 Btu/hr/sq ft/in/°F over the density range of 2.4 to 6.7 lb/cu ft.

Feasibility of producing foamed-in-place, flexible and rigid structures at arctic temperatures (-40 to -65°F) was demonstrated. The polymeric systems were initiated by ionic catalysts. Lack of fluidity of most monomers and additives (foam stabilizers) at -65°F is the most restrictive factor for foaming at this temperature.

B. FIELD PRODUCTION AND TESTING OF FOAMS

Mixing effected by kneading of material poured into plastic films held in the shape of a bag proved simple and efficient. A Klauder-Williams foam machine was adapted for producing formulations 100C and 108C. Methods were established for calibrating the machine, for mixing the two formulations and for foaming at desired densities. Foams were satisfactorily cast into paperboard cartons as large as 48 × 48 × 6 inches. A hand-mixer for use under field conditions was designed, built, and tested. It supplied 1.5 cu ft (from 1 gallon of liquid mix) of 6 lb/cu ft density foam per minute.

Spray applications onto tents, shelters, or inflated bags proved the foams well-suited for the preparation of durable insulated structures.

Reduced exotherm during foaming was achieved by substitution of polyols for Quadrol, but the foams so produced were unsatisfactorily resilient. Experiments indicated that in the absence of unsaturated polyol, such as castor oil, the heat of reaction of diisocyanate with saturated polyol such as Quadrol would induce homopolymerization of added vinyl monomers to give foamed-in-place, energy-dissipating structures that were more brittle. Styrene monomer combinations yielded more brittle foams than the other monomers, and reduced the exotherm. Tests demonstrated siloxanes to be better stabilizers than ethyl cellulose in the 100C formulation.

Flame-retarding foams were produced by the incorporation of phosphate polyols in the polymer chain, and by the addition of borax. A modified 108C formulation foamed successfully at 35°F.

Tests made on the stability of the components and component mixes, as affecting packaging, handling, and foaming under field conditions, indicate deterioration in from two weeks to six months, far short of the desired two-year storage period.

Tests for flexural strength indicate that ultimate load varies as the 3/2 power of the foam density. The ultimate deflection decreases slightly as the density increases. These foams are superior to non-reinforced concrete,

which fails at a maximum fiber stress of 1000 psi. Results are available for design purposes. Further tests indicate that energy dissipation of the foams varied with density, but conclusions were clouded by disagreement of data. Dimensional stability of foams made with formulations 100C and 108C was excellent when cycled between -65 and 160°F.

II. DEVELOPMENT OF FOAMS

A. REQUIREMENTS

1. Background and Objectives

There was an urgent requirement for more efficient energy-dissipating structures to protect supplies and equipment delivered by aerial drop, so that packages could be delivered from higher altitudes and at higher rates of descent. This would reduce hazards to personnel and aircraft during delivery, decrease size of parachute for drag and stabilization of packages during fall, and increase accuracy in placing dropped material.

The Quartermaster Research and Engineering Command, in previous research on cushioning materials, had found that plastic foams offered possibilities as energy-dissipating structures. Since the transport of low-density, bulky structures was impracticable, this program was initiated for research on the development of foamed-in-place, plastic, energy-absorbing materials which could be produced under field conditions.

Specific objectives for the principal area of research were to investigate and determine materials, methods, and equipment suitable for foamed-in-place, plastic, energy-absorbing structures to be foamed in the field for later assembly with aerial drop containers. The investigation was to include theoretical studies, laboratory investigations, equipment evaluation, and development pertinent to the objective. Suitability was to be based on the following requirements.

a. Raw Materials

Raw materials were to be safe to handle and effective over a period of two or more years of storage under arctic temperate or tropical climates.

b. Process

The foam was to be producible in blocks up to 4 square feet and 6 inches thick at temperatures from 42 to 125°F. The foam was to develop the necessary energy-absorption requirements (as indicated

below) within 12 hours after the foaming operation, without application of an accessory source of heat. Consideration was to be given to development of kits or units suitable for preparation of individual aerial drop packages.

c. Properties of Plastic Foam Structure

The material was to be capable of absorbing up to 200 in-lb of energy per cubic inch without transmitting stresses exceeding 300 lb/sq in when 6-inch-thick structures are impacted at 50 ft/sec with a flat metal hammer having a static weight up to 1.25 lb/sq in of foam. The foam was to be relatively unaffected by water and high or low temperatures. The density of the foam was not to exceed 6 lb/cu ft.

d. Cost

The combined cost of all materials needed for preparation of the foam plastic structures in large quantities in the field was not to exceed $2.00/cu ft for a packaged unit from 2 to 8 cu ft.

e. Availability of Materials

Materials needed for proposed plastic foams were to be commercially producible in quantities necessary for preparation of 2,000 tons of foam per month.

f. Personnel

Procedures required to handle materials and produce foam were to be sufficiently simple to be carried out with a minimum of training by military personnel.

g. Transportability

All materials necessary for the preparation of the foams were to be readily and safely transportable by air.

2. Polyurethanes Selected

Polyurethane foaming systems were selected as the most promising of the resin systems for the proposed application. Since the screening of experimental foams entailed the design and construction of a simple laboratory drop-tester, this task was assigned as part of the program. Other phases of this project included:

(1) The production of selected, energy-absorbing structures for field testing;

(2) studies on the basic criteria for equipment suitable for producing promising foamed-in-place, energy-absorbing materials; and

(3) basic investigations on the thermal balance of the highly exothermic foamed-in-place plastic systems which may have application as energy absorbers and as flexible and rigid insulating materials.

Thermal studies, such as heat of polymerization, specific heats, and heat conductivities, were initially to be limited to polyurethane systems. In view of the desirability of producing foamed-in-place structures in the field under arctic conditions (-40 to -65°F), these studies were extended to ionic systems to permit exploratory investigations of the feasibility of preparing foams at very low temperatures in the absence of an accessory source of heat.

B. RIGID, FOAMED-IN-PLACE POLYURETHANES

1. Theoretical Basis for the Experimental Approach

A survey of the literature at the time the project was initiated revealed that all of the commercially available rigid, foamed-in-place polyurethane systems were based on the use of polyhydroxy polyesters and the reaction products of polyhydroxy polyesters with diisocyanates. The process for foaming the polyhydroxy polyesters was termed the "one-shot" procedure. It was a three component system of (1) polyhydroxy polyester and additives (foam stabilizers, emulsifiers, coupling agents), (2) diisocyanate, and (3) catalyst and water. These were mixed, poured into molds, and allowed to foam. The two component systems or "prepolymer" systems were composed of (1) polyhydroxy polyesters prereacted with an excess of diisocyanate and (2) water plus catalyst. These were mixed, poured, and allowed to foam. Most of these systems did not generate sufficient heat during foaming to cure to optimum properties and heat was applied for complete curing.

The foaming systems developed in the United States and the United Kingdom were based on processes disclosed by the Germans at the end of World War II. The Germans prepared polyhydroxy polyesters by esterifying and tranesterifying dibasic acids, such as adipic acid, with an excess of mixtures of diols (such as ethylene glycol, propylene glycol), and triols (such as glycerol, trimethylol propane, or hexanetriol). These polyhydroxy polyesters were used in "one-shot" and two-component foaming systems.

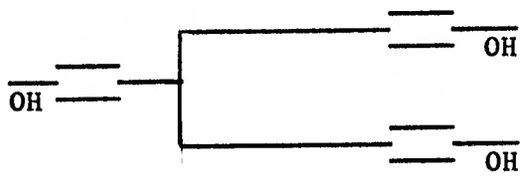
Rigidity of the foam was a function of the distance between cross-linking sites: the higher the triol content in the polyester, the greater the rigidity. The prepolymer systems were more popular than the "one-shot" because the reaction products of the hydroxy polyesters with diisocyanates were much less volatile and less irritating than the unreacted diisocyanates. Recent research in the United States on the preparation of foamed-in-place, rigid polyurethanes of low density (used for insulation, core materials for radomes, and high-strength, low-density materials) has led to replacement of part of the adipic acid used in the preparation of polyhydroxy polyesters by phthalic anhydride

and maleic anhydride. Diols are omitted. Cross-linking monomers, such as diallyl maleate and triallyl cyanurate, may be added with peroxides, and copolymerization effected with the unsaturated polyester at temperatures of 75 to 85°F. In Great Britain, adipic acid is omitted: sebacic-, succinic-, glycerol-alkyd polyesters are considered among the best for the preparation of rigid foams with good strength to weight ratios.

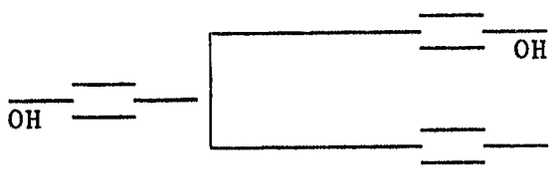
These polyhydroxy polyesters and their reaction products with diisocyanates do not meet the specifications outlined above for foamed-in-place, energy-absorbing plastic materials. Esterification of the starting materials to obtain esters of the desired molecular weight, hydroxyl number, and acid number is expensive. The price of polyester would range from approximately $0.50 to $1.00/lb. Nor could foams be produced over an ambient temperature range of 42 to 125°F. The aromatic diisocyanate component normally used solidifies slightly below room temperature. Viscosities of polyesters at low temperature are too high for ready mixing. In addition there is insufficient exotherm for curing over the range of temperature specified. Prepolymers prepared by reacting these polyesters with an excess of diisocyanate have the disadvantage of shelf-life of only six months.

The materials needed for the present application were inexpensive monomeric polyols and diisocyanates of low molecular weight that were fluid and reactive at low temperatures, and yielded sufficient exotherm for foaming, setting up, and curing between 42 to 125°F without an accessory source of heat. Castor oil, a natural trihydroxyester that has been widely used in prepolymer systems for the production of semirigid urethane foams, was selected as one of the monomers for the development of highly exothermic, "one-shot" foaming systems. It is readily available and inexpensive (less than $0.30/lb). Castor oil is a triglyceride of 18-carbon fatty acids, chiefly ricinoleic acid. The fatty acids consist of approximately 90 per cent hydroxy acids (practically all ricinoleic) and 10 per cent nonhydroxy acids (chiefly oleic and linoleic). There is virtually no chance of nonhydroxy triglycerides and little chance of monohydroxy triglycerides being present in castor oil. Castor oil from the viewpoint of isocyanate functionality is about 70 per cent trifunctional (70 per cent

glyceryl triricinoleate) and 30 per cent difunctional (30 per cent diricinoleate triglyceride). This accounts for the semirigid nature of the polyurethanes prepared from castor oil. However, all the fatty acids of the triglycerides of castor oil, 12-hydroxy-9-octadecenoic acid (ricinoleic acid), 9-octadecenoic acid (oleic acid), and 9,12-octadecadienoic acid (linoleic acid), possess double bonds at the ninth carbon. Cross-linking and chain extension at these sites as well as at those of the -OH group should yield highly cross-linked, three dimensional, rigid urethane polymers. Thus, functionality for the glyceryl triricinoleate fraction (70 per cent) of the castor oil with three -OH groups, may be illustrated in the following manner:



The diricinoleic triglyceride fraction (30 per cent), with two -OH groups would be:



A variety of unsaturated monomers is available for copolymerization with castor oil. Preference was given those that are (1) fluid at low temperature, (2) high boiling, and (3) good solvents for aromatic diisocyanates. Thermal initiation should be feasible and should yield, at the temperatures expected during the foaming reaction, copolymers with physical properties better than those obtained by initiation by peroxide free-radicals.

Castor oil with secondary hydroxyls reacts very slowly with diisocyanates at room temperature, even in the presence of catalysts. Cocondensation with highly reactive polyols of lower molecular weight,

such as the strongly basic polyol N,N,N',N',-tetrakis(2-hydroxypropyl)-ethylene diamine, could be used to obtain the exotherm required for foaming and complete reaction of all the hydroxyls of castor oil with diisocyanate, and for initiating the thermal copolymerization of various unsaturated monomers with castor oil.

2. Development of Foamed-in-Place Systems

The hydroxyls of castor oil react so slowly with diisocyanates that prepolymer systems are used for commercial foaming. The castor oil is reacted at elevated temperature with diisocyanate to form the prepolymer. The prepolymer with additives is then mixed with water and catalyst to produce the foam. Because prepolymers have a guaranteed shelf life of about six months, they were not suitable for this program. Since no information was available on systems suitable for the preparation of foamed-in-place castor oil polyurethanes by the "one-shot" technique, such systems had to be developed.

The essential components of "one-shot" foam systems are (1) polyol, foam stabilizer, emulsifier and coupling agent; (2) catalyst and water; and (3) diisocyanate. At the time of foaming, (1) and (2) are blended. The diisocyanate is then added and mixed. Fillers may or may not be added.

In the foaming reaction, the diisocyanate reacts with the hydroxyl groups to link them together into long-chain molecules, and with the water to form carbon dioxide gas. At the same time, isocyanate groups on the growing chains are reacting with water to form urea links and more carbon dioxide. Since the hydrogens on the urea links of the large molecules react readily with diisocyanates, cross-linking occurs at these sites. If the original viscosity is favorable and if chain extension and cross-linking increase the viscosity at an appropriate rate, the carbon dioxide gas is trapped in the gel structure to yield a stable foam. If sufficient heat is generated, these foams are self-curing.

Since water liberates gas, the amount of water controls the density of foam. Carboxylic acids, if present or added, react with diisocyanates to form acid anhydrides which break down at elevated temperatures to form an acid amide and carbon dioxide gas. Acetic acid has been used as a source of gas for the preparation of rigid foams. Water is generally used.

The emulsifier acts as a dispersing and solubilizing agent for the water. It promotes rapid mixing of components and the interaction of the water with diisocyanate. In its absence, water and most diisocyanates are relatively immiscible and react slowly.

Foam stabilizers (or "bubble stabilizers") improve uniformity and fineness of pore size. At low densities they reduce the tendency to fissure and collapse. Some of these are viscosity regulators, others are not.

The most widely used catalysts are amines. Catalytic activity, steric influences excepted, is a function of basicity. Tertiary amines are good catalysts. Type and amount of catalyst control rate of reaction, exotherm, and cure. The catalyst may enhance the rate of reaction of diisocyanate with water relative to that of polyol and alter polymer properties. Strong inorganic bases as catalysts are unpredictable, and reactions may be violent. Heavy metal salts, such as iron acetylacetonate and lead naphthenate, are employed as catalysts. Mild inorganic acids are mild inhibitors, but Lewis acids are catalysts.

The type of diisocyanate is an important factor in controlling rate of reaction, foam rise, and polymer properties. Aromatic isocyanates are more reactive than aliphatic. Reactivity of the aromatic diisocyanates may also be varied by appropriate substitution on the nucleus; the more negative the substituent, the more reactive the diisocyanate. Steric hindrance affects reactivity; for example, the ortho-NCO group of 2,4-toluene diisocyanate is much less reactive than the para.

These were the variables investigated to obtain acceptable castor-oil and modified castor-oil formulations for the production of foamed-in-place resins by the one-shot technique.

a. Castor Oil Systems

Two industrial grades of castor oil, AA and DB oils, were used as polyols. The properties of interest in the preparation of polyurethanes* are included in Table I.

Table I

Properties of DB and AA Castor Oils

Castor Oil	Molecular Weight	Hydroxyl Value	Volatile Moisture (per cent)	Acid Value	Isocyanate Equivalent (grams per OH group)
DB	926	163	0.02	1	342
AA Standard	926	163	0.02	2	340

An isocyanate equivalent of 311 was used for these oils in most of the experimental work. This was based on information available at that time, which estimated a molecular weight of 933 (mean), assuming trifunctionality. Glyceryl monoricinoleate S,** other glyceryl esters, and various polyesters tried were assigned isocyanate equivalents.*** The standard isocyanate equivalent values of 87 (grams per NCO group) for toluene diisocyanates, 9 for water, and 73 for N,N,N',N',-tetrakis-(2-hydroxypropyl)ethylene diamine (Quadrol) were used. Functional groups on foam stabilizers and catalysts were not compensated for with additional isocyanate.

Batches were hand-mixed in paper cups using 0.1 or 0.2 equivalent quantities of reactants. In early work, the mixtures were poured into aluminum molds coated with mold release (Johnson's floor wax) and allowed to foam. Later, hand-made cardboard boxes lined with aluminum foil were substituted as molds to obtain more uniform foams and to eliminate surface stickiness caused by rapid heat loss at contact points with metal, and consequent incomplete cure. During seasons with night temperatures below 70°F, the toluene diisocyanate was preheated

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* As described in technical bulletins of the Baker Company.
** Glyco Products
*** Published by the Baker Company in Technical Bulletin 31.

20 minutes at 150°F, and subsequently cooled to room temperature before use, to avoid inconsistencies in foaming because of solid particles of toluene diisocyanate.

The secondary hydroxyls of castor oil were found to react too slowly with toluene diisocyanates for the rate of heat generation needed for foaming and self-cures. Hence, a survey was made of some of the catalysts recommended for commercial use, and of other compounds whose rates of reaction might be sufficiently rapid. Castor oil was used as a polyol with 100 per cent 2,4-toluene diisocyanate (Hylene T) and the 80:20 mixture of the 2,4- and 2,6-isomers (Hylene TM) as sources of the NCO group. An equivalent ratio of NCO:OH of 3:1 was used for the initial trials, since this ratio is optimum for good foam properties.* The catalysts were tried in the formulation in Table II at a concentration level of 1.3 per cent by weight based on the weight of the mix.

Table II

Formulation Used to Evaluate Catalysts

Ingredient	Content (gm)	Isocyanate Equivalent (mol)
Castor oil (Baker DB)	20.0	0.064
Ethyl cellulose (Hercules N-100, 86 cps)	2.0	-
Water (tap)	0.25	0.028
Emulphor EL-719 (Antara)	0.20	-
Diisocyanate	23.70	0.27

Processing was by the "one-shot" technique at room temperature (24 to 25°C). All components except the diisocyanate were thoroughly mixed by hand. The diisocyanate was then added and well mixed until foaming began. The results of the tests are described in Table III.

* Reported by National Aniline.

Table III

Survey of Catalysts for Increased Rate of Heat Generation

Catalyst (1.3 per cent by wt of total mix)	NCO Source	Mixing Time (sec)	Rise Time (min)	Maximum Temperature (°C)	Foam Properties
No catalyst	Hylene T	60	3	67	Good foam; after 12 hours no cure, collapsed.
	Hylene TM	60	3.5	65	Good foam; after 12 hours no cure, slight collapse, creamy consistency.
N-methyl morpholine (Eastman)	Hylene T	60	3.5	82	Collapsed
	Hylene TM	60	2	70	Collapsed
N-ethyl morpholine (Eastman)	Hylene T	60	2.5	82	Collapsed
	Hylene TM	60	3	82	Collapsed
Glyceryl monoricin-oleates (Glyco) S	Hylene T	60	2	110	Good foam; good cure, some shrinkage; density 6 lb/cu ft
	Hylene TM	60	2.5	112	Good foam; smooth rise, higher than T; little shrinkage; density 4.7 lb cu ft.
Triethylamine (Eastman)	Hylene T	15	1.1	82	Collapsed
	Hylene TM	20	2.5	80	Good rise, no cure, shrinkage in center; foam rise higher than T.
Triethanolamine (Carbide & Carbon)	Hylene T	40	3.5	83	Collapsed
	Hylene TM	40	4.75	80	Collapsed
Sodium stearate (Fisher)	Hylene T	60	6	100	Fair foam, tacky cure, some shrinkage.
	Hylene TM	60	3	106	Some shrinkage, fast cure; foam rise higher than T.
Dibutylamino-ethanol (Sharples)	Hylene T	60	3	80	Collapsed
	Hylene TM	60	3	80	Collapsed
Sodium salt of resorcylic acid	Hylene T	60	2	70	Collapsed
	Hylene TM	60	7	72	Collapsed

Table III (Cont'd)

Catalyst (1.3 per cent by wt of total mix)	NCO Source	Mixing Time (sec)	Rise Time (min)	Maximum Temperature (°C)	Foam Properties
Sodium salicylate (H. B. Gilpin)	Hylene T	40	4	124	Good foam, some shrinkage, smooth skin; density 4.8 lb/cu ft.
	Hylene TM	60	5	122	Good foam, some shrinkage, smooth skin; density 4.1 lb/cu ft.
Dimethylaminoethanol (Eastman)	Hylene T	20	1.5	100	Fair foam, shrunk in center; cured 12 hours, inside collapsed.
	Hylene TM	20	2	101	Good foam, no shrinkage; cured 12 hours, inside collapsed.
Sodium ricinoleate (Baker)	Hylene T	40	5	100	Excessive shrinkage.
	Hylene TM	60	5	105	Excessive shrinkage.
Diethanolamine (Carbide & Carbon)	Hylene T	60	4	85	Collapsed
	Hylene TM	60	4.5	85	Collapsed
Quinone dioxime	Hylene T	60	2	80	Collapsed
	Hylene TM	60	3	80	Collapsed
Quadrol (Wyandotte)	Hylene T	60	4	95	Collapsed
	Hylene TM	60	5	95	No cure after 12 hours.

The catalysts that proved best for this system at the concentration level used were glyceryl monoricinoleate, sodium stearate, sodium salicylate, and sodium ricinoleate. These were not those recommended for commercial formulations, which use N-methyl morpholine, triethylamine, triethanolamine, and diethanolamine. All of the foams with temperatures of reaction of 80°C or less failed to cure in 12 hours at room temperature. Hylene T (2,4-toluene diisocyanate), as reported in the literature, produces foams with greater tendency to collapse than the 80:20 mixture of 2,4- and 2,6-isomers (Hylene TM). Hylene T also yielded slightly higher temperatures of reaction. Glyceryl monoricinoleate is not only a good coupling agent but is also a good catalyst.

Since reaction rates of aliphatic polyols with toluene diisocyanates are base-catalyzed, basicity of polyol is an important factor in catalysis. Samples of some of the polyols currently used for the preparation of polyurethane foams were shaken thoroughly with equal parts of water and the pH of the dispersions were measured (while agitating) with a Beckman pH meter (glass electrode). Results are summarized in Table IV.

Glyceryl monoricinoleate, a basic polyol with primary as well as secondary hydroxyls, was found to be an excellent coupling agent and foam stabilizer for castor oil polyurethanes. It was highly reactive; 24.8 grams of glyceryl monoricinoleate when mixed with 17.4 grams of toluene diisocyanate (Hylene T, DuPont 100 per cent 2,4-toluene diisocyanate) at 25°C, began to react within 30 seconds, and temperature rose from 25 to 140°C within 5 minutes. When applied as a coupling and emulsifying agent in combination with Antara's Emulphor EL-719 ("a polyoxyethylated vegetable oil"), castor oil foams of uniform, small pores of controlled density ranging from 1.7 to 8 lb/cu ft were readily prepared. These foams at 1:1 NCO:OH ratios were resilient.

The NCO:OH ratio was increased to reduce foam resilience. Four-inch cubes were cut from foams prepared with the formulation in Table V. Energy absorption characteristics were measured by drop-testing.*

Table IV

pH of Polyol-Water Mixtures

Polyol	pH (1:1 mixture with water)
Castor oil (Fisher AA VSP)	5.95
Castor oil (Fisher dark lubrication)	5.50
Castor oil (Baker DB)	5.70
Glyceryl monoricinoleate S	8.75
Flexricin 9 (Baker) (propylene glycol monoricinoleate)	3.90
Quadrol (Wyandotte) N,N,N',N',-tetrakis(2-hydroxypropyl)-ethylenediamine	
light	10.70
dark	10.40
Tetronic 701 (Wyandotte)	7.55
Tetronic 702 (Wyandotte)	10.55
Tetronic 704 (Wyandotte)	10.10
Tetronic 904 (Wyandotte)	9.25
Pluronic L-61 (Wyandotte)	6.55
Multron R-16 (Mobay)	4.00
Foamrez 50 (Witco)	4.00

Table V

Formulations T38C using 4:1 and 3:1 NCO:OH

Ingredient	4:1 NCO:OH Content (gm)	3:1 NCO:OH Content (gm)
1. Castor oil, DB	30.0	30.0
2. Glyceryl monoricinoleate S	3.0	3.0
3. Ethyl cellulose N-199, 86 cps	2.0	2.0
4. Water	0.25	0.25
5. El-719	0.20	0.20
6. Nacconate 80	50.0	40.26

Note - Mixing sequence: 1 and 2 mixed thoroughly, followed by 3, 4, 5 and 6.

The foams made at the 3:1 NCO:OH ratio ranged in density from 2.7 to 3.1 lb/cu ft; those at the 4:1 NCO:OH ratio ranged from 3.6 to 4.0 lb/cu ft. The foams prepared at 4:1 NCO:OH ratios were more rigid than those made at the 3:1 ratio and had little resilience. However, they exhibited much lower energy absorption values (Table VI).

Table VI

Drop-Test Results for Formulations T38C

Material	Range of Density (lb/cu ft)	Range of Energy Absorption (in-lb/cu in)	Resilience
Foam T38C (4:1)	3.6 to 4.0	32 to 55	small
Foam T38C (3:1)	2.7 to 3.1	38 to 77	small

Fillers were utilized to modify the resilience of glyceryl monoricinoleate S-castor oil foams, and to reduce the exotherm of foams at high ratios of glyceryl monoricinoleate to castor oil. Fillers such as calcium oxide, magnesium oxide, aluminum oxide, silicates, silica, and aluminum powder at high loadings reduced resilience but did not enhance the strength of the foam. Dimensional stability of low-density foams was improved.

Foams of very low density were produced by using calcium sulfate as the filler. The formulation in Table VII yielded foams with a density of 1.5 lb/cu ft.

Table VII

Formulation Containing Calcium Sulfate Filler

Ingredient	Content (gm)
Calcium sulfate·H_2O	20.0
Castor oil, DB	20.0
Glyceryl monoricinoleate S	5.0
Emulphor EL-719	0.4
Water	0.8
Ethyl cellulose (N-100, 86 cps)	1.0
Nacconate 80 (80:20 2,4-:2,6-isomers)	43.5

This type of foam was of interest since items of high fragility, such as eggs, encased in it could be dropped from a height of six feet without fracture.

The plastisol technique was used to introduce organic fillers. Plastisol-grade polymers* (spherical products of 1 to 25 microns in diameter) of nitrocellulose (11.5 per cent nitrogen), cellulose acetate, ethyl cellulose, polyvinyl chloride, and copolymers of vinyl chloride with other monomers (vinyl acetate, maleates) were blended with equal parts by weight of castor oil and its derivatives to form viscous fluid suspensions. The fluid suspensions were then foamed and cured in the usual manner with diisocyanate.

The ethyl cellulose-castor oil foams were tough but flexible Castor oil was a good plasticizer for ethyl cellulose.

The nitrocellulose-castor oil foams were rigid. In cases for which the heat of reaction was high, these foams decomposed and charred with the evolution of dense clouds of smoke.

Cellulose acetate yielded rigid foams, but there was evidence of incompatibility with the castor oil polyurethane. This system seemed less promising than others of the group.

The polyvinyl chloride foams were rigid and strong. The heat of reaction in most cases sufficed for fusion of the resins. Decomposition of polymer in some instances was quite marked.

b. Modified Castor Oil Foams

Quadrol,** N,N,N',N',-tetrakis(2-hydroxypropyl)ethylene diamine, with four hydroxyl groups available for chain extension and cross-linking should improve rigidity of castor oil foams. Since it contains two tertiary nitrogens, it is basic and should serve as an excellent catalyst for the condensation of polyols with diisocyanates. It was investigated thoroughly at varied ratios as catalyst, cross-linking agent, and comonomer in castor oil systems.

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* Prepared by Atlantic Research Corporation process.
** Wyandotte Chemicals Corporation

Quadrol admixed with castor oil at ratios of 1:1 or greater yields highly reactive systems with toluene diisocyanates, although it did not perform as well as expected as a cross-linking agent for castor oil polyurethanes. Foamed products based on a 1:1 equivalent ratio of NCO:OH lacked the rigidity desired. It is suspected that the OH groups of Quadrol, being more reactive with NCO groups than the OH groups of the castor oil, are removed from the site of reaction as the polyurethane before the castor oil reacts. Four-inch cubes were prepared for an evaluation of energy absorbing properties with typical formulation in Table VIII.

Table VIII

Formulation T63C,
Typical for Polyurethanes Containing Quadrol

Ingredient	Content (gm)
Quadrol	25.0
Castor oil, AA	75.0
Ethyl cellulose (N-100)	7.5
Water	0.63
Emulphor EL-719	0.50
Toluene diisocyanate (100 per cent 2,4)	70.0

The results, discussed later, indicated that strength of foam was improved by using Quadrol as a comonomer for castor oil, but resilience was not eliminated.

The next approach to the problem was to try to impart more rigidity to the polyurethane chain by utilizing the double bonds of the castor oil as reaction sites for copolymerization with other unsaturated monomers. There was little probability of obtaining high molecular weight products at the temperatures reached during foaming by the one-shot procedure if initiation were by peroxide free-radicals. Emphasis was, therefore, placed on initiation by thermal radicals, induced by the heat of condensation of polyol with diisocyanate during the foaming process.

A qualitative experiment with distilled and inhibited styrene indicated that diisocyanate would react with and remove the inhibitor, p-tert-butyl catechol, at relatively low temperatures. For example, tubes containing 25 ml of distilled styrene, 25 ml of styrene containing 10 ppm p-tert-butyl catechol, and 25 ml of styrene containing 10 ppm p-tert-butyl catechol plus 1 ml of 2,4-toluene diisocyanate were heated at 80°C until the mixtures were noticeably viscous. The distilled styrene became viscous in 9 hours at 80°C; the styrene plus inhibitor became viscous in 14 hours; and the inhibited styrene plus diisocyanate thickened in 12 hours. Styrene, when added to Quadrol-castor oil systems, increased rigidity of foam, but the styrenated foams were characterized by coarse, nonuniform cell structure. This was attributed to heterogeneity of mixes prior to foaming of mixes containing styrene.

Several compounds were compared with Emulphor EL-719 as emulsifier and coupling agent for styrene in the formulation in Table IX.

Table IX

Formulation Used to Compare Emulsifiers

Ingredient	Content (gm)
Quadrol	30.0
Castor oil, AA	20.0
Styrene (distilled)	10.0
Emulsifier	3.0
Ethyl cellulose (N-100)	3.0
Water (tap)	0.25
Nacconate 80	43.7

The control, Emulphor EL-719, a polyoxyethylated vegetable oil, yielded rigid, glassy foams of nonuniform, coarse texture. Foam density was 5.8 lb/cu ft.

Nacconal NRSF, an alkyl aryl sulfonate, produced rigid, glassy foams with more uniformity of pore size than the Emulphor EL-719. Density was similar, 5.3 lb/cu ft.

Aerosol OT (sodium dioctyl sulfosuccinate) was difficult to disperse but gave foams similar in structure and rigidity to the control. Density was 6.2 lb/cu ft.

Witco 77/86 (composition unknown) gave foams of smaller pore size and greater uniformity than the Emulphor EL-719. Density of foam was 7.2 lb/cu ft.

Petromix #9, a "built" emulsifier, based on long-chain petroleum sulfonates (C_{18} or higher) with sodium oleate and other coupling agents added, proved to be an excellent emulsifier and coupling agent for foaming systems containing styrene. Pores were small and uniform, and foam density was 3.2 lb/cu ft. This emulsifier appears to contain inhibitors which retard polymerization during foaming. These foams lacked the glassy appearance of the other foams and were less rigid and brittle. This tendency of Petromix #9 to inhibit polymerization is reduced markedly by replacing half of the Petromix with Witco 77/86. Of a large number of emulsifiers and coupling agents tried in the course of this project, only sulfated monoglyceride of coconut fatty acid was as effective as Petromix #9. It is produced on a large scale by Colgate Palmolive-Peet Company and sold as Arctic Syntex M or L, and for household use as "Vel".

The polymeric materials designated "foam stabilizers" are also indispensable for the production of foams. In the United States the most widely used foam stabilizers are low-viscosity "silicone oils" (polydimethyl siloxanes) and ethyl cellulose (N-100). In Britain, Cellulose acetatebutyrate (Eastman Kodak EAB 272-3) is also used for rigid foams.

Effectiveness as foam stabilizers in formulations containing styrene was compared for cellulose acetates (variable acetyl content), ethyl celluloses (variable ethoxyl content), polyvinyl alcohol, silicone oils, polyvinyl methyl ether—maleic anhydride, casein, gum arabic, and Zein. Ethyl cellulose (N-100 type, 86 cps) and Zein, an alcohol-soluble protein, were the best of the group. Silicone oils (50 and 100 cps) are effective but expensive.

Rigid styrenated foams were prepared by the formulations in Table X.

Table X

Formulations T62A and T60A for Rigid Styrenated Foams

Ingredient	T62A Content (gm)	T60A Content (gm)
1. Quadrol	30.0	30.0
2. Castor oil		
AA	20.0	-
DB	-	30.0
3. Styrene	10.0	10.0
4. Ethyl cellulose N-100, 86 cps	3.0	2.0
5. Water	0.25	0.5
6. EL-719	0.20	0.5
7. Nacconate 80	43.7	49.0

Note - Mixing sequence: 1, 2, and 3 are thoroughly mixed, 4 is added, then followed by 5, 6, and 7.

Energy-absorbing characteristics were determined by drop test. The results (Table XI) indicate that reduction in resilience by styrenation is accompanied by a decrease in foam strength.

Improvement in the strength-to-density ratio and the rigidity of castor oil-based polyurethanes was attempted by modification with monomers other than styrene. Several monomers (undistilled) were used in the high-concentration Quadrol-castor oil system for interpolymerization with the castor oil. The basic formulation, the monomers used, and the characteristics of the foams are shown in Table XII. All of the monomers increased the brittleness of foam. The most promising monomers of the group were diallyl phthalate, diallyl succinate, and triallyl cyanurate. The foamed products were uniform and tough.

Many blocks of the castor oil polyurethane foams modified with monomer were prepared to evaluate energy-absorbing properties. The foams were tested about two weeks after preparation. The formulations for the foams are described in Table XIII. They are arranged

Table XI

Summary of Drop-Test Data Used for Screening Foam Formulations[a]

Foam Formulation	Sample Density (lb/cu ft)	Loading (lb/sq in)	Impact Energy per Vol. Crushed (in-lb/cu in)	Impact Velocity (ft/sec)	Hammer Bounce (in)
T62A	5.21	1.00	69	29	0.4
	4.49	1.00	53	29	0.2
	5.50	1.00	67	29	0.2
	5.76	1.00	81	29	0.2
	6.36	1.00	94	29	0.2
	4.58	0.59	59	20	0.2
	4.40	0.58	45	23	0.2
	4.26	0.59	37	25	0.2
	4.14	0.59	29	25	0.2
T63C	2.86	0.99	94	21	1.2
	3.18	0.99	72	21	2.0
	2.98	0.99	90	21	1.2
	2.98	0.99	86	21	1.6
	3.43	1.00	96	18	1.0
	3.40	1.00	62	25	1.0
T60C	4.23	0.98	65	25	0.2
	4.39	0.99	70	28	0.4
	4.32	0.99	66	29	1.6
	4.39	0.99	59	23	0.4
	4.39	0.98	73	20	1.6
	4.42	0.98	77	23	0.4
	3.75	0.99	42	25	1.0
	3.80	0.98	75	29	0.2
91A	3.05	0.58	41	29	0.5
	1.74	0.59	32	23	0.2
	2.60	0.58	24	25	2
	2.52	0.59	22	20	0.5
89A	4.73	0.58	46	27	0
	4.96	0.58	57	27	0
	4.89	0.58	55	29	0
	4.77	0.58	47	24	0.5
	4.70	0.58	36	27	0
	4.69	0.58	39	30	0.3
100D	7.48	2.72	185	29	1
	7.08	1.80	176	29	0.2
	6.66	1.83	140	29	0
	6.36	1.80	115	29	0

a. Drop-test procedures are discussed in Section G.

Table XI (Cont'd)

Foam Formulation	Sample Density (lb/cu ft)	Loading (lb/sq in)	Impact Energy per Vol. Crushed (in-lb/cu in)	Impact Velocity (ft/sec)	Hammer Bounce (in)
85B	3.21	0.60	19	20	0
	2.40	0.59	14	20	0
	2.64	0.59	14	20	0.3
	2.88	0.59	18	20	0
Honeycomb Paper	2.4	1.38	51	25	0.4
	2.4	1.38	51	20	0
	2.4	1.38	56	16	0
	2.4	1.38	43	23	0.2
Styrofoam	1.58	0.73	62	25	4.0
	1.57	0.73	62	20	2.0
	1.56	0.73	62	16	2.0
	1.55	0.73	60	23	3.2
	1.56	0.73	70	29	6.0
	4.26	1.66	445	25	7.0
	4.26	1.65	582	29	8.0
	2.77	0.77	107	29	2.0
	2.76	0.75	125	29	0.5
	2.76	1.37	119	29	5.0
T38C (3:1)	2.66	0.99	50	20	1.5
	2.93	0.58	38	29	1.6
	2.87	0.58	77	29	3.6
	2.97	0.58	50	29	1.6
	2.89	0.58	47	29	2.4
	3.12	0.58	52	29	2.0
	2.93	0.58	48	29	0.4
T38C (4:1)	3.55	0.57	44	25	1.0
	3.77	0.58	55	25	0.4
	3.77	0.57	32	25	1.0
	3.82	0.57	37	25	0.6
	4.04	0.57	35	29	1.6
91B	3.95	0.58	41	29	0
	3.96	0.58	57	24	0
	3.89	0.59	55	27	0.5
	4.28	0.58	49	27	0
	4.35	0.59	59	27	0.3
91C	4.31	2.70	67	20	1
	3.95	2.66	60	14	0
	4.13	2.70	74	11	0
	4.50	2.67	68	16	0.5

Table XI (Cont'd)

Foam Formulation	Sample Density (lb/cu ft)	Loading (lb/sq in)	Impact Energy per Vol. Crushed (in-lb/cu in)	Impact Velocity (ft/sec)	Hammer Bounce (in)
108C	4.88	1.82	106	20	0.2
	4.94	1.82	105	23	0.2
	5.76	1.85	137	25	0.2
	4.94	1.82	102	28	0.2
108C 1 day old	4.92	1.40	96	29	0.2
	5.05	1.40	100	29	0.5
	5.08	1.38	103	29	0.5
	5.14	1.39	98	29	0
	5.20	1.40	113	29	0.4
	5.24	1.40	110	29	0.5
108C 13 days old	4.84	1.41	102	29	0
	4.98	1.40	100	29	0
	5.07	1.41	110	29	0.5
	5.23	1.40	119	29	0
	5.36	1.40	148	29	0
113B	8.08	3.10	159	25	0
	8.13	3.10	168	25	0
117B	2.08	0.44	110	29	4
	2.23	1.09	98	29	6
	1.98	1.09	92	29	6
120A1	7.02	2.20	115	29	0
	6.31	1.71	77	24	0
Glass foam	8.36	2.66	226	29	0
	8.36	2.62	185	29	0
125A	4.62	2.01	54	16	0
Hooker Electrochemical 126	3.66	1.38	64	24	0
	3.82	1.38	105	24	0
	3.95	1.38	102	24	1
U308 Dayton Rubber	3.98	1.38	178	25	4
American Rubber Products	4.73	1.38	188	25	3
	4.72	1.38	198	25	0
	4.76	1.38	204	29	0

TABLE XI (Cont'd)

Foam Formulation	Sample Density (lb/cu ft)	Loading (lb/sq in)	Impact Energy per Vol. Crushed (in-lb/cu in)	Impact Velocity (ft/sec)	Hammer Bounce (in)
Al Honeycomb 3/8 inch Hexcel	2.29	2.01	108	25	0
	2.28	2.01	104	25	0
	2.18	2.01	109	25	0
	2.24	2.01	109	25	0
Al Honeycomb 1/8-inch Hexcel	8.39	2.58	694	29	0
	8.70	3.34	792	29	0
P-508 Nopco Chemical Co.	6.34	1.38	353	29	3
93D	3.68	2.68	147	29	2-3
	4.07	2.67	120	25	2-3
	4.36	2.68	131	23	0.5
	4.42	2.66	98	20	0.5
	4.65	2.66	126	14	1
100C	5.80	1.84	176	29	0
	5.56	1.84	143	29	0
	4.62	1.87	116	25	0.2
	3.76	1.81	77	20	0.5
	3.35	1.85	61	16	0.2
99BD	5.57	1.39	159	29	0
	4.39	1.44	107	29	1
	3.85	1.39	82	29	0
	3.41	1.41	62	25	0.5
	3.39	1.43	51	20	0.2
	5.86	1.80	177	29	0.1
	6.25	2.70	196	29	0.2
	6.33	2.71	196	29	0

Table XII

Improvement in Strength-to-Density Ratio and Rigidity
of Castor Oil Polyurethanes by Modification with Various Monomers

Control Formulation 91 (Density 4.33 gm/cu cm)

Ingredient	Weight (gm)
Quadrol	60.0
Castor oil, AA	40.0
Petromix #9	2.0
Witco 77/86	2.0
Ethyl cellulose (N-100)	6.0
Water	0.5
Nacconate 80	74.0 ml (87.4 gm)

Formulation 91 with Additives

Formulation	Additive (20 gm) to Control Formulation	Density (gm/cu cm)	Foam Characteristics
91B	Styrene	4.33	Hard, brittle, fairly large irregular cells.
98B	Methyl methacrylate	2.36	Coarse, brittle, large cells.
99A	Ethyl methacrylate	2.44	Very coarse, brittle, large cells.
99B	Diallyl succinate	4.42	Very uniform cells, hard, strong, brittle.
99C	Ethyl acrylate	2.26	Very coarse, brittle, large irregular cells.
99D	N-butyl acrylate	3.14	Nonuniform, coarse, brittle.
100C	Diallyl phthalate	5.25	Uniform small cells, very strong, less brittle than 99B.
100D	Triallyl cyanurate	6.26	Uniform, tough, small cells, brittle.

Table XIII

Compositions of Foams of Various Energy-Absorbing Characteristics

Group I. Highest Energy Absorption
(136 in-lb/cu in of crushed volume at foam density of 5 lb/cu in)

Ingredient	Content (gm)		
	100C	99BD	93D
Quadrol	60	60	70
Castor oil, AA	40	40	30
Diallyl phthalate (distilled)	20	-	-
Petromix #9	2	2	1.0
Witco 77/86	2	2	-
Ethyl cellulose (N-100)	6	6	-
Water (deionized)	0.5	0.5	0.5
Nacconate 80	87.4	87.4	-
Diallyl succinate (undistilled)	-	20	-
Zein	-	-	6.0
Triethanolamine	-	-	1.0
Hylene TM	-	-	73.0

Group II. Second Highest Energy Absorption
(118 in-lb/cu in of crushed volume at foam density of 5 lb/cu in)

Ingredient	Content (gm)	
	91A	108C
Quadrol	60	60
Castor oil, AA	40	40
Styrene (undistilled)[a]	20	-
Petromix #9	12	2
Witco 77/86	-	2
Ethyl cellulose (N-100)	6	6
Water	0.5	0.5
Hylene TM	87.4	-
Vinyl toluene (undistilled)	-	20
Nacconate 80	-	87.4

Table XIII (Cont'd)

Group III. Third Highest Energy Absorption
(82 in-lb/cu in of crushed volume at foam density of 5 lb/cu in)

Ingredient	Content (gm)		
	100D	91D	91C
Quadrol	60	60	60
Castor oil, AA	40	40	40
Triallyl cyanurate	20	-	-
Styrene	-	20	20
Petromix #9	2	2	2
Witco 77/86	2	2	2
Ethyl cellulose (N-100)	6	6	6
Water	0.5	0.5	0.5
Nacconate 80	87.4	87.4	-
Hylene TM[b]	-	-	96.1

Group IV. Lowest Energy Absorption
(52 in-lb/cu in of crushed volume at foam density of 5 lb/cu in)

Ingredient	Content (gm)	
	89A	85B
Quadrol	60	70
Castor oil, AA	40	(DB) 30
Styrene (undistilled)	20	10
Zein	-	10
Witco 77/86	4	-
Emulsifier-719	-	0.5
Ethyl cellulose (N-100)	6	0
Hylene TM	87.4	229.5

a. Styrene kept over Drierite; this removed most of the inhibitor.
b. NCO:OH = 1:1 + 10 per cent excess.

in groups based on energy-absorption levels as determined by drop-tests (Table XI).*

The three foams of highest energy absorption values, Group 1, were the 60:40 Quadrol-castor oil systems modified with diallyl phthalate, with diallyl succinate, and the unmodified 70:30 Quadrol-castor oil system. The unmodified foam, with a high exotherm and an NCO:OH ratio of less than 1.0, was a "dead" foam of more resilience than the modified foams. Although the use of Zein as a foam stabilizer made preparation of the foam possible, the product contained some fissures. Higher ratios of NCO:OH gave unstable foaming systems. The modified systems, containing diallyl phthalate or diallyl succinate, were quite stable and yielded rigid, uniform foams with small pores.

The styrene- and vinyl toluene-modified foams of Group II, as expected, were similar in energy-absorbing properties. Although these foams exhibited only slight bounce upon impact, they were not as rigid as the styrenated foams of Groups III and IV. Explanation of the difference between the styrenated castor oil foams on the basis of past experience is tentatively ascribed to the inhibition of polymerization due to the presence of the Petromix #9; the more complete the polymerization of the styrene (Witco 77/86 and Emulphor-719 as emulsifiers), the more rigid the foam and the lower the energy absorption.

In view of the marked differences in energy-dissipating characteristics and rigidity of monomer-modified castor oil-Quadrol foams, the screening program was extended to other monomers. These formulations and foams are described in Table XIV. Vinyl stearate monomer produced uniform nonresilient foams. Energy absorption of this foam, as indicated by the drop-tests (Table XI), was much lower than expected.

The effect of aluminum powder as a filler on energy-absorbing properties of foam was determined. Foam 100C was altered by the addition

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* Energy absorption data are included in Figure 4, page 84.

Table XIV

Improvement of Castor Oil-Quadrol Foams by Varying Amount of Water, Emulsifier and Coupling Agent, and Monomer in Formulations

Control Formulation

Ingredient	Weight (gm)
Castor oil, AA	40.0
Quadrol	60.0
Ethyl cellulose (N-100)	6.0
Nacconate 80	87.4
Water	variable
Emulsifier and coupling agent	variable
Monomer	variable

Control Formulation with Additives

Formulation	Monomer Type	Monomer Weight (gm)	Witco 77/86 (gm)	Petromix #9 (gm)	Vel[a] (gm)	Water (gm)	Density (lb/cu ft)	Properties of Foam
108B	Diallyl maleate	20	2	2	-	0.5	5.21	Uniform
109C	Dimethyl maleate	20	2	2	-	0.5	3.28	Tough, uniform cells.
109B	2-ethyl hexyl acrylate	20	2	2	-	0.5	4.09	Tough, dead cells.
119A	MPL monomer	20	2	2	-	0.5	6.16	Small, uniform cells, tough, dead.
119C	Vinyl acetate	20	2	-	2	-	-	Foamed rapidly and collapsed.
119D	Divinyl benzene (50-60 per cent)	20	2	-	2	-	4.10	Irregular cells, brittle.
113B	Vinyl stearate	20	2	2	-	0.5	6.30	Very tough, uniform cells.
111B	MG-1	20	2	2	-	0.5	5.40	Uniform, tough.
124A	MG-1	20	2	-	2	-	-	Tough
111C	MG-1 Vinyl toluene	5 15	2	2	-	0.5	5.10	Very uniform cells, tough, dead.

Control Formulation with Additives (Cont'd)

Formulation	Monomer Type	Monomer Weight (gm)	Witco 77/86 (gm)	Petromix #9 (gm)	Vel[a] (gm)	Water (gm)	Density (lb/cu ft)	Properties of Foam
122D	MG-1 Vinyl toluene	15 5	2	-	2	-	4.66	Tough cells, uniform.
122C	MG-1 Methyl butenol	10 10	2	-	2	-	2.62	Large cells, brittle.
108C	Vinyl toluene	20	2	2	-	0.5	4.46	Uniform cells, tough, dead.
119B	Vinyl toluene	20	2	-	-	0.5	5.20	Uniform cells, tough.
118B	Diallyl phthalate	20	2	-	2 pwd	0.5	4.98	Cells uniform, small, dead, tough.
117A	Diallyl phthalate	20	2	2	-	0.5	4.48	Very small cells, fairly tough, dead.
125B	Methyl butenol	10	2	2	-	-	3.51	Dead, brittle, uniform.
121B	Methyl butenol	20	2	2	-	-	3.09	Uniform cells, brittle.
122E	Methyl butenol MG-1	10 10	-	-	-	-	-	Uniform cells, very dense.
125A	N,N'-diallyl-melamine	20	2	-	2	-	4.58	Tough, brittle uniform cells.
121A	N,N'-diallyl-melamine	20	2	2	-	0.5	4.90	Uniform, small cells (crunchy).
125C	N,N'-diallyl-melamine Methyl butenol	5 5	2	2	-	-	4.15	Small, uniform cells, dead, brittle.
122F	N,N'-diallyl-melamine MG-1	10 10	2	-	0.5	-	-	Very dense, uniform.
122A	N,N'-diallyl-melamine MG-1	10 10	2	-	2	-	3.77	Dead, brittle.
122B	N,N'-diallyl-melamine MG-1	10 10	2	-	-	-	8.96	Tough, uniform minute cells, numerous fissures.

a. Sulfonated monoglyceride of coconut fatty acids.
b. All pours made in a 5-cubic-inch mold.

of 20 parts of aluminum powder (formulation 120A1) and 60 parts of aluminum powder (formulation 120A2). Energy absorption of these foams (Table XI) was less than that of the unfilled product. Modification with N,N'-diallylmelamine (formulation 125A) yielded very rigid, brittle foams, characterized by poor energy-absorbing properties (Table III).

Commercially available materials for the production of foamed-in-place, rigid polyurethane foams were obtained, and 4-inch cubes of foam prepared for evaluation of energy-absorption properties with the laboratory drop-tester. Samples of preformed polyurethane foams, Styrofoam, aluminum honeycomb, foamed glass, and paper honeycomb of this size were cut and used as reference materials for drop testing. The following foams and materials were used for drop-tests:

Hooker Electrochemical foam 126

Dayton Rubber Products foam U308

American Rubber Products, urethane foam

Hexcel Products

Aluminum honeycomb, 3/8-inch cells
Aluminum honeycomb, 1/8-inch cells

Nopco Chemical Company, foam P-508

Foamed glass (from Natick)

Styrofoam (from Natick)

Pittsburgh Plate Glass Company, Selectrofoam

Selectrofoam was prepared by mixing components A and B (Formulation 117B) of Table XV, and pouring into molds.

Table XV

Formulation 117B Used to Prepare Selectrofoam

	Ingredient	Content (gm)
Part A:	Selectrofoam resin 6002 (polyester)	58.0
	Tween 40	1.0
	2-dimethylaminoethanol	0.25
	Water	2.75
Part B:	Selectrofoam prepolymer 6003 (contains excess diisocyanate)	100.0

Results of drop-tests for these materials (Table IX) are discussed in the physical testing section.

Foams of materials from the Freeman Chemical Corporation were evaluated at several densities as energy dissipators. Chempol resins 30-1323 and 30-1427 were used for the preparation of foamed blocks for drop-testing, using the laboratory drop-tester. Trichloromonofluoromethane was applied as blowing agent. The formulation in Table XVI was used.

Table XVI

Formulation Containing Chempol Resins

Ingredient	Content (parts)
Chempol 30-1427	100
Trichlorofluoromethane (Freon 11)	10 to 20
Chempol 30-1323	115

Trichloromonofluoromethane was weighed at 15°C and blended with the resin, which was at room temperature (22 to 24°C).

Blocks were prepared for energy-dissipation measurements by casting into aluminum-lined molds, 5 × 5 × 8 inches, and curing overnight at room temperature. These foams were cut to 4- × 4- × 4-inch blocks and drop-tested. The results appear in Table XVII.

Table XVII

Drop-Test Results for Foams Containing Chempol Resins

Density (lb/cu ft)	Energy Absorbed (in-lb/cu in crushed)	Remarks
6.62	224	Hammer bounce of about 2 inches
6.48	314	Hammer bounce of about 2 inches
5.36	224	High hammer bounce
5.66	195	Hammer bounce of about 2 inches
5.66	224	Hammer bounce of about 2 inches
5.52	262	Hammer bounce of about 2 inches
5.59	262	High hammer bounce

Table XVII (Cont'd)

Density (lb/cu ft)	Energy Absorbed (in-lb/cu in crushed)	Remarks
+.1	112	Hammer bounce of about 2 inches
4.1	89	Low hammer bounce
3.97	175	High hammer bounce
3.97	134	Hammer bounce of about 2 inches

The hammer bounce indicated that these foams were resilient over the density range of 3.97 to 6.62 lb/cu ft.

3. Production of Large Blocks of Foam for Field Tests

The experimental foams prepared by formulations 100C and 108C are characterized by little or no resiliency and good energy-absorbing characteristics (Table IX and Figure 4). These formulations were selected for the production of large blocks of foam (24 × 24 × 6 inches) to be used in more extensive testing. The processing variables which require control for preparing by hand larger blocks of foam by these formulations were studied. The rate and heat of reaction and the ratio of surface to volume were found to be important factors regulating size of pour and density of foamed-in-place blocks. Some of the experimental work on processing variables follows.

Four 24- × 24- × 6-inch blocks of foam were prepared by random pouring of hand-mixed batches of the 108C formulation into large molds lined with cardboard covered with aluminum foil. The quantity mixed per batch was three times that of the standard 108C formulation shown in Table XVIII. Several batches were required to fill the 24- × 24- × 6-inch mold. The expected density of the foamed blocks, based on the use of laboratory molds, was approximately 6 lb/cu ft; the measured densities ranged from 7.5 to 8.0 lb/cu ft. The ratio of surface to volume alters foam density. The higher the surface-to-volume ratio, the denser the foam; thus, the thinner the foam layer, the denser will be the foam.

Table XVIII

Standard 108C Formulation

Ingredient	Content (gm)
Quadrol	60.0
Castor oil, AA	40.0
Vinyl toluene	20.0
Petromix #9	2.0
Witco 77/86	2.0
Ethyl cellulose (N-100)	6.0
Water	0.5
Nacconate 80	87.0

Heat buildup in foams of 5 to 6 lb/cu ft density limits the thickness of foam that can be poured at one casting to less than 4 inches. Heat loss from thicker foams is too slow to prevent charring and melting (referred to as "burning").

Formulation 108C was modified to permit the foaming of large blocks of densities from 2 to 6 lb/cu ft. Water was varied in this formulation (with compensating diisocyanate) to determine the amount required for the preparation of large blocks of foam of any desired density. Batch size for 108C was tripled and blocks of foam 15 × 15 × 10 inches were prepared for each experiment. The cardboard-lined molds were tilted 15 degrees to reduce the surface-to-volume ratio on pouring (less loss of gas during foaming, hence lower density). The standard formulation for 108C, the modifications (water and diisocyanate), and the foam densities obtained are listed in Table XIX.

Table XIX

Densities of Foams of Formulation 108C
Modified with Various Amounts of Water and Toluene Diisocyanate

Ingredient	Content (gm)	Foam	Modification		Foam Density (lb/cu ft)
			Water (gm)	Toluene Diisocyanate (gm)	
Quadrol	60.0	1	0.50	87.0	7.6
Castor oil, AA	40.0	2	0.75	89.4	6.2
Vinyl toluene	20.0	3	0.90	90.8	5.5
Petromix #9	2.0	4	1.00	91.8	4.5
Witco 77/86	2.0	5	1.20	93.3	4.8
Ethyl cellulose (N-100)	6.0	6	1.40	95.7	3.9
Water	0.5 or variable	7	1.80	99.6	2.72[a]
Nacconate 80	87.0 or variable	8	2.00	102.5	collapsed

a. Partial collapse.

Modifications 3 and 6, which gave foam densities of 5.5 and 3.9 lb/cu ft, respectively, were selected for the pouring of 24- × 24- × 6-inch blocks. Aluminum molds (30 × 30 × 10 inches) lined with cardboard and an inner facing of aluminum foil were used. The molds were partitioned into four sectors and hand-mixed batches, using triple the quantity of material indicated for formulation 108C, poured alternately into each sector at intervals of 3 minutes or more between pours. This delay between consecutive pours is necessary to prevent overheating and consequent "burning" of foam.

When the molds were filled with foams, the partitions were removed and the sectors fused with the final pour. The block of foam was then removed and cut to 24 × 24 × 6 inches. Ten blocks with density from 5.4 to 5.6 lb/cu ft, and ten of density from 4.0 to 4.3 lb/cu ft, and the four blocks of 7.5 to 8.3 lb/cu ft density made previously were shipped to Natick.

In view of possible interest in foams of densities of less than 4 lb/cu ft, considerable effort was spent on the development of formulations for the preparation of unfilled, rigid low-density foams of the 108C type. Formulation 108, shown in Table XX, was found satisfactory.

Table XX

Formulation 108

Ingredient	Content (gm)
Quadrol	60.0
Castor oil, AA	40.0
Vinyl toluene	20.0
Vel (solution)	2.0
Glyceryl monoricinoleate S	8.5
Triethylamine	0.5
Ethyl cellulose N-100	6.0
Water	1.0
Toluene diisocyanate (Nacconate 80)	99.6

The rigid foams prepared by this formulation had densities of 2.5 to 3.0 lb/cu ft and energy-absorption values of 30 to 45 in-lb/cu in of crushed volume.

Many difficulties were encountered in attempts to prepare large blocks of foam by formulation 100C. Burning and fissuring were hard to control. A 15-minute interval between pours is the minimum for preventing over-heating. Fissuring may be reduced or eliminated by a 10 per cent reduction in diisocyanate from the equivalent (NCO:OH), but this results in a sharp decrease in foam rigidity and in energy-absorbing capacity. Further study of processing variables revealed that satisfactory products of varied density may be produced by merely increasing the ethyl cellulose content of the standard 100C formula 50 per cent (from 6 to 9 grams), and varying the water content (with compensating diisocyanate).

Ten blocks with densities of 4.5 to 5.0 lb/cu ft and ten blocks with densities in the 6 to 7 lb/cu ft range were made and shipped to Natick. The denser foams of 100C were made in molds 30 × 30 × 10 inches, using for each pour triple the quantities shown in Table XXI.

Table XXI

Formulation 100C Used for Foams of 6 to 7 lb/cu ft Density

Ingredient	Content (gm)
Quadrol	60.0
Castor oil, AA	40.0
Diallyl phthalate	20.0
Petromix #9	2.0
Witco 77/86	2.0
Ethyl cellulose (N-100)	6.0
Water	0.8
Nacconate 80	88.5

These were then cut to blocks 24 × 24 × 6 inches.

In adjusting this formulation for the pouring of foams with densities in the 4.0 to 5.0 lb/cu ft range by varying water and Nacconate 80 content, the following relationship between water content (with compensating diisocyanate) and density of foam was observed.

Table XXII

Effect of Water and Diisocyanate Content on Density of Foam 100C

Water (gm)	Toluene Diisocyanate (80:20 2,4-:2,6-isomers) (gm)	Density (lb/cu ft)
0.5	87.0	7.95
0.8	88.5	6.06[a]
1.0	89.5	5.20
1.2	90.4	4.62
1.4	91.4	4.12
1.7	92.8	3.29[b]

a. Used for the ten large blocks; densities, 6.0 to 7.0 lb/cu ft.
b. Used for ten large blocks; densities, 4.5 to 5.0 lb cu ft.

These densities were for foams poured at random, using triple quantities of the materials indicated (Table XXI) for each pour. An interval of 20 minutes between pours was required to avoid excessive heat buildup (170 to 180°C) and consequent degradation of foam. Heat emissivity of foam was too low to permit the pouring of foam layers greater than 3 inches in thickness without "burn" and deterioration in properties, regardless of interval between pours.

The tendency to fissure of foams made by formulation 100C becomes more marked as density is lowered. Fissuring at low density was reduced by increasing the amount of ethyl cellulose (N-100).

The large blocks of low-density foam (4.5 to 5.0 lb/cu ft) were made by the following modification of the 100C formulation.

Table XXIII

Formulation 100C Used to Prepare Foams of 4.5 to 5.0 lb/cu ft Density

Ingredient	Content (gm)
Quadrol	60.0
Castor oil, AA	40.0
Diallyl phthalate	20.0
Petromix #9	2.0
Witco 77/86	2.0
Ethyl cellulose (N-100)	18.0
Water	1.7
Nacconate 80	92.8

These blocks were prepared by single pours of the above formulation, using twelve times the quantities indicated, into a breakdown plywood mold, lined with aluminum foil, and with inside dimensions of 28 × 28 × 3-1/8 inches. Two of these blocks were cemented together with a small amount of the foam mix and cut to 24 × 24 × 6 inches.

4. Thermal Studies

a. Heat Conductivity Measurements

Thermal conductivity measurements on selected experimental semirigid and rigid foams were carried out at the National Bureau of Standards under the supervision of Mr. H. E. Robinson, Chief, Heat Transfer Section. Castor oil foams, castor oil-Quadrol foams, and modified castor oil-Quadrol foams (modified with diallyl phthalate (100C), and vinyl toluene (108C)) were prepared. Density was varied. Some of the foams were filled with varying amounts of aluminum powder. This was done at Mr. Robinson's suggestion that reflective surfaces on the pores of the foam, assuming discontinuity of the aluminum-powder phase, might reduce heat transfer. The samples of foam submitted were 12 inches square and 1 to 3 inches thick. Formulations used for the preparation of the samples, and the foam densities are shown in Table XXIV.

The thermal conductivities of the specimens were measured in an apparatus of the type described by Lang.* The heat flow meter of the apparatus was calibrated just prior to the measurements, using a National Bureau of Standards 8-inch guarded hot plate conforming to ASTM C177-45, and 1-inch specimens of 0.22 Btu/hr/sq ft/in/°F conductivity.

The test results are given in Table XXV. Cell sizes are approximate values considered to be representative averages for the specimens; actual cell diameters varied over a ratio of 5 or 10 to 1 in some specimens locally, as well as exhibiting trends in typical sizes from one face of the specimen to the other.

The values for thermal conductivity of the experimental foams are similar to those reported by C. J. Harrington of DuPont for castor oil foams. The K values given for castor oil foams ranged from 0.26 to 0.30 Btu/hr/sq ft/in/°F at densities of 2 lb/cu ft to 8 lb/cu ft. The

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* Technical Paper TP170, ASTM Bulletin 216, September 1956.

Table XXIV

Formulations of Foams for Heat Conductivity Studies

Sample	Formulation	
	Ingredient	Content (gm)
A (108C)	Quadrol	60.0
1 × 12 × 12 inches	Castor oil, AA	40.0
Density, 6.04 lb/cu ft	Vinyl toluene	20.0
Density, 4.33 lb/cu ft	Petromix #9	2.0
	Witco 77/86	2.0
	Ethyl cellulose, N-100	6.0
	Water	0.5
	Nacconate 80	74.0 ml
B (108)	Quadrol	60.0
1 × 12 × 12 inches	Castor oil, AA	40.0
Density, 2.49 lb/cu ft	Glyceryl monoricinoleate	8.5
Density, 2.56 lb/cu ft	Vel (liquid)	2.0
	Ethyl cellulose, N-100	6.0
	Triethylamine	0.5
	Water	1.0
	Nacconate 80	99.6 ml
C (PA)	Castor oil, AA	120.0
1 × 12 × 12 inches	Glyceryl monoricinoleate	12.0
Density, 3.03 lb/cu ft	Witco 77/86	1.0
Density, 3.54 lb/cu ft	Ethyl cellulose, N-100	8.0
	Nacconate 80	112.0 ml
E (100C)	Quadrol	60.0
1 × 12 × 12 inches	Castor oil, AA	40.0
Density, 2.58 lb/cu ft	Diallyl phthalate	20.0
Density, 2.50 lb/cu ft	Glyceryl monoricinoleate	8.5
	Triethylamine	0.5
	Vel (liquid)	2.0
	Nacconate 80	99.6 ml
H (PA)	Castor oil, AA	120.0
3 × 12 × 12 inches	Glyceryl monoricinoleate	12.0
Density, 3.19 lb/cu ft	Aluminum powder	12.0
Density, 3.20 lb/cu ft	Witco 77/86	1.0
	Ethyl cellulose, N-100	8.0
	Water	1.5
	Nacconate 80	112.0 ml

Table XXIV (Cont'd)

Sample	Formulation	
	Ingredient	Content (gm)
J and K (108C) 1 × 12 × 12 inches Density, 6.39 lb/cu ft Density, 6.25 lb/cu ft	Quadrol	60.0
	Castor oil, AA	40.0
	Vinyl toluene	20.0
	Aluminum powder	6.6
	Witco 77/86	2.0
	Petromix #9	2.0
	Ethyl cellulose, N-100	6.0
	Water	0.5
	Nacconate 80	74.0 ml
L and M (108C) 1 × 12 × 12 inches Density, 6.69 lb/cu ft Density, 6.64 lb/cu ft	Quadrol	60.0
	Castor oil, AA	40.0
	Vinyl toluene	20.0
	Aluminum powder	16.0
	Witco 77/86	2.0
	Petromix #9	2.0
	Ethyl cellulose, N-100	6.0
	Water	0.5
	Nacconate 80	74.0 ml
N (108) 1 × 12 × 12 inches Density, 2.28 lb/cu ft Density, 2.36 lb/cu ft	Identical formulation to sample B, cut from different block.	

Table XXV

Results of Thermal Conductivity Measurements of Foams

Specimen	Mean Temperature (°F)	Thermal Conductivity	Density (lb/cu ft)	Cell Size, Approximate Average (mm)	Thickness (in)
A1	83.2	0.300	6.04	1.0	0.99
A1	83.5	0.295	6.04	1.0	0.99
A2	64.6	0.282	4.33	0.8	1.03
B1	83.3	0.306	2.49	0.8	0.99
B2	64.5	0.291	2.56	0.8	1.00
C1	82.9	0.274	3.03	0.5	1.00
C1	64.7	0.272	3.03	0.5	1.00
C2	64.2	0.273	3.54	0.5	1.01
E1	83.5	0.266	2.58	0.8	0.96
E2	64.7	0.257	2.50	0.8	1.00
N1	83.0	0.290	2.36	1.0	0.99
N2	64.4	0.275	2.36	1.0	1.02
I	83.7	0.322	3.20	3.0	2.04
H	65.1	0.275	3.19	1.5	2.05
J	83.1	0.345	6.36	2.5	1.00
K	64.3	0.334	6.25	2.5	1.00
L	83.2	0.405	6.69	2.5	0.98
M	64.4	0.398	6.64	2.5	1.00

K values for the experimental foams were 0.26 Btu/hr/sq ft/in/°F to 0.40 Btu/hr/sq ft/in/°F over the density range of 2.4 to 6.6 lb/cu ft. The foams are good insulating materials. Aluminum powder as filler did not reduce rate of heat transfer.

b. Specific Heats

The heat capacities of foams prepared by formulations 100C and 108C, and of the principal components for which specific heats were not available, were determined. The measurements were made at the Crippen and Ehrlich Laboratories.

The bomb in which the samples were weighed was blanked by heating it empty in a water bath to the desired temperature (80°C) for half an hour to ensure equilibrium. The bomb was then transferred quickly to a calorimeter containing a measured quantity of water at 20°C. The water was agitated continuously and measured to 0.001°C on a regular calorimeter thermometer every 15 seconds until equilibrium was again established. This value was then subtracted from that of the samples run under identical conditions. It was not necessary to apply corrections for radiation loss since the samples were treated identically. Materials of known specific heat were measured and showed the accuracy to be ±5 per cent. Measured specific heats are shown in Table XXVI.

Table XXVI

Measured Specific Heats: Foams and Components

Material	Specific Heat (cal/gm-°C)
Formulation 100C (density = 6.07 lb/cu ft)	0.49
Formulation 108C (density = 5.8 lb/cu ft)	0.47
Diallyl phthalate	0.32
Sulfated monoglyceride of coconut fatty acids (Vel)	0.61
Triethylamine	0.51
Ethyl cellulose (N-100)	0.34
Glyceryl monoricinoleate S (Glyco Products)	0.50
N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine (Quadrol)	0.48

Table XXVI (Cont'd)

Material	Specific Heat (cal/gm-°C)
Toluene diisocyanate (Nacconate 80)	0.29
Castor oil (Fisher's AA)	0.45
Witco Emulsifier 77/86 (composition unknown)	0.38
Petromix #9 emulsifier ("built" sulfonated petroleum soap containing free oil and sodium stearate)	0.49

The published value for the specific heat of vinyl toluene at 30°C is 0.42 cal/gm.

c. Rates and Heats of Reaction

Research by industry and government on reaction rates of various polyol-isocyanate systems has shown the kinetics of these systems to be complex. There are several reactions that may occur when a diol or polyol is reacted with a di- or polyfunctional isocyanate. The predominant reaction is the formation of urethane.

$$-RNCO + -R-OH \longrightarrow RNHC(=O)-OR \qquad (1)$$

If more than equimolar amounts of isocyanate are used, a secondary reaction takes place:

$$-RNCO + RNC(=O)(H)-OR \longrightarrow RNC(=O)-OR,\ C(=O)HNR \qquad (2)$$

The rate of the reaction forming carbanilide is much slower than that forming urethane; therefore, in polyurethane formation (where exact equivalence is required) the rate of carbanilide formation is negligible. If water is present, other reactions disrupt the original equivalence between -RNCO and -R-OH:

$$-RNCO + H_2O \longrightarrow RNHCOOH \longrightarrow RNH_2 + CO_2 \qquad (3)$$

$$-RNH_2 + RNCO \longrightarrow RNHCNHR \quad (O)$$

The hydrogens of the urea groups are much more reactive with diisocyanates than those of the urethane group and hence much more useful as cross-linking sites. These are the important reactions for the preparation of foams without an accessory source of heat.

Relative reactivity of the -NCO group with various compounds with active hydrogen has been found to be R-OH > HOH > urea > urethane. The relative rates of reactivity between an isocyanate group and a primary and a secondary hydroxyl group is approximately 3:1. These reactions are accelerated by bases, metallic salts, and Lewis acids. They are inhibited by traces of hydrogen chloride, certain other acid chlorides, sulfur dioxide, and even carbon dioxide. With appropriate catalysis, isocyanates react more readily with water than with the hydroxyls of alcohols, diols, or polyols. Water retards reactions catalyzed by ferric acetyl acetonate by destroying the catalyst.

The para-NCO group of toluene diisocyanate (the least expensive of the diisocyanates sold in the United States) is about 10 times as reactive as the ortho-NCO at 15°C; 8 times as fast at 20°C, and 2.7 times as fast at 100°C. The activation energy of the para-NCO group has been estimated to be 6 kcal/mol and that of the ortho-NCO about 10.4 kcal/mol. Solvents used as additives have a marked effect on reaction rates. For example, the effect of solvent on the reaction of phenyl isocyanate with methanol at 20°C has been found to vary 71-fold in the order benzene > toluene > nitrobenzene > di-n-butyl ether > n-butyl acetate > methyl ethyl ketone > dioxane > acetonitrile. The rate depends primarily upon the dielectric constant of the solvent.

As part of the present study at Atlantic Research, experimental work on heats of reaction dealt chiefly with the influence of the various components of the foaming systems on the exotherm and the use of catalysts to modify it. The total heat liberated and the rate of liberation are two important factors in the processing of highly exothermic, foamed-in-

place systems. The reactions were carried out in paper containers placed in an insulating block of polyurethane foam. Temperatures were measured by thermocouples and thermometers placed slightly below the center of the reacting mixtures. Important aspects of this work are discussed below.

Equivalent quantities of toluene diisocyanates and water did not give a perceptible heat of reaction when mixed at 23°C. This was attributed to immiscibility in the absence of a coupling (solubilizing) agent.

The rate and heat of reaction of 0.2 equivalent each of castor oil (Fisher AA grade) with toluene diisocyanate (Nacconate 80, an 80:20 mixture of 2,4- and 2,6-isomers) was studied with and without catalysts at 23°C. Castor oil, in the absence of catalysts, reacted very slowly with toluene diisocyanate. It failed to gel on standing overnight at room temperature. The addition of catalysts improved the rate of reaction with a maximum exotherm that increased the ultimate temperature to 56°C and permitted set-up in some cases upon standing overnight. The different catalysts used and their effect on exotherm and gelation are discussed below and tabulated in Table XXVII. None of these blends foamed.

On a humid day, when the experiment with the most basic catalyst, triethylamine, was repeated with twice the quantities of reactants, the mixtures foamed slightly within 30 seconds of mixing, and the temperature rose to a maximum of 67°C. Gelation occurred within 11 minutes of mixing. The enhanced rate of reaction and short gelation time were attributed to more atmospheric moisture and larger mass of reactants.

Quadrol, an important component of the foaming systems, is a basic polyol. Its reactions with toluene diisocyanates are highly exothermic. An equivalent of Quadrol, when reacted with an equivalent of toluene diisocyanate (100 per cent of the 2,4-isomer) attained a temperature of 195°C in 5.5 minutes. The exotherm produced by reacting various blends of the 2,4- and 2,6-isomers of toluene diisocyanate at the one equivalent level were similar. The results are shown in Figure 1. At these temperatures the polymers which are formed melt and degrade.

Table XXVII

Rates and Heats of Reaction of Castor Oil with Toluene Diisocyanate (Nacconate 80)

Catalyst	Molecular Weight	Equivalent Weight	Equivalents Used	Equivalents (gm)	Mixing Time (min)	Maximum Temperature (°C)	Standing for 24 hours
Zinc stearate	632.3	632.3	0.01	6.32	8	36.5	Rubbery, tacky
Zinc stearate	632.3	632.3	0.02	12.64	9	36.0	Rubbery, tacky
n-Methyl morpholine	101	101	0.1	10.1	5	55	Rubbery, tacky
n-Methyl morpholine	101	101	0.2	20.2	5	55	Rubbery, tacky
Triethylamine	101	101	0.1	10.1	4.5	56	Rubbery, tacky
Triethylamine	101	101	0.2	20.2	4	56	Rubbery, tacky
Triethanolamine	149.2	49.7	0.075	3.73	6	48	Viscous, liquid
Triethanolamine	149.2	49.7	0.15	7.46	6	49	Viscous, liquid
Sodium tartrate	190.1	47.5	0.1	4.75	8.5	40	Viscous, liquid
Sodium tartrate	190.1	47.5	0.2	9.5	8	37	Viscous, liquid
Sodium stearate	306.5	306.5	0.02	6.12	13	42	Viscous, liquid
Sodium stearate	306.5	306.5	0.04	12.24	14	39	Viscous, liquid
Sodium salicylate	160.1	80.05	0.1	8.0	13	38	Rubbery, tacky
Sodium salicylate	160.1	80.05	0.2	16.0	13	39	Rubbery, tacky
Sodium citrate	249.1	73.5	0.1	7.35	10.5	41	Rubbery, tacky
Sodium citrate	249.1	73.5	0.2	14.7	7	37	Rubbery, tacky

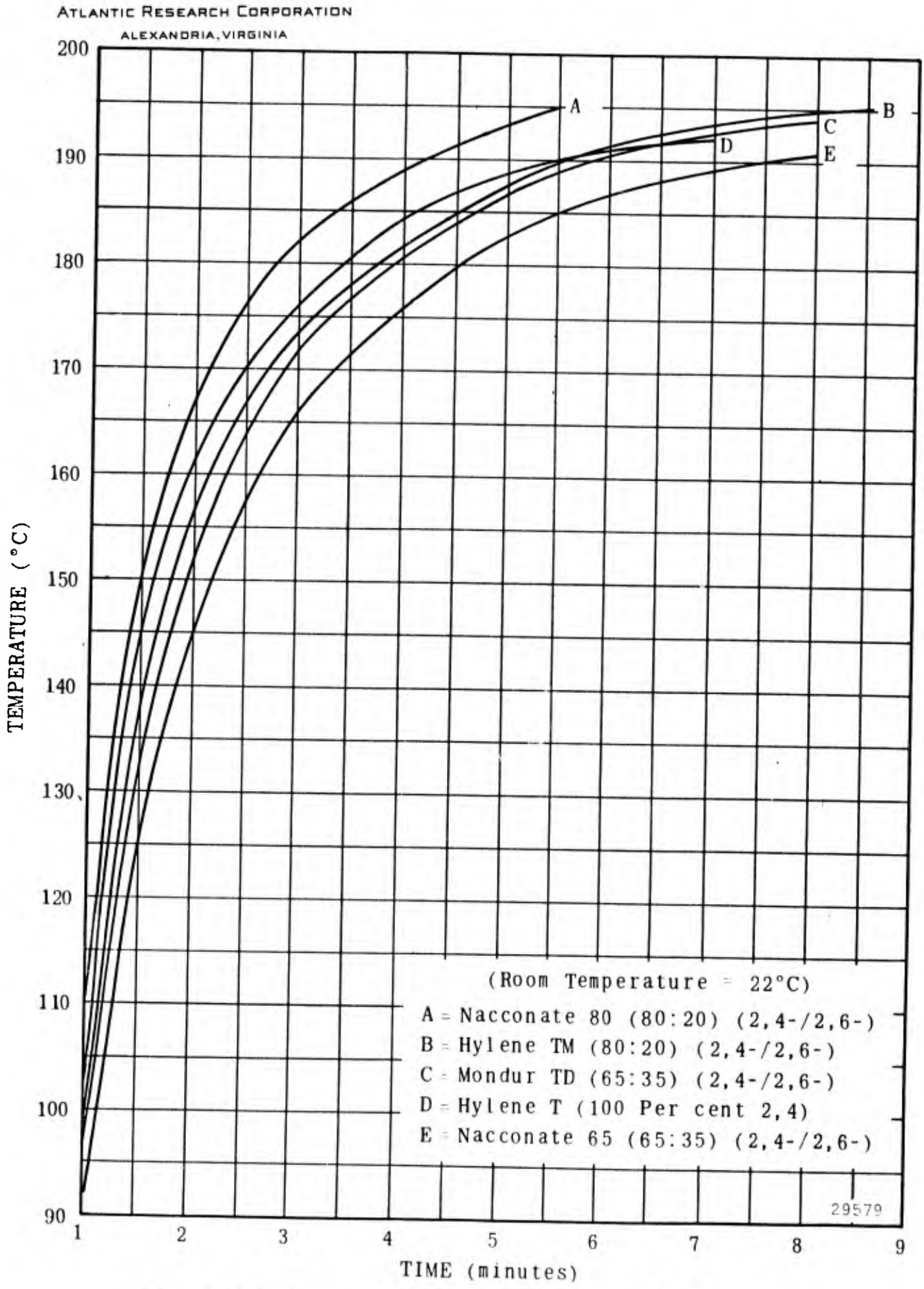


Figure 1. Influence of Isomeric Ratio (2,4-: 2,6-Toluene Diisocyanates) on Rate and Heat of Reaction of Toluene Diisocyanate with Quadrol (one equivalent each).

Quadrol, as used in formulations for the production of foamed-in-place energy-absorbing structures, such as formulations 100C and 108C, gives a higher exotherm than desired. Reduction in the heat of reaction would permit the casting of larger sections without the risk of overheating and degradation. Reduced reaction rates and lower exotherm were sought by adding functional organic acids. The effect of adding various organic acids on heat of reaction of Quadrol and toluene diisocyanate (100 per cent 2,4-isomer)(one equivalent each, with compensating toluene diisocyanate for the acids added) is shown in Figure 2 and Table XXVIII. The behavior of beta-propiolactone, which reacts with water to form beta-hydroxypropionic acid, and that of lactic acid, alpha-hydroxypropionic acid, should be noted. The lactone enhances the exotherm, but lactic acid is an effective agent for reducing it.

The reaction between Quadrol and toluene diisocyanates was even more vigorous in foaming systems when emulsifiers, water, and foam stabilizers were added. Some of these formulations, when mixed at 23°C, attained temperatures as high as 238°C.

Saran-filled mixtures of the type shown in Table XXIX also decompose with the evolution of much gas and smoke.

The exotherm of the foamed-in-place systems based on Quadrol, selected for use over a wide range of temperature (formulations 100C and 108C), approach the maximum that can be tolerated, 165°C, without loss in strength-to-density ratio of material. Modification of these formulations to reduce the exotherm may be necessary to permit use in the field at ambient temperatures higher than the maximum (85°F) used in the laboratory.

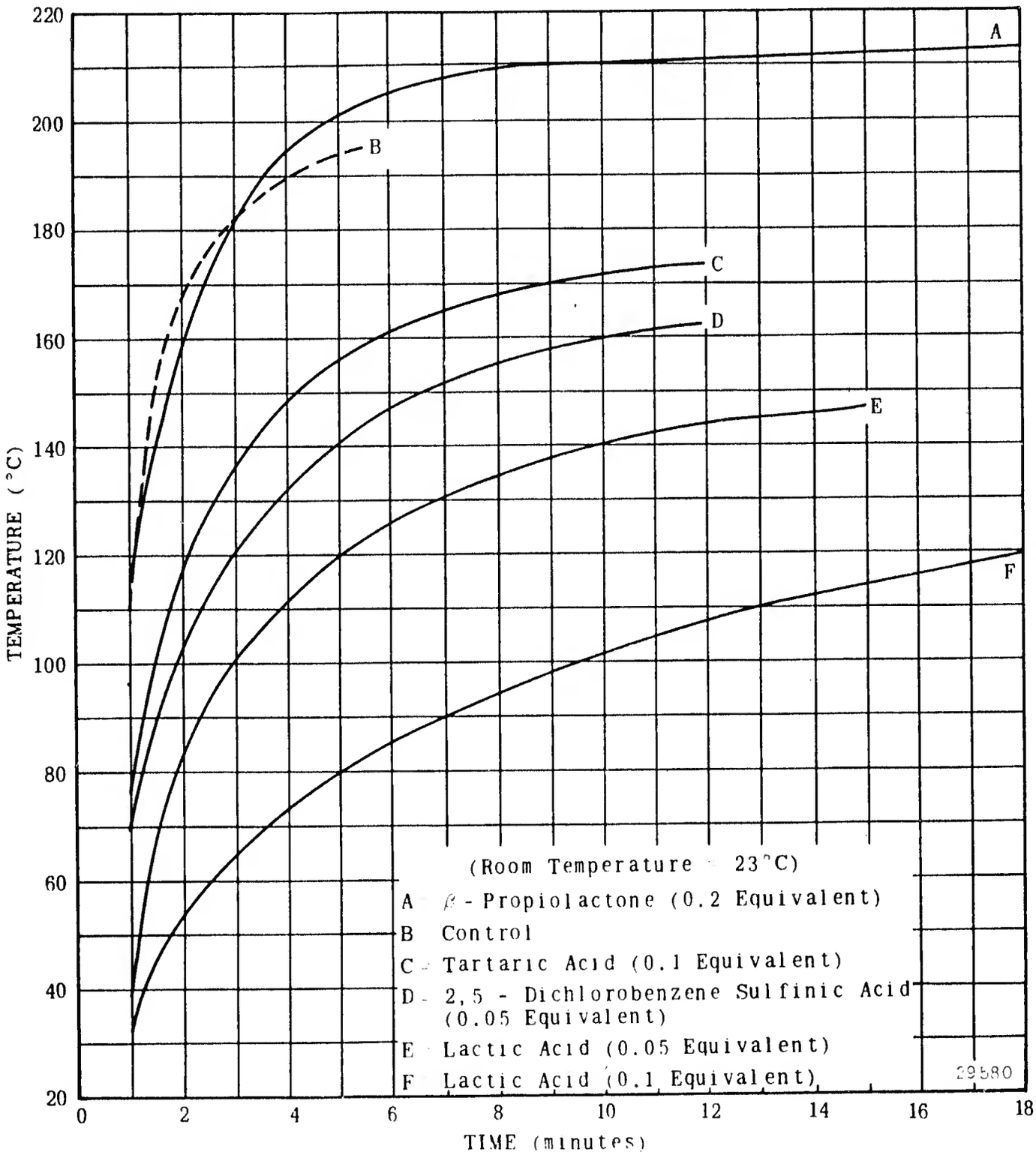


Figure 2. Effect of Acidic Materials on Rate and Heat of Reaction of Quadrol with Toluene Diisocyanate (one equivalent each).

Table XXVIII

Effect of Functional Organic Acids on the Heat of Reaction of Quadrol with Toluene Diisocyanate (One Equivalent Each) with Compensating Equivalent of Toluene Diisocyanate

Compound	Content (gm)	Equivalent	Toluene Diisocyanate (gm)	Maximum Temperature (°C)	Time to Reach Maximum Temperature (min)
Control	-	-	87	195	5.5
Beta-propiolactone	7.2	0.2	104.4	213	18
Tartaric acid	4.75	0.1	95.7	173	12
2,5-dichlorobenzene sulfinic acid	10.5	0.05	91.4	162	12
Lactic acid	2.25	0.05	91.4	147	15
Lactic acid	4.5	0.1	95.7	122	21

Table XXIX

Foam Formulation Containing Saran

Ingredient	Content (gm)
Quadrol	73
Saran F-120, 1000 cps	40
Nacconate 80	87

C. IMPROVED FORMULATIONS

1. Reduction of Isotherm

a. Modification of Foaming Systems

Reduced exotherm was needed for the pouring of thicker foams. There were several obvious approaches to the problem of controlled exotherm for polyurethane foam systems.

(1) Dissipation of part of the heat of reaction of -NCO and -OH groups in a prepolymer step preceding the final reaction at the time of foaming. This approach was rejected as impracticable at the start of this program principally because of unpredictable shelf life. Moisture present at the time of processing and packaging and which gains access to package on storeage, reacts with the prepolymer with consequent chain extension, cross-linking, and gelation.

(2) Increased distance between -NCO and -OH groups along the molecular chains of the reactants to reduce the -NCO:-OH concentration per unit of mass of reactants and hence the total exotherm. This approach has some promise for systems of interest in this study if the increases in distances are small. Otherwise, the foams may have too much resilience for foamed-in-place, energy-dissipating applications.

(3) Reduction in reactivity of reactants to reduce the rate and increase the period over which heat is released. This method when used with appropriate catalysts, polyols, diisocyanates, and polyisocyanates for the control of reaction rate has been widely used. The method has merit and could be used to modify the foam formulations for the control of exotherm.

(4) The use of diluents to reduce heat buildup has been tried. Some mineral fillers act as "heat-sinks" but these are too bulky for transport to the field. Liquid, nonreactive diluents, such as Freons, have been used instead of water as blowing agents to prepare foams of exceptionally low heat conductivity. These were tried but were found to have too high vapor pressures for successful blowing of foam systems as "hot" as those required in this study, when reactions were started at room temperature.

(5) Reduction of diisocyanate relative to polyol to reduce heat of reaction. This method was tried in order to determine the level of concentration of reactants, such as -NCO + -OH, for a given exotherm, and the effect of the reduction of diisocyanate on foam properties by the 100C formulation.

b. Reduction of Diisocyanate:Polyol Ratio

These foams were prepared in a mold 5 × 5 × 5 inches, lined with aluminum foil. The diisocyanate (Nacconate 80), using the standard 100C formulation and 0.85 gram of water, was varied from 87 to 57.3 grams. Effect of reduction of diisocyanate on exotherm and properties of the foam prepared at 26°C is summarized in Table XXX.

Table XXX

Foams Properties and Exotherm at Reduced Diisocyanate Content

Nacconate 80 Content (gm)	Maximum Temperature at Center of Foamed Sample (°C)	Foam Rise (in)	Foam Characteristics
87 (control)	189	4-5/16	Fissures, discoloration, rigid.
81.9	179	4-1/8	Fissures, discolored rigid.
75.6	168	3-13/16	Fissures, no discoloration, rigid.
69,5	160	3-5/8	No fissures, no discoloration, rigid.
57.3	142	3-3/4	No fissures, no discoloration, rigid.

Quadrol reacts preferentially with diisocyanate but cross-linking of the castor oil, depending on the exotherm produced, may be adequate for the rigidity desired.

c. Negative Catalysts

The major source of heat developed during the preparation of foams by formulations 108C and 100C was that derived from the reaction between Quadrol and TDI. Although a highly exothermic reaction was essential for the preparation of self-curing foams at low temperatures, the heat evolved at elevated temperatures (ambient) limits the quantity of material (and the thickness of foam) that one can pour at one casting of liquids.

Since reaction of -NCO/OH groups are base-catalyzed, acids were tried as means of reducing the exotherm. The formulation used was one in which silicone oil (Union Carbide L-520) could be substituted effectively for ethyl cellulose as the foam stabilizer (Table XXXI).

Table XXXI

Formulation Used for Silicone or Ethyl Cellulose Stabilizer

Ingredient	Content (gm)
Quadrol	60
Caster oil, AA	40
N,N-diallylmelamine	20
Witco 77/86	2
Silicone L-520	.0.2
Water	.1.7
Nacconate 80	87

For the control without acid added, the maximum exotherm produced a rise of the foam temperature to 183°C. Foam rise was 8.25 inches and the density was 3.5 lb/cu ft.

The substitution of 1.7 grams of glacial acetic acid for water (1.7 grams) in the control formulation gave a temperature rise to 192°C, a foam rise of only 3.25 inches and a density of 9.7 lb/cu ft. Hydrochloric acid (1.7 grams concentrated acid) and 1.5 grams of water were then substituted for the water of the control formulation. This gave a temperature rise to 173°C, a foam rise of 10 inches and a density of 2 lb/cu ft.

The following weakly acidic materials compounds were tried at varied concentration levels as negative catalysts in the 108C formulation: dodecyl succinic anhydride, fumaric acid, 4-tert-butyl catechol, nonyl phenol, resorcinol. None gave a significant reduction in exotherm. Since lactic acid in previous tests with formulation 100C had shown considerable activity as a negative catalyst, it too was tried in 108C. A sample of lactic acid, said to be 100 per cent pure was obtained from the U. S. Department of Agriculture. This

material when applied at concentrations of 2 to 4 parts per hundred of foam mixture 108C, caused the foam to collapse.

d. Substitution of Polyols for Quadrol

An experimental Quadrol (Wyandotte Polyol III), a propylene oxide adduct of Quadrol, of lower basicity than Quadrol, higher molecular weight and with more carbon atoms between the -OH groups and the nitrogen atoms, was substituted for Quadrol in formulation 108C. The reduction in exotherm was marked: maximum temperature was 160°C compared to 180°C for the control.

Two other polyols, Niax Triol LK-380 (Union Carbide) and Pluracol TP 440 (Wyandotte Chemical), now used for the commercial production of rigid foams, were substituted for Quadrol in formulation 100C. Hydroxy equivalents are shown in Table XXXII.

Table XXXII

Hydroxy Equivalents for Three Polyols

	Hydroxy Equivalent
Niax LK-380	147
Pluracol TP 440	138.6
Quadrol	73.0

A master batch of the composition was made and in Table XXXIII these polyols substituted for Quadrol to determine their effect on foam properties.

Table XXXIII

Formulation of Master-Batch Y

Ingredient	Content (gm)
Caster oil, AA	38.6
Diallyl phthalate	19.3
Witco 77/86	1.9
Petromix #9	1.9
Silicone L-520	0.08
Water	0.05
	66.83

These polyols were much less reactive than Quadrol and produced less heat during foaming. Relative heats of reaction during foaming are shown in Table XXXIV.

Table XXXIV

Exotherms for Polyols in Master Batch Y

Formulation	Composition: Ingredient	Composition: Content (gm)	Maximum Temperature in Sample (°C)
60526T1	Master-batch Y	66.8	188
	Quadrol	60	
	TDI	90	
60526T2	Master-batch Y	66.8	145
	Niax Triol LK-380	120	
	TDI	90	
60527T1	Master-batch Y	66.8	152
	Pluracol TP440	110	
	TDI-80	90	

Reaction time for these polyols was much less than for Quadrol. The time for maximum foam rise for Quadrol was approximately 45 seconds; the other polyols required 10 minutes. The Niax and Pluracol foams, in contrast to the Quadrol, remained tacky for hours. Foams based on the substitution of these polyols for Quadrol in formulation 100C were resilient and were not tested for energy dissipation. Partial replacement of Quadrol with these polyols, using 10 per cent increments, yielded foams which were more resilient than foams based on Quadrol. This approach was abandoned.

e. Modification of Foams for Increased Brittleness

Experiments proved that, in the absence of an unsaturated polyol such as castor oil, the heat of reaction of diisocyanate with saturated polyol such as Quadrol, would induce homopolymerization of added vinyl monomers to give more brittle foamed structures. Table XXXV shows the base formulation and the monomers used for these tests.

Table XXXV

Foam Formulation Used for Increased Brittleness

Ingredient	Content (gm)
Quadrol	60
Nacconate 80	78
Silicone L-520	0.2
Water	None or variable
Monomer[a]	Variable
Filler	None or variable

a. The monomers used were diallyl phthalate, styrene, ethyl methacrylate, methyl methacrylate, and vinyl propionate.

Styrene monomer combinations yielded more brittle foams than the other monomers. The styrene acted as the blowing agent, and addition of water was unnecessary. Polyvinyl chloride fillers (Geon 126, Geon 121, Pliovic VO) behaved as heat sinks and lowered the exotherm. The optimum ratio of styrene to Quadrol appeared to be 50:60. The foam formulation of Table XXXVI was typical.

Table XXXVI

Typical Formulation of Foams Modified with Styrene

Ingredient	Content (gm)
Quadrol	60
Styrene	50
Geon 126	10
Silicone L-520	0.2
Nacconate 80	78

This foam gave a temperature rise to 150°C and a density of 6.4 lb/cu ft. No fissures or discoloration were present. It powdered on impact.

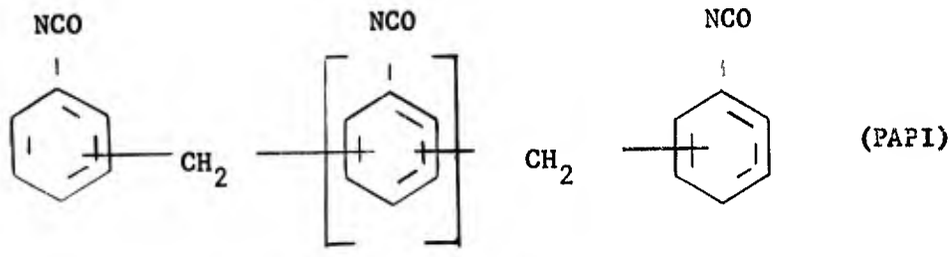
The heat-induced homopolymerization of diallyl phthalate did not appear to proceed rapidly enough for the formation of brittle polymers with high molecular weights.

f. Replacement of TDI with Polymethylene Polyphenyl Isocyanate

Polymethylene polyphenyl isocyanate* (PAPI), when reacted with certain polyols, yields rigid polyurethanes characterized by stability at high temperatures. Since the high heat of reaction of components of foaming systems designed for the production of self-curing foams under field conditions over a wide range of temperatures, frequently resulted in degradation of foam, modification of formulation to improve heat stability of product was attempted.

PAPI was substituted for toluene diisocyanate in formulation 100C and castor oil omitted. Water was also omitted to permit evaluation of brittleness, flexibility, and toughness of unfoamed polymer sheets.

PAPI has an equivalent weight of approximately 135. After exploratory trials with various ratios of olefinic monomer to Quadrol to obtain low viscosity of mix, the basic formulation of Table XXXVII was selected for an evaluation of the PAPI.



(PAPI)

Table XXXVII

Formulation Used to Evaluate PAPI

Ingredient	Content (gm)
Quadrol	60
Diallyl phthalate	53
Silicone L-520	1
PAPI	variable

* Carwin Company, North Haven, Connecticut (Trade Name, PAPI).

The PAPI was used in this formulation at the -NCO group equivalent ranges of 1.12, 1.0, 0.88, 0.76, 0.63, and 0.51, based on the Quardol -OH group equivalent of 1.0. After mixing in paper cups for 20 seconds the mixtures were cast into metal molds to form sheets approximately 0.25 inch thick. Other mixes at the same ratios of isocyanate to polyol were left in the paper cups and heat of reaction measured. All of the mixtures were tack-free approximately one minute after casting.

The polymers formed were brittle, but not glassy, at high ratios or 1:1 ratio of -NCO to -OH; and were tough, impact-resistant materials at the 0.63 equivalent of isocyanate to 1.0 equivalent of polyol. Flexibility increased as the ratio of isocyanate to polyol was decreased below this level. The maximum temperature rose to 155°C at the highest ratio of -NCO to -OH.

Other monomers were substituted for diallyl phthalate in the formulation of Table XXXVII. These were styrene, divinyl sulfone, diallyl maleate, and ethylene glycol dimethacrylate. Only styrene and ethylene glycol dimethacrylate, gave tough, brittle polymers. The formulation containing styrene in Table XXXVIII was typical. Silicone stabilizer was unnecessary.

Table XXXVIII

Formulation Containing PAPI and Styrene

Ingredient	Content (gm)
Quadrol	38
Styrene	10
PAPI	70

The polymer was brittle. The temperature rose to 169°C. There was no discoloration.

2. Handling and Processing Modification of Foam Formulations

a. Foam Stabilizers Other Than Ethyl Cellulose

Ethyl cellulose was not a practical stabilizer in formulation 100C designed for packaging as a two-component system of liquid polyol and diisocyanate. Ethyl cellulose was only partially soluble in the polyol portion. When incorporated, it raised the viscosity of the polyol portion and the undissolved fraction settled out. A soluble foam stabilizer was needed to avoid the necessity of adding it at the time of foam preparation in the field.

Silicone L-520 (Union Carbide), a widely used foam stabilizer, was substituted for ethyl cellulose in formulation 100C to compare its influence on foam properties with that of ethyl cellulose. A resin master batch of the composition in Table XXXIX was prepared.

Table XXXIX

Formulation of Master Batch for Silicone L-520 as a Substitute Stabilize for Ethyl Cellulose

Ingredient	Content (gm)
Quadrol	60
Castor oil, AA	40
Diallyl phthalate	20
Witco 77/86	2
Petromix #9	2

Aliquots of 124 grams of this mixture blended manually with Silicone L-520, 90 grams of toluene diisocyanate (Nacconate 80), and water (as required for variations in density of foam). Mixing time after addition of diisocyanate was 15 seconds. The mixtures were cast and foamed in cardboard boxes, 5 × 5 × 8 inches, lined with aluminum foil. Ethyl cellulose (6 grams) was used in the control series. The variables and their effect on density of foam are shown in Table XL.

Table XL

Effect of Silicone L-520 on Foam Density

Formulation	Water (ml)	Ethyl Cellulose (gm)	Silicone L-520 (gm)	Density (lb/cu ft)
60518T1	0.5	6	---	5.15
60519T1	0.5	---	0.7	5.78
60526T1	0.5	---	0.08	5.71
60620T1	2.0	6	---	2.51
60616T2	2.0	---	0.08	1.94
60620T2	1.8	6	---	2.77
60617T1	1.8	---	0.08	1.99
60620T3	1.6	6	---	3.11
60617T2	1.6	---	0.08	2.06

At the time foaming started resin mixtures containing Silicone L-520 were more fluid than those stabilized with ethyl cellulose. Time available for mixing before start of foaming and time for foam rise were less. Maximum exotherm, though similar to that obtained with ethyl cellulose, was attained more rapidly. The tendency to fissure and "burn" was enhanced by the silicone oil. Except where only small amounts of water were used, the silicone oil gave products of lower density.

Blocks 4 × 4 × 4 inches were cut from these foams and energy-dissipating properties measured, on the drop-tester. Substitution of Silicone L-520 for ethyl cellulose did not alter the energy-dissipating characteristics of the foams.

Siloxanes other than Union Carbide's L-520 were substituted for ethyl cellulose. Foam rise is more rapid with the siloxanes than with ethyl cellulose. Their effect on foam rise and cell structure is summarized as follows:

(1) Union Carbide L-520. Foam rise more rapid than with ethyl cellulose; cell structure similar.

(2) Dow Corning 199. Foam rise similar to L-520 but smaller cells.

(3) Union Carbide L-45. Very rapid foam rise but larger cells than with L-520.

(4) Union Carbide X-521. More rapid foam rise but larger cells than with L-520.

Zein, like ethyl cellulose, is insoluble in the resin components of the formulation 100C and is ill-suited for two component systems. Solubility of Zein in various diols and polyols available on the market, was determined at room temperature and at 100°C. It was found that Zein was quite soluble at room temperature in the lower-molecular-weight diols, i.e., ethylene and propylene glycols. It was not soluble in Quadrol, higher-molecular-weight diols, nor polyols.

Solutions of Zein in propylene glycol (25 per cent by weight) were prepared and substituted for ethyl cellulose in formulation 100C. The Zein did not precipitate when added to the castor oil-monomer mixture. Although it was satisfactory foam stabilizer, it offered no advantage over the siloxanes in formulation 100C. However, in some flexible foam systems such as those based on Pluronic L-62 with glyceryl monoricinoleate, it was a better foam stabilizer than the siloxanes.

b. Substitution of Freon-11 for Water as Blowing Agent

When Freon-11 (b.p. 24°C) was used as a blowing agent for the production of urethane foams, insulation properties were attained that were better than those of the standard foams blown with carbon dioxide generated by the water-isocyanate reaction. The effectiveness of freons as viscosity depressants for the castor oil-monomer component of formulation 100C were studied, for their use would facilitate foaming at low temperatures.

Feasibility of their use in formulation 100C was examined, using Nacconate 65 (65:35 blend of 2,4- and 2,6-isomer of toluene diisocyanate) instead of Nacconate 80 (the 80:20 blend of isomers). Nacconate 80 solidifies at approximately 15°C, whereas Nacconate 65 solidifies about 10 degrees lower. Foams were prepared from a master batch of composition shown in Table XLI.

Table XLI

Formulation of Master Batch (100C) Used to Evaluate Freon-11 Blowing Agent

Ingredient	Content (gm)
Quadrol	60
Castor oil, AA	40
Diallyl phthalate	20
Witco 77/86	2
Petromix #9	2
Silicone L-520	0.7

This liquid mixture was precooled to 9°C and blended with 15 grams of Freon-11 before mixing with the Nacconate 65. The density of the foamed products varied from 2.0 to 9.8 lb/cu ft.

Freon-11 (15 grams) was very effective as a viscosity depressant at low temperatures for the castor oil-monomer component, using the composition in Table XLII, which includes triethylamine as a catalyst.

Table XLII

Formulation Used for Freon-11 as a Viscosity Depressant

Ingredient	Content (gm)
Quadrol	60
Castor oil	40
Diallyl phthalate	20
Witco 77/86	2
Petromix #9	2
Silicone L-520	0.7
Triethylamine	0.7

D. FLAME-RETARDING FOAMS

Two types of additives were examined in an attempt to develop a flame-retardant, rigid, brittle foam: (1) inorganic materials normally used as fillers in flame-extinguishing mixtures, and (2) phosphate polyols that could react to become a part of the polymer chain. A third type of flame retardant, the halogenated plasticizers, was excluded, since such materials would increase the resilience of the foam.

Materials of the first type, with the exception of borax, proved to be ineffective; the second type was effective. Three basic formulations were compared. One, HP 88-1 (Table XLIII), containing no olefinic monomer, was used for comparison with formulations 100C and 108C, in order to determine the influence of the olefinic monomer on flame-retardant compositions.

Table XLIII

Formulation HP 88-1

Ingredient	Content (gm)
Quadrol	60
Castor oil	40
Dapon (solid polymer of diallyl phthalate)	5
Water	2
Silicone L-520	6 drops
Nacconate 80	79

At room temperature, HP 88-1 yielded a very uniform foam with a density of 3.2 lb/cu ft.

The fillers applied for flame retardancy of foam were blended thoroughly into the castor oil-Quadrol fraction, and the diisocyanate was then added. The fillers were added, up to 25 parts by weight, in 5-part increments, to 107 parts of the castor oil-Quadrol mixture. Silica (Cabosil) was used at 5 parts only, because of excessive increase in viscosity of the mixture on blending. The fillers used were potassium carbonate, calcium phosphate, potassium oxalate, and polyvinyl chloride.

Twenty-four hours after preparation of the foams, samples were cut into sections approximately 0.5 inch thick, which were then ignited with a torch and observed for burning characteristics. None of these compositions was self-extinguishing.

Borax was tried in a formulation using 60 grams of Quadrol, 50 grams of diallyl phthalate, and 70 grams of PAPI at levels of 6, 12, and 24 grams. Foamed compositions containing 24 parts of borax were slowly self-extinguishing after removal of the source of ignition (burning ceased in 30 seconds).

A phosphate polyol, VC-3-382,* of unknown chemical structure, was added to the three foam formulations, as 5-part increments to 107 parts of the castor oil-Quadrol mixture.

The control formulation HP 88-1, containing no olefinic monomer, became self-extinguishing after the incorporation of only 10 parts (by weight) into the castor oil-Quadrol mixture of the phosphate polyol. Twenty-five parts of the castor oil-Quadrol-olefinic monomer mixture of formulation 100C were needed to render these foams self-extinguishing, and 35 parts, correspondingly, for formulation 108C. The difference in flame retardance of the three foams after incorporation of the phosphate polyol is attributed to the presence of unreacted olefinic monomer in the cells of the foam. Samples were stored 24 hours before testing.

Introduction of the phosphate polyol increased the exotherm, even in the absence of a compensating diisocyanate. These flame-retardant formulations should be useful for the spray-on applications, although they would have higher raw-materials costs.

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* Virginia-Carolina Chemical Company

E. FOAMING AT NEAR-FREEZING AND FREEZING TEMPERATURES

Experiments were set up to determine foaming behavior at 35°F, including mixing time, time for foam to rise, and time for foam to solidify. An ice-bath was used for cooling the ingredients, and maintaining the temperature of all compounds, and the mold, at 35°F, at the time of mixing.

A modified formulation 108C was used. The vinyl toluene (20 grams) was mixed with Nacconate 80 (87 grams) before chilling. This mix was very fluid when cooled to 35°F. Quadrol (60 grams), castor oil AA (40 grams), Witco 77/86 (2 grams), Petromix #9 (2 grams), water (0.5 gram), and Silicone L-520 (0.1 gram) were then blended and chilled to 35°F. At this temperature, the resulting mixture was very viscous.

The castor oil-Quadrol mix was transferred to a water-proofed paper mold partly immersed in the ice bath, and the cold Nacconate 80-vinyl toluene mixture added. The resulting mixture, after being stirred with a wooden paddle, became homogeneous and fluid after 30 seconds, and began to foam after 90 seconds of mixing. The foaming continued for 75 seconds and the foam was set after an additional 15 seconds (non-tacky to the touch). The temperature rose to 160°C. The density of the foam was 4.26 lb/cu ft, and the foam was not discolored. A similar foam prepared at 88°F reached a maximum temperature of 187°C and discolored because of the heat generated. Its density was 6.1 lb/cu ft.

The field production of foams based on castor oil-Quadrol, olefinic monomer-TDI systems of the 100C and 108C types, at temperatures as low as 32°F, were deemed feasible if effective inhibitors were developed for preventing polymerization of olefinic monomer-toluene diisocyanate blends (which are fluid at 32°F) over storage periods of at least two years under field conditions. An alternate procedure would be to add inert liquids, such as Freons, which would maintain fluidity of diisocyanate at low temperature and serve as nonplasticizing blowing agents when blended with the polyol ingredients.

Several variants of the problems that might be encountered in selecting a good inhibitor of polymerization for the monomer-diisocyanate mixtures were considered. Those cases were considered where:

(1) The diisocyanate does not react with the polymerization inhibitor added. Depending upon the concentration required for long-term storage stability, polymerization inhibitors of this type may interfere with polymerization at the time of foaming. The extent of interference would likely depend on the heat of the condensation reaction at the time of foaming, and the use of appropriate additives for removing the inhibitor at the time of foaming.

(2) The diisocyanate reacts with inhibitor and removes it as an insoluble and noninhibiting compound. Inhibitors of this type would be of no value for long storage.

(3) The diisocyanate reacts with inhibitor to yield soluble or partially soluble compounds that behave as redox catalysts, particularly in the presence of trace quantities of certain heavy metals. The redox catalysts in turn promote polymerization of monomer on storage, especially if there is access to air. Inhibitors of this type are obviously undesirable.

(4) The diisocyanate reacts with the inhibitor or with impurities in the monomer, such as water or other compounds with active hydrogens (normally present or added), to form soluble or partially soluble compounds which are effective polymerization inhibitors. This approach is attractive since removal of these inhibitors in the field at the time of foaming should not be difficult, and might not be necessary.

(5) The diisocyanate reacts with monomers containing active hydrogens. This type of monomer would not maintain fluidity of toluene diisocyanates at low temperature. Some of the reaction products might be useful as polymerization inhibitors for other monomer-diisocyanate combinations.

(6) Traces of certain heavy metals, such as copper, manganese, and iron are powerful inhibitors of polymerization. They are not normally used because of the deleterious effects of the metals on resistance to oxidation of polymers prepared from the metal-stabilized monomers. This type of stabilization has possibilities for the present work, since the metallic compounds do not react with diisocyanates and can be converted to highly active catalysts at the time of foaming in the field by the addition of reductants to form redox systems.

Several of the more widely used inhibitors for preventing polymerization of vinyl and diene monomers during shipment and storage, such as quinone, hydroquinone, 4-tertbutyl ortho-cresol, and 2,5-ditert-butyl hydroquinone, were added at concentrations of 20 parts per million to the undistilled monomers such as vinyl toluene, which contains ditertbutyl catechol inhibitor and is used in formulation 108C. Stability of these samples in the presence and absence of toluene diisocyanates (80:20 mixture of the 2,4- and 2,6-isomers) was compared after 60 days storage at 24 to 28°C with that of similar samples containing no added inhibitor. Increase in viscosity as measured by a Brookfield viscometer was used to indicate the relative degree of polymerization during storage.

The results were significant even though some of the viscosity changes after storage are not easily interpreted. The addition of di-isocyanates to undistilled monomers tended to decrease stability, depending on type of monomer, type of stabilizer present, and possibly the kind of unknown impurities. Diallyl phthalate-TDI combinations appeared to be quite stable, since diallyl phthalate does not require the addition of inhibitor. The reason for the decrease in stability caused by the addition of more inhibitor of the types used and the relatively greater efficiency of the hydroquinone group compared to quinone as the inhibitor was not apparent. The excellent stability of the vinyl toluene-hydroquinone-Nacconate 80 combination, as indicated by its low viscosity, was attributed to the formation of a reaction product between hydroquinone and toluene diisocyanate that was highly effective as a polymerization inhibitor. The marked increase in viscosity after 48 hours exposure to air leads one to suspect the presence of an oxygen-initiated redox system.

Undistilled vinyl toluene, to which was added 20 parts per million of one of each of the inhibitors mentioned above, was used within 24 hours of mixing in formulation 108C to determine the effect of the inhibitors on foaming properties. Foam rise and foam density were not affected.

F. FOAMING-IN-PLACE AT LOW TEMPERATURES

1. Modified Polyurethane System

The experimental work in this field was exploratory and limited to trials to determine feasibility of foaming at low temperature. The major obstacle is lack of fluidity of reactants. Toluene diisocyanates solidify at temperatures above 0°C: the 65:35 mixture of 2,4- to 2,6-isomers solidifies at 5°C; the 80:20 mixture at 12°C; and the 100 per cent 2,4-isomer at 22°C.

Styrene and vinyl toluene were used as depressants for the solidification of toluene diisocyanates and as comonomers for castor oil-Quadrol and castor oil-propylene glycol, foamed-in-place systems, and foaming attempted over a temperature range of -28 to 10°C. Styrene and vinyl toluene were satisfactory depressants for toluene diisocyanate (80:20 2,4- to 2,6-isomers) when used at 1:1.5 monomer:toluene diisocyanate ratios over the 0 to 10°C range. Rigid foams were prepared over this temperature range with the styrene-castor oil-Quadrol systems by using strong bases as catalysts. These foams were coarser and denser than those made at room temperature by similar formulations.

Vinyl toluene, with a melting point of -82.5°C (mixed isomers), is a better solidification depressant for toluene diisocyanates for low temperature systems than styrene, which solidifies at -30°C. Flexible foams, although dense, were prepared at -28°C by using vinyl toluene to maintain the diisocyanate in solution and as a comonomer for castor oil-propylene glycol systems. A 2:1 ratio of vinyl toluene to diisocyanate was necessary to maintain fluidity at -28°C. Strong bases were used to initiate reaction. Glycerine could be used as a cross-linking polyol in these systems. The foams failed to cure when left overnight at -28°C but hardened slowly over a 16-hour period when brought to room temperature.

Systems with greater exotherms, and diisocyanates or diisocyanate adducts which are fluid at lower temperatures, are needed. Nacconate 1080H, an adduct of one mole of hexane triol and three moles of toluene diisocyanate, was found to be a useful source of active -NCO groups at 0 to 10°C. This compound, in contrast to the toluene

diisocyanates, was fluid, with no depressant added, over this temperature range. It reacted with polyols and water over this temperature range when catalyzed with triethylamine to produce foams.

2. Ionic Catalyzed Systems

Acid-catalyzed polymerization of unsaturated monomers was selected as the most promising procedure for the production of foams at very low temperatures. Cationic polymerization, instead of anionic, was tried first, since the catalysts are better adapted for field use and reaction rates are faster at low temperatures.

The sources of gas for foaming were liquids, or gases solubilized in the monomers which were released as gas during polymerization, and solids suspended in the monomers which decomposed upon addition of the polymerization catalysts to form gas. Viscosity modifiers were added to thicken the monomers and facilitate entrapment of gas during the polymerization step. The experimental work described below was restricted to trials to determine feasibility of producing foamed-in-place rigid or flexible foams at sub-zero temperatures for possible use as insulating materials.

Styrene was distilled under reduced pressure and dried with cobalt chloride-free drierite. Aliquots of the monomer were then saturated with carbon dioxide* at -28°C by adding crushed dry ice, and left overnight at -28°C. (The freezing point lies between -30°C and -32°C.) The next day, aluminum chloride in methylene chloride was added to the saturated monomer (approximately 0.5 per cent $AlCl_3$ based on the monomer) to initiate polymerization. The monomer slowly became viscous, with liberation of some gas, and hardened overnight at -28°C. There was little foaming, since the liberated gas escaped before gelation occurred. Boron fluoride-etherate was then tried as catalyst. Reaction was instantaneous. Gas was trapped, but crumbled the resinous product.

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* The solubility of CO_2 in styrene at room temperature is 2 cu cm/cu cm of styrene.

Isobutylene, which dissolves more carbon dioxide than styrene does, was saturated with the gas by addition of dry ice. The CO_2-saturated monomer was then polymerized at dry-ice temperature using aluminum chloride in methylene chloride, and boron fluoride etherate, as catalysts. Most of the liberated gas escaped before viscosity increased enough to trap it. There was some foaming. Polymerization rates were slower than anticipated.

Various monomers were saturated with propane and polymerizations effected with boron fluoride, stannic chloride, or aluminum chloride at -30°C. The solvent for the catalysts was ethyl ether. Isobutylene and an isobutylene-styrene mixture (90:10) were saturated with propane and polymerized at -65°C with boron fluoride-etherate. All these monomers foamed vigorously during polymerization but little gas was trapped. Viscosities were too low during the period of gas release.

Polymerization of styrene, vinyl toluene, and vinyl 2-chloroethyl ether initiated with boron fluoride-etherate was instantaneous at -30°C. It was too fast for uniform dispersion of catalyst by hand-mixing. Aluminum chloride was slower. Stannic chloride began to react after 30 seconds, and was readily incorporated into the monomers.

Bentone 38, aluminum stearate, zinc stearate, lead stearate, ethyl cellulose, liquid natural rubber (depolymerized), Butarez (Phillips liquid polybutadiene), and Hycar 1312 (liquid butadiene-acrylonitrile) copolymer, were used to raise the viscosities of monomers and enhance gas-entrapment during polymerization. Aluminum stearate and Hycar 1312 were the most effective materials of the group.

Hycar 1312 dissolved in vinyl toluene gels immediately on contact with stannic chloride. The liquid polymer itself reacts with stannic chloride to form a highly viscous fluid which gradually hardens to a solid which resembles (and probably is) a cyclized rubber. It is very useful as a viscosity modifier.

Pure dinitrosopentamethylene tetramine (Opex 100)* decomposes in the presence of Lewis acids, even at low temperatures, to liberate

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* Opex 100, National Polychemicals, Boston, Massachusetts

nitrogen. This reaction does not appear to interfere with polymerizations initiated with this type of catalyst. It was an effective blowing agent for monomer systems.

Foamed structures of low density were prepared from vinyl toluene at -30°C by using Hycar 1312 as the viscosity modifier, dinitrosopentamethylene tetramine as the source of gas, and either aluminum chloride, boron fluoride-etherate, or stannic chloride as catalyst. These foams were coarse and brittle.

The temperature of foaming was reduced from -30 to -40°C. The monomers selected were vinyl toluene and vinyl-2-chloroethyl ether. Stannic chloride (in ethyl chloride), boron trifluoride-etherate, and aluminum chloride (in ethyl ether) were used as catalysts. Hycar 1312 and aluminum stearate were applied as foam stabilizers, and Opex 100 as the blowing agent. The formulation is shown in Table XLIV.

Table XLIV

Formulation Used at -40°C

Ingredient	Content (gm)
Monomer (containing 5 per cent Hycar 1312)	23.0
Aluminum stearate	1.0
Opex 100	0.1
Catalyst (in solution)	0.8

The monomers with blowing agent and foam stabilizers were cooled to -40°C and the cold catalyst solution (-40°C) added and mixed.

At this temperature vinyl toluene, with aluminum chloride and stannic chloride as catalysts, yielded brittle, non-uniform foams. Aluminum chloride began to react on contact but produced foams of lower density than those produced with stannic chloride. The latter reacts in about 10 seconds after mixing. Boron fluoride-etherate reacted quickly but failed to trap gas and produce foam; it did not gel the Hycar 1312 before the liberated gas escaped.

Vinyl-2-chloroethyl ether reacted instantly with all three catalysts without foaming. Polymerization was violent and in some cases the polymer was blown from the container. Foam stabilizers were not used, since neither Hycar 1312 nor aluminum stearate was soluble in the monomer at -40°C.

G. PHYSICAL TESTING

1. Description of Tester

The purpose of the physical testing program was to recommend those formulations which were most likely, with improvement of chemical composition and techniques of production, to prove satisfactory. Quantitative results of testing were required. A simple laboratory drop-tester was constructed to meet these needs. A sketch of the drop-tester is given in Figure 3. The base, made of cold rolled steel, and the anvil, made from hardened vanadium steel, together weighed 480 pounds and rested on a concrete slab. The guide rods, made from 0.5-inch-diameter steel rod, extended from the ceiling to the anvil. Linear ball bearings* were used to reduce the friction between the hammer and guide rods. The hammer weight could be varied from 7 to 60 pounds. The hammer was held in position by an electromagnet** and was released by cutting off the current to the magnet. The maximum drop-height was 13.25 feet, corresponding to an impact velocity of about 29 ft/sec.

For testing, the sample was placed on the anvil and centered by eye. The hammer was then released from the chosen height and impinged on the sample. The anvil was designed for a sample 4 × 4 inches in cross-section.

2. Measured and Calculated Quantities

The following measurements were made: hammer height and weight; original length, width, and thickness of the sample; final thickness of the sample; height of bounce of the hammer. The bounce height, used to give an indication of the resilience of the sample, was estimated by eye; the measurement was rough and the resulting approximations were erratic. In making computations of the impact energy per unit volume crushed, it was assumed that all energy was dissipated in the sample.

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* Thompson Industries No. A81420.

**Central Scientific No. 79647.

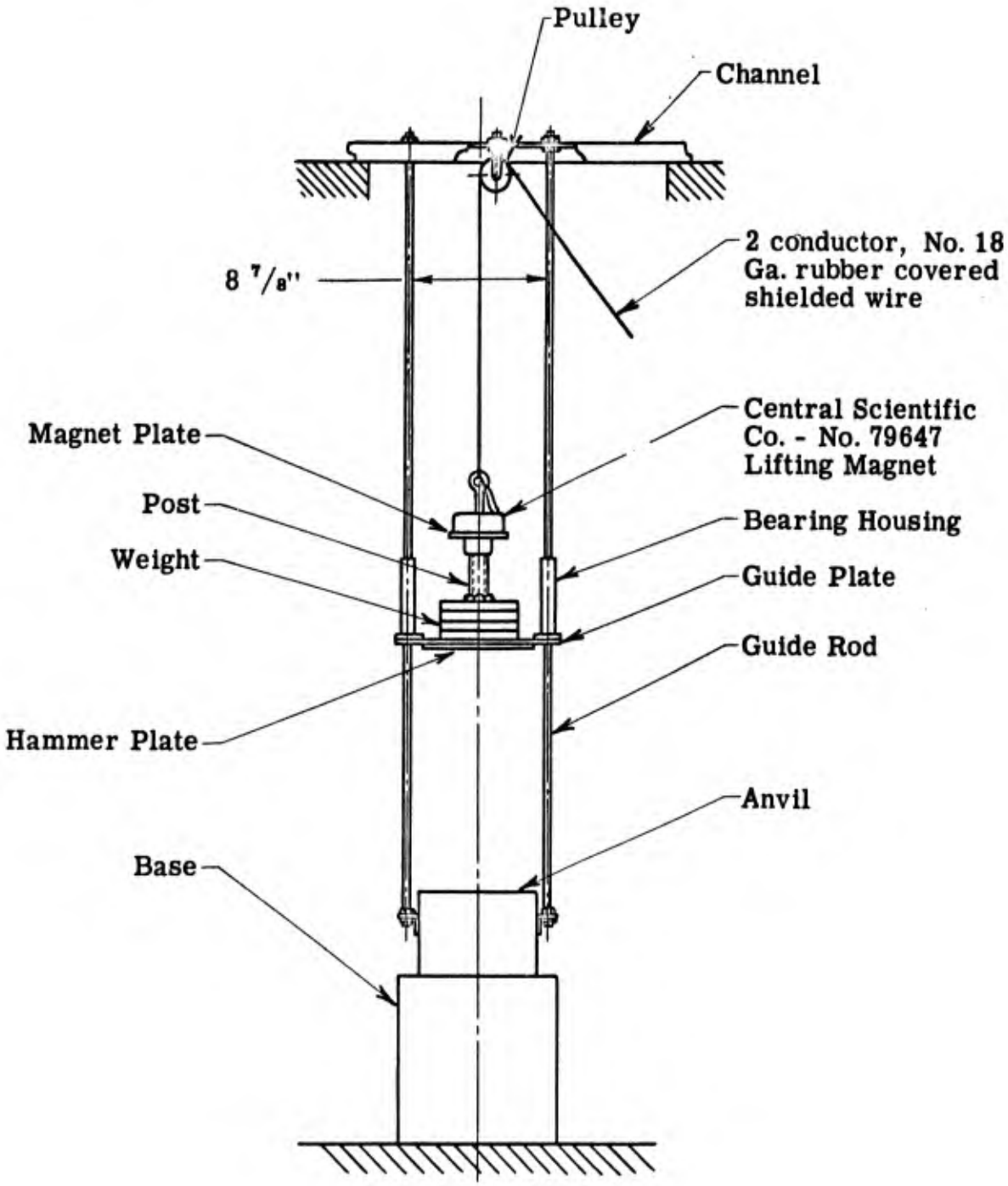

Figure 3. Drop-Tester.

3. Effect of Experimental Parameters

When a given foam sample is to be tested, the only experimental parameters which can be varied are the height and weight of the hammer. A few experiments were carried out with a series of foam samples of the same density using various hammer heights and weights. Variations in kinetic energy of the impacting hammer gave the same measured values of energy absorbed per unit volume crushed, within the (rather large) experimental error. Hence, it was assumed, for purposes of our screening tests, that effects of kinetic energy, impact velocity, or hammer weight on the measured energy-absorption characteristics of foams could be considered negligible. Obviously, however, the energy had to be great enough to cause some crushing and not great enough to "bottom".

H. COMPARISON OF FOAMS WITH DIFFERENT DENSITIES

Early in the testing program it became clear that the density of a foam sample has an important effect on the measured energy-absorption properties of the sample. Although it is possible to control the density of a foamed structure over rather wide limits, it is not in general possible to obtain a sample with a predetermined density in the early investigations of a given foam. Hence a means of comparing foams of different densities was desired. An analysis of energy absorption was carried out using a simplified model of the structure and behavior of a rigid plastic foam.

Consider a honeycomb structure with cubical cells. Let the repeating unit be a cubical space, the length of an edge being ℓ, with three walls of thickness, x. The cell is completely enclosed, of course, by the walls of neighboring structural units, except that the cells at three of the surfaces bounding a foam sample in the shape of a rectangular parallelopiped will lack one wall and the cells at four corners will lack two walls. This is a close approximation to an actual foam sample.

Because all cells are alike, the density of the foam will equal the density of the structural unit. Let the density of the wall material be d. The density of the foam, D, will be given by

$$D = (3\ell^2 + 3\ell x + x^2)\, xd/(\ell + x)^3$$

Let the ratio of the length of the cubical space to the wall thickness be k, so that

$$\ell = kx$$

We then have

$$D = (3k^2 + 3k + 1)d/(k + 1)^3 \qquad (1)$$

as the relation between the density of the foam and the density of the foam material in terms of the parameter describing the structural unit. The density of the gas filling the cubical space is neglected here in comparison with the much greater density of the wall material.

When the value of k is 30, we calculate that D = 0.094d, giving a foam density of 5.9 lb/cu ft for a plastic material whose specific gravity is 1.0. This value is in the range of interest. For light foams, k will be large, and an approximation to Equation (1) is given by

$$D = 3d/k \qquad (2)$$

This approximation is in error by 6 per cent when the value of k is 30.

Equation (1) shows that foams can be constructed with the same density but with different pore sizes, provided the ratio of wall-thickness to pore-size remains constant. We now need to know whether the variation of pore-size, keeping the density constant, will cause a variation in strength characteristics.

Assume that a vertical load is applied to a foam sample and that the walls of the cells are arranged vertically and horizontally. Assume, further, that the horizontal walls serve only to constrain the load-bearing vertical walls and that the vertical walls comprise a series of long columns which fail by buckling, one after the other, when the load is applied.

Euler's formula* for the failure of a long column by buckling is

$$P = n\pi^2 EI/\ell^2$$

where P is the critical load, n a constant depending on the constraints, E Young's Modulus, I the moment of inertia, and ℓ the length. Consider one cell wall as one column. We then have

$$P = n\pi^2 EAx^2/12\ell^2$$

where A is the cross-sectional area of the column. Assume the cross-section

*Marks Handbook, McGraw-Hill Book Company, Inc., New York, 1951, p. 465.

of the sample is square, the length of the side being L. The number of cells in one layer is $L^2/(\ell + x)^2$ and the cross-sectional area of the load-supporting columns is

$$A = L^2(2k + 1)/(k + 1)$$

Substituting in the previous equation, we find for the critical (distributed) load

$$P = C(2k + 1)/k^2(k + 1) \qquad (3)$$

where C is constant for a given material and involves numerical constants, Young's Modulus of the material, the constraints applied to the column, and the size of the sample. When k is large, an approximation to Equation (3) is

$$P = 2C/k^2 \qquad (4)$$

This approximation is about 1 per cent in error when the value of k is 30.

Equation (3) shows that the load-bearing ability of the foam is determined by the parameter, k, which also determines the density, and that the load-bearing ability of several foams made of the same wall-material can be changed only by changing the density.

Substituting Equation (2) in Equation (4) we find that

$$P = KD^2 \qquad (5)$$

where K is constant for a given material.

The energy absorbed (per unit volume crushed) for a number of foam formulations is plotted in Figure 4 against the square of the density. Within experimental error, the data are consistent with Equation (5). As a result of this analysis, the following assumptions were made for purposes of the screening test: (1) the energy-absorbing properties of a given foamed material depend only on the nature of the material and

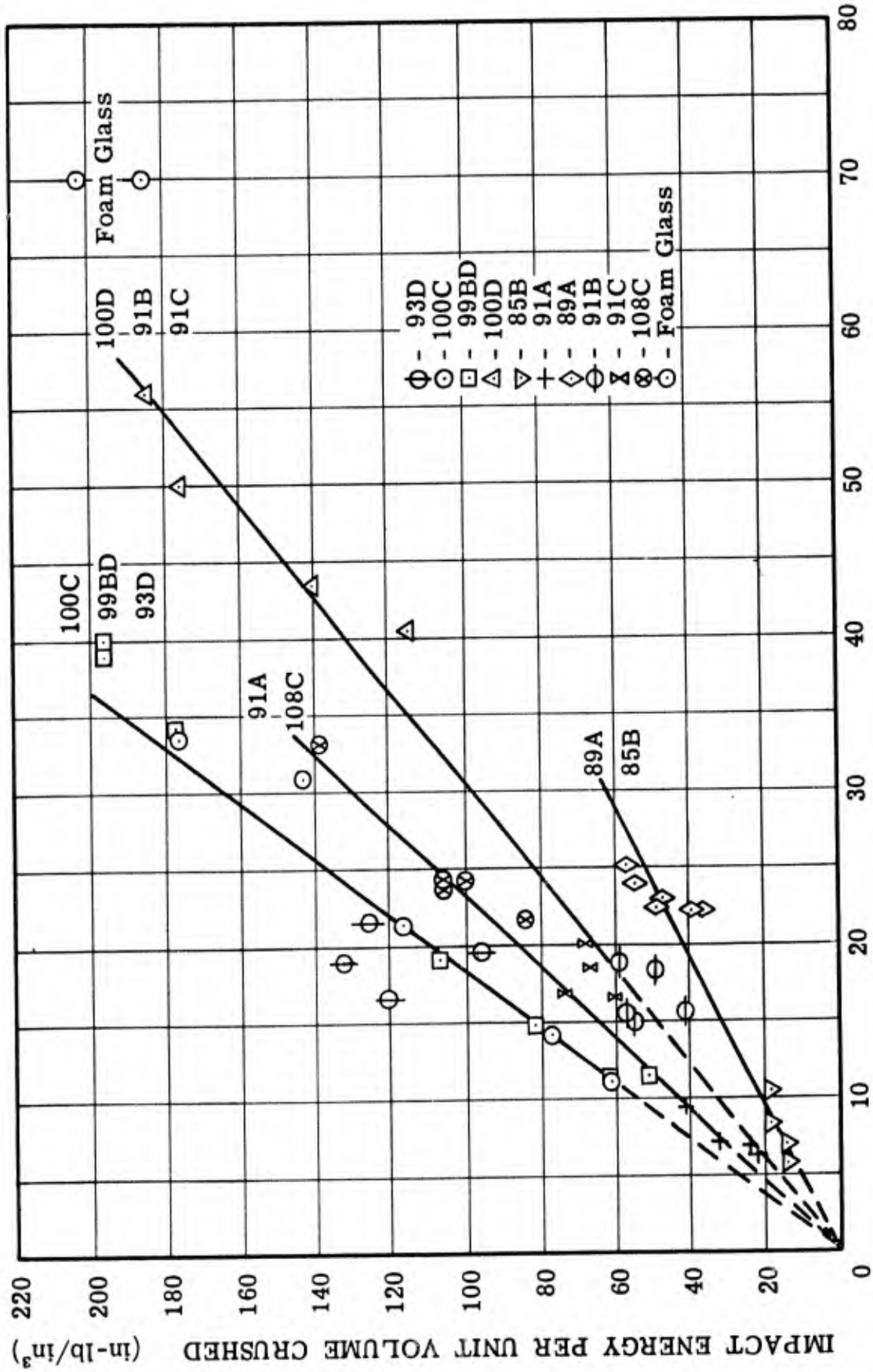

Figure 4. Energy Absorbed per Unit Volume Crushed for Several Foam Formulations.

on the density of the foam; (2) the energy absorbed per unit volume crushed at one density can be computed from the energy absorbed at a different density on the basis that the energy absorbed per unit volume crushed is proportional to the square of the density.

The compressive strengths of samples of Moltopren, a rigid polyurethane foam, are reported by Dombrow* over the density range from 3 to 18 lb/cu ft. The data are rather accurately approximated by a power law, the exponent of the density being 1.8. The exponent 1.8 is not inconsistent with our measurements; the density range and accuracy of our data are such that we cannot distinguish between the exponents 2 and 1.8. Hence, these data on Moltopren are regarded as supporting our procedure for comparing foams of different densities for screening purposes.

1. Comparison of Texas and Instron Tests

Four samples, in the form of 4-inch cubes, of each of foam formulations 91B (with styrene), 100C (with diallyl phthalate), and 108C (with vinyl toluene), were drop-tested.** The reported stress-strain curves, giving the quantitative data which our screening test did not give, are informative regarding the foams and our screening test.

Two of the foams, 91B and 108C, give stress-strain curves not far from the ideal rectangular shape. After the initial peak stress, a long plateau of essentially constant stress is found, extending from 10 to nearly 70 per cent strain. After the plateau, the stress rises rapidly as the sample bottoms. The form of the stress-strain curve for foam formulation 100C is somewhat different; after the initial peak stress, the stress decays gradually to a minimum at about 45 per cent strain and then increases. We surmise that plastic phenomena as well as crushing are involved in the energy-absorption mechanism of 100C, whereas 91B and 108C absorb energy primarily by the fracture of a brittle structure. Much more evidence would be required, of course, to verify this supposition.

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*Dombrow, Bernard A., Polyurethanes, Reinhold, New York, 1957, p. 30. .

**Tests performed at the University of Texas.

The two sets* of screening tests were carried out under different conditions of hammer weight, drop height, maximum strain, and sample density; nevertheless, a comparison of the results is informative. We have reported energy absorbed per unit volume of sample crushed, assuming no losses, from tests in which the maximum strain fell in the range from 30 to 60 per cent. The energy absorbed per unit crushed volume has been calculated from the University of Texas stress-strain curves, assuming that the stress reported is the measured force divided by the original area of the sample (16 sq in) and that the strain is the change in sample thickness divided by the original thickness (4 inches). The energy absorbed has been calculated at the 50 per cent strain level, assuming that this strain level is representative of our screening test. To obtain a comparable value from our screeinging test, the value of energy absorbed per unit crushed volume is read from Figure 4 at the average density of the samples tested by the University of Texas. Results of this comparison are listed Table XLV.

TABLE XLV

Comparison of Energy-Absorption Results:
Atlantic Research and University of Texas

Foam Formulation	Average Density of Samples Tested by Univ. of Texas (lb/cu ft)	Energy Absorbed per Unit of Crushed Volume (in-lb/cu in)	
		Univ. of Texas Stress-Strain Curves, Average at 50 per cent Strain	Value from Figure 4
91B	5.0	68	82
100C	7.4	132	300
108C	5.3	75	118

It is gratifying that the two tests rank the foam samples in the same order. It would appear that the energy absorptions of the samples in our screening tests are 20 per cent (or more) higher than the values obtained at the University of Texas.

*From the University of Texas and from Atlantic Research Corporation.

The value of the energy absorption given in Table XLV for foam formulation 100C is obtained from Figure 4 by a long extrapolation beyond the experimentally measured points; apparently the straight line given in Figure 4 does not represent the behavior of formulation 100C at high densities.

Samples of foam formulation 91B, 108C, and 100C were tested by the Instron tester at the Quartermaster Research and Engineering Center, Natick, Massachusetts. The force required to crush 91B, as measured by the Instron tester, was approximately the same as the average retarding force measured by the drop-tester. The forces required to crush 108C and 100C, however, were noticeably less than the average retarding forces calculated from drop-tester measurements. These results show the same trend as the University of Texas results and may well be caused by energy losses which occur in the laboratory drop tester.

2. Results of Tests

The numerical results, mentioned previously, are summarized in Table XI. The data for several of the foam formulations are also shown graphically in Figure 4. The data of Figure 4 appear to fall naturally into four groups and the lines have been drawn to represent the energy-absorbing characteristics of these groups.

These conclusions may be drawn from the physical testing program:

(1) The laboratory drop-tester performed satisfactorily for screening purposes.

(2) Plastic foams were tested which were equivalent to glass foam in energy-absorbing characteristics, but lighter.

(3) The energy absorbed by a foamed plastic appears to depend on a power of the foam density, the exponent being approximately 2.

(4) The plastic foams tested at Atlantic Research developed most of their strength within the first day; increase in strength between the first and thirteenth days appeared to be about 10 per cent.

(5) A number of commercial foam or honeycomb structures were tested. Aluminum honeycomb had the most favorable ratio of density to energy absorption and showed no resilience. Glass foam showed no resilience and paper honeycomb almost none. The commercial plastic foams tested had favorable ratios of density to energy absorption, but one showed high resilience and the others showed significant resilience in at least one sample tested.

III. FIELD PRODUCTION AND TESTING

A. REQUIREMENTS

The primary objective of the field production and test program was to develop techniques, methods, and equipment to produce foamed plastic energy dissipators in the field.

Under the previous program these energy-dissipating, foamed-in-place structures could be prepared in the field only by skilled personnel at temperatures at which currently available dissocyanates remain the liquid state. More work was required for the development of less highly exothermic and simple systems for handling by unskilled personnel.

Preliminary experiments on foaming in the field at very low temperatures demonstrated this approach to be feasible. Compositions of these foamed plastics were to be similar to formulations 100C and 108C. Modification of these formulations was permissible if necessitated by the requirements for field foaming. The following modifications were anticipated: control of exotherm during foaming; maintenance of fluidity of diisocyanate at low temperature; improved shelf-life of foam components; and nonaqueous systems for catalysis and foaming at low temperatures.

The equipment used was to be as simple as possible, consistent with the production of satisfactory foams at temperatures of 0 to 125°F at rates up to 200 cu ft/hr with a minimum number of personnel for operation. It was to be lightweight, compact, free of hazard to operating personnel. It should be capable of producing foams in blocks up to 4 feet square and 6 inches thick. Serious consideration should be given to expendable type plastic equipment capable of producing one to five units of 200 cu ft each.

Both machine and hand mixing was proposed for the preparation of foams in the field. Field conditions were to be simulated and the limitations of both procedures relative to feasibility of use under field conditions were to be determined, as well as rate of production of foam, personnel requirements, hazards to personnel, and cost.

Requirements for availability, handling, and transport of raw materials as indicated in the statement of work were to be observed. Suitability of the foams as energy-dissipating structures was to be determined by the drop-tester previously constructed.

A secondary objective was to perform basic investigations on the thermal balance of highly exothermic, foamed-in-place plastic systems, which may have application as energy absorbers and as flexible and rigid insulating materials.

It was planned to study further the thermally induced copolymerization of monomers of the vinyl and diallyl types used with castor oil systems, other unsaturated polyol systems and mixed systems based on polyhydroxy polyethers (which are less expensive than polyesters), triol diisocyanate adducts, and other new raw materials as they might appear on the market which could be useful for foaming under field conditions.

B. MACHINE MIXING

1. Klauder-Williams Machine

Machine-mixing was studied with a Klauder-Williams foam machine, producing formulations 108C and 100C. The machines were calibrated for use of the resin system of each formulation. Variables were investigated which affect the preparation of machine-mixed foams of controlled density under field conditions.

a. Preparation of Modified Formulation 108C

A 55-gallon drum was placed on a platform scale, the tare weight noted, and 60 pounds of vinyl toluene and 120 pounds of castor oil AA were added to it. A Lightning mixer, suspended on a hoist, was lowered into the drum and stirring was begun as 180 pounds of Quadrol were added. Petromix #9 and Witco 77/86 (6 pounds each) were added after the first three components were thoroughly mixed. More ethyl cellulose was used in the large modified batch than was used in the normal 108C formulation, to improve foam stability in the large molds. Ingredients in order and amount of their addition are shown in Table XLVI.

Table XLVI

Modified Formulation 108C for Machine Mixing

Ingredient	Content (lb)
Vinyl toluene	60
Castor oil, AA	120
Quadrol	180
Petromix #9	6
Witco 77/86	6

Thirty pounds of this stock mixture were weighed into a 5-gallon container and just before a run began, 680 grams (1.5 pounds) of ethyl cellulose N-100, 86 cps*, were added. Water was the last component added and was variable in amount. A hand paddle was used to blend the composition to a homogeneous mixture before adding it to the feed tank.

* Hercules Powder Company.

(1) Calibration of Machine for Modified 108C.

For the resin of formulation 108C (170 grams of water/30 pounds of stock resin mixture), mixing-head speed was 2100 rpm and the resin temperature 35°C. The large amount of water (regular amount was 43 grams) was necessary to produce the low-density foam desired. The variable meter-pump dial was set at 5 and readings of pump rpm taken several times at intervals of 5 seconds. This same procedure was repeated at dial settings of 10, 15, 20, 25, and 30 (Table XLVII). The amount of resin delivered was measured by collecting samples directly at the mixing head and weighing. Results are shown in Figure 5.

Table XLVII

Calibration Mixing Data for Resin of Formulation 108C

Dial Setting of Variable Meter Pump	Average Pump rpm/5 Seconds	Average Weight (gm) Delivered in 5 Seconds
5	10	79
10	18	160
15	27	232
20	34	283
25	40	335
30	45	375

The amount delivered was independent of the speed of the mixing head whether at 0 or 2100 rpm.

For the toluene diisocyanate (Nacconate 80) the mixing head speed was 2100 rpm, and the temperature of the TDI was 32°C. The same procedure was repeated at dial settings of 5, 10,15, 20, 25, and 30. Samples were collected directly from mixing head and weighed (Table XLV). Results are shown in Figure 6.

Table XLV III

Calibration Mixing Data for Toluene Diisocyanate (108C)

Dial Setting of Variable Meter Pump	Average Pump rpm/5 Seconds	Average Weight (gm) Delivered in 5 Seconds
5	11	48
10	19	90
15	27	133
20	35	168
25	40	202
30	45	219

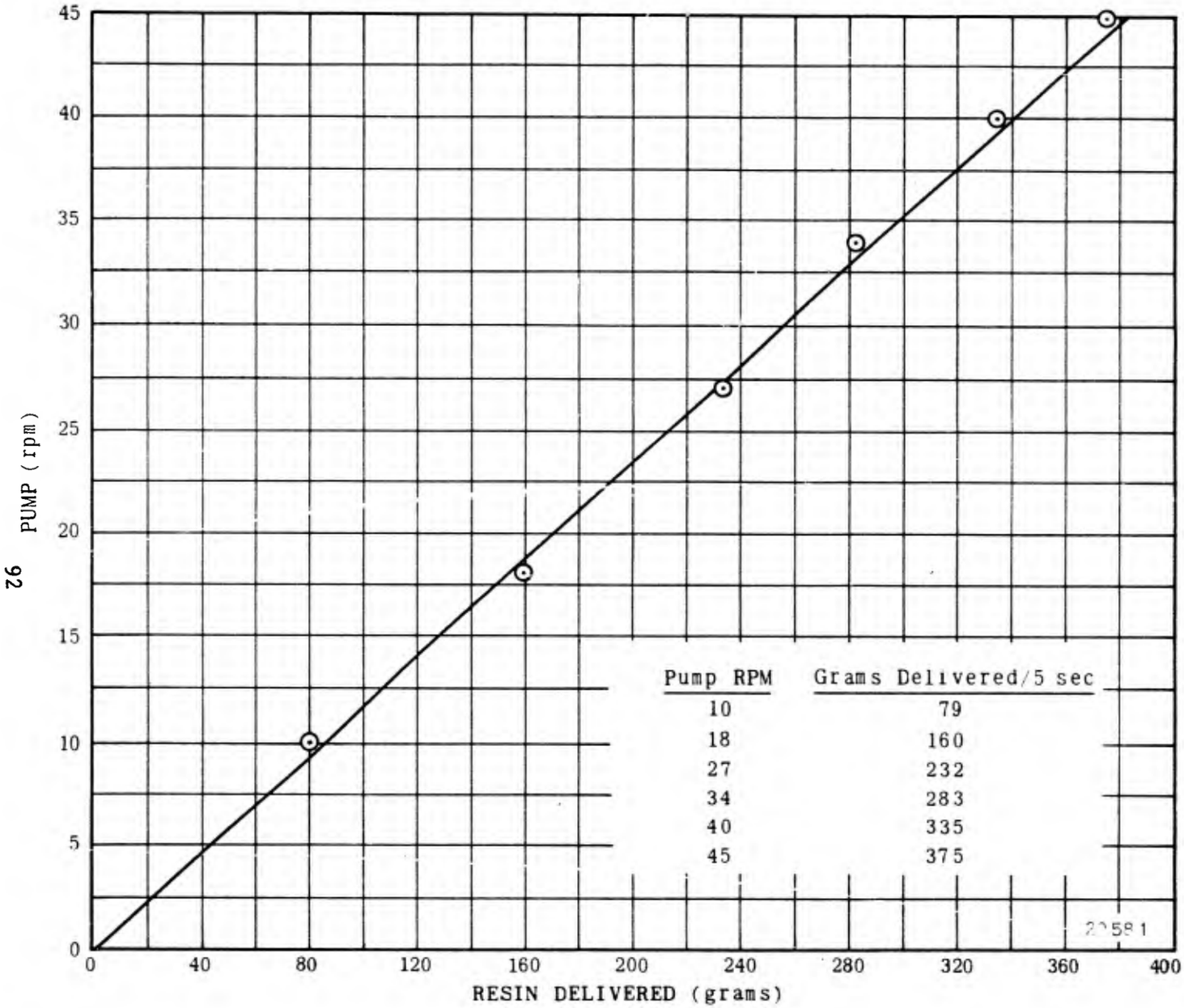

Figure 5. Flow of Resin for Formulation 108C at 5-Second Intervals at 32°C.

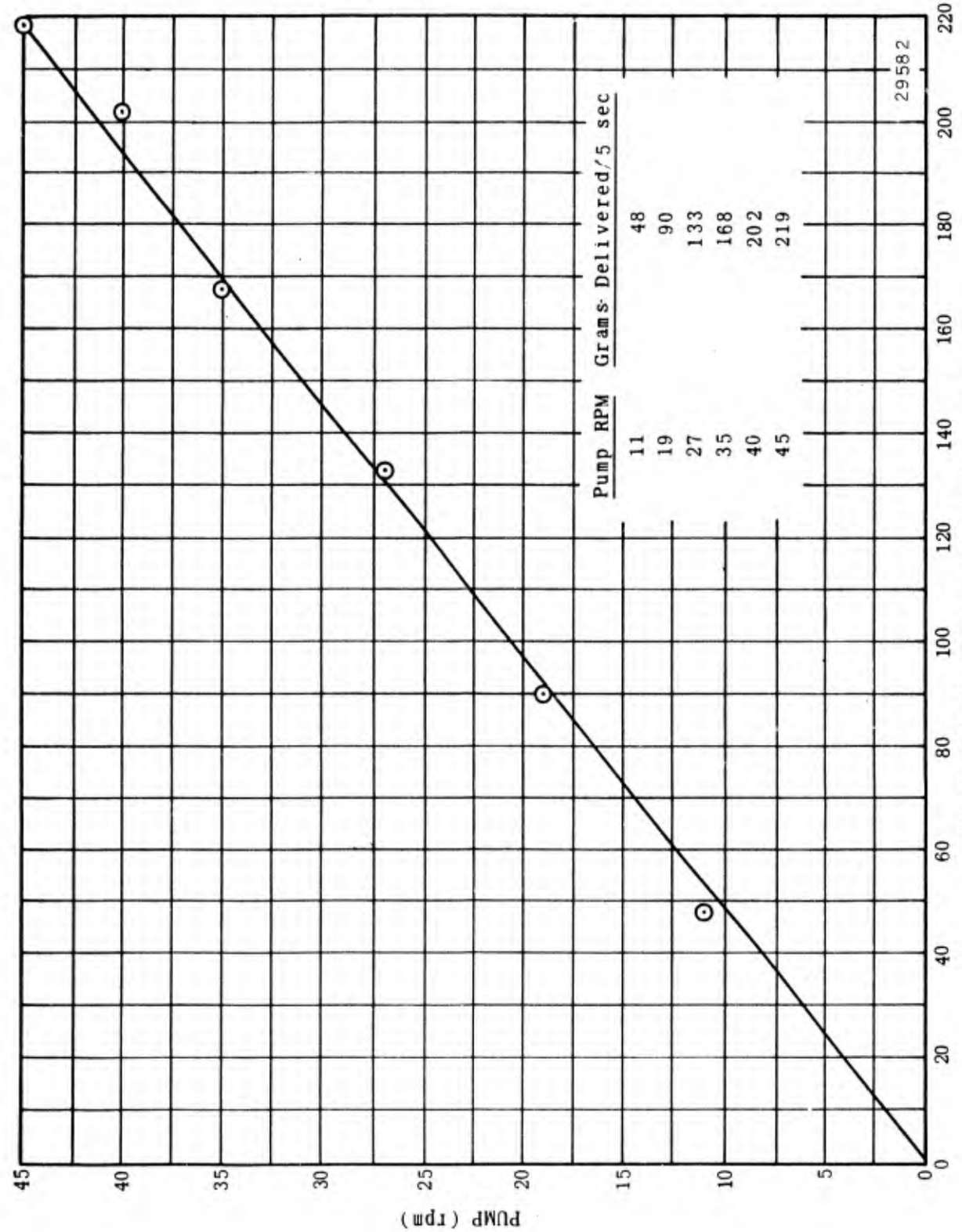

Figure 6. Flow of Toluene Diisocyanate for Formulation 108C at 5-Second Intervals at 32°C.

The following procedures were followed for machine settings for 1:1.36 ratio of TDI resin, a modified formulation 108C. (Ratio for regular 108C is 1:1.5.) For the toluene diisocyanate the variable speed dial was set at 15-1/4, pump rpm 26 delivering 125 grams of TDI in 5 seconds. For the resin, the variable speed dial was set at 11, pump rpm 21 delivering 170 grams of resin in 5 seconds. Mixing head speed was 1200 rpm. No variations in weight of either toluene diisocyanate or resin was delivered evident from 23 to 32°C, due to the positive displacement metering pumps.

There was no difficulty in transferring the Nacconate directly from a 55-gallon container to the feed tank of the positive displacement pump. This was accomplished by having a Y-shaped fitting threaded to fit the drum and through which a stainless steel tube would reach the bottom of the 55-gallon container. The Nacconate was then pressurized with dry nitrogen, forced up the tube, and through polyethylene tubing to the feed tank. Two floats (aluminum pie pans welded one on top of the other) were constructed, each with an aluminum tube attached which came out through a hole in the tops of the toluene diisocyanate and resin feed tanks. This enabled the operator to ascertain the level of the components from a distance. The toluene diisocyanate feed tank was kept moisture free by a constant flow of dry nitrogen over the surface, as shown in Figure 7.

(2) Control of Density of 108C Foams

Water in varied quantities was added to batches of the resin system and its effect on the density of the machine-mixed foams determined. Temperature of components at time of mixing was measured. The temperature of the batches varied from 15 to 28°C. From these measurements it was computed that approximately 50 grams of water per 30 pounds of resin would be required for foams with densities in the 7 lb/cu ft range, about 116 grams for foams in the 5.0 lb/cu ft range, and about 150 grams for the 4.0 lb/cu ft range. Temperature at the time of mixing is an important factor: a resin system which yielded a foam with a density of 5.0 lb/cu ft at a mixing temperature of 15°C gave a foam of 4 lb/cu ft density at 27°C.

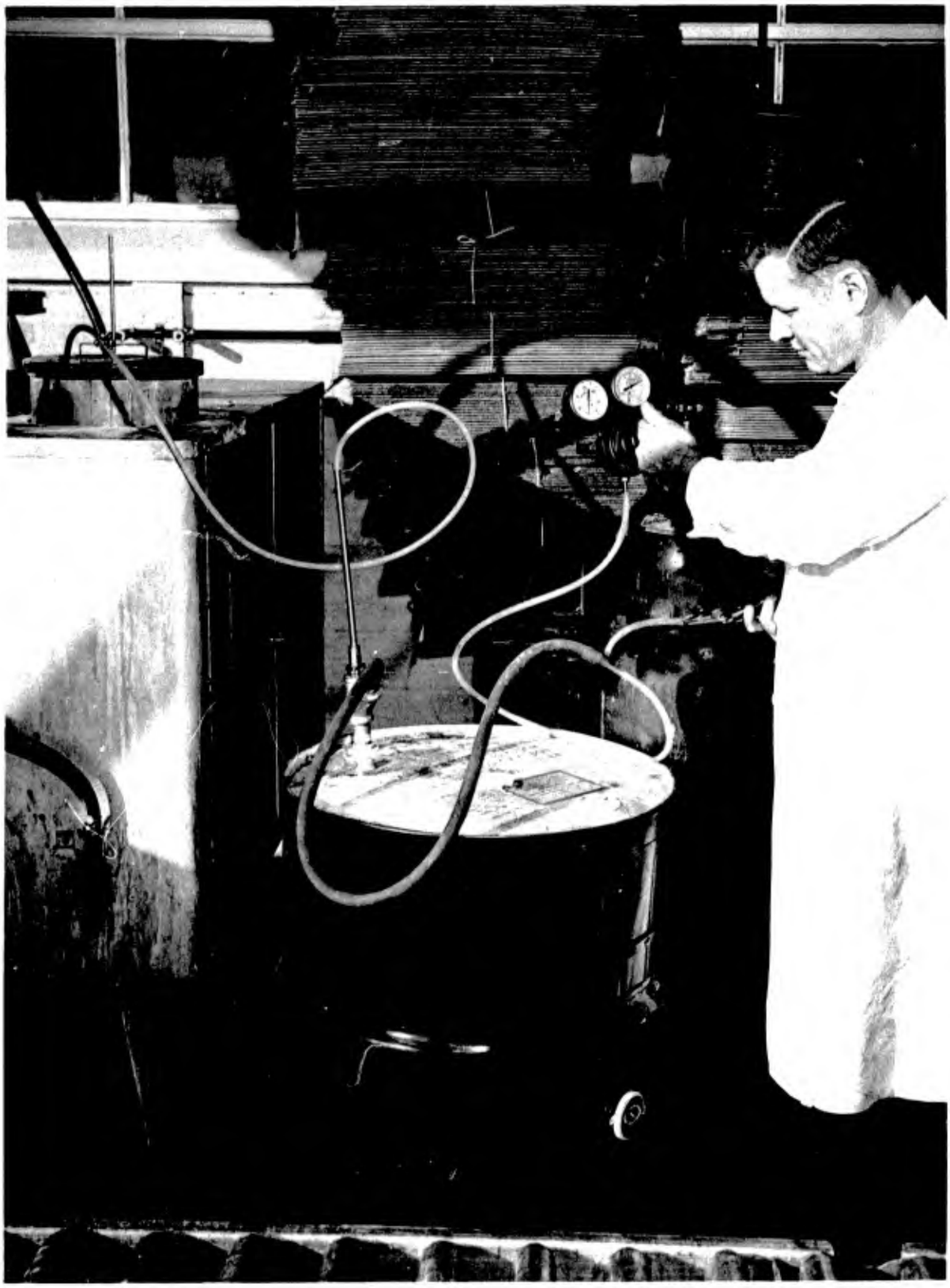

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Figure 7. Technique of Delivering Toluene Diisocyanate from Drum to Machine Reservoir by Nitrogen Pressure.

(3) Molds for Casting Foams of 108C

Paper-board cartons were assembled, with and without liners, and moved continuously, or at intervals of several seconds, beneath the mixing head of the machine to receive the foaming mixture. Some of the cartons were placed in wooden frames to prevent excessive bulging of carton by the rapidly expanding foam. It was found that confining frames could be dispensed with for cartons as large as 24 × 24 × 6 inches by using repeated pours of small amounts of foam mix. The procedure recommended for use is as follows.

Use paper-board boxes 24 × 24 × 6 inches, the open end being 24 × 6 inches. Stand the boxes side by side, open ends up, tape several together as a unit, and place on a board frame mounted on the conveyor. Move the unit of boxes under the mixing head, using a 5-second pour for the introduction of about 300 grams of TDI-resin mix to each box. Repeat the pours at 5-minute intervals until the boxes are filled. Trim off excess foam and close the package. Arrangement for this procedure is shown in Figure 8.

(4) Cleaning the Machine After Use with Formulations 108C

At the end of each run the mixing head had to be removed quickly and immersed in acetone. Toluene diisocyanate and resin were drained from the feed-pump tanks, and the system flushed with dry acetone. This procedure was repeated three times. Residual acetone was blown out of the hoses with compressed air. The disassembled mixing head after cleaning is shown in Figure 9. Although the mixing head was removed immediately after each pour and immersed in acetone, a deposit of foam build-up was experienced which was easily removed by soaking the entire head in nitric acid occasionally.

b. Preparation of Formulation 100C

A 55-gallon drum was placed on a platform scale, the tare weight noted, and 60 pounds of diallyl phthalate and 120 pounds of castor oil AA added. The Lightning mixer was lowered into the mix and 180 pounds of Quadrol blended in. The Petromix #9 and Witco 77/86 (6 pounds each) were added and thoroughly mixed. Amounts of ingredients

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Figure 8. Arrangement for Casting Foam in Cartons 24 × 24 × 6 inches.

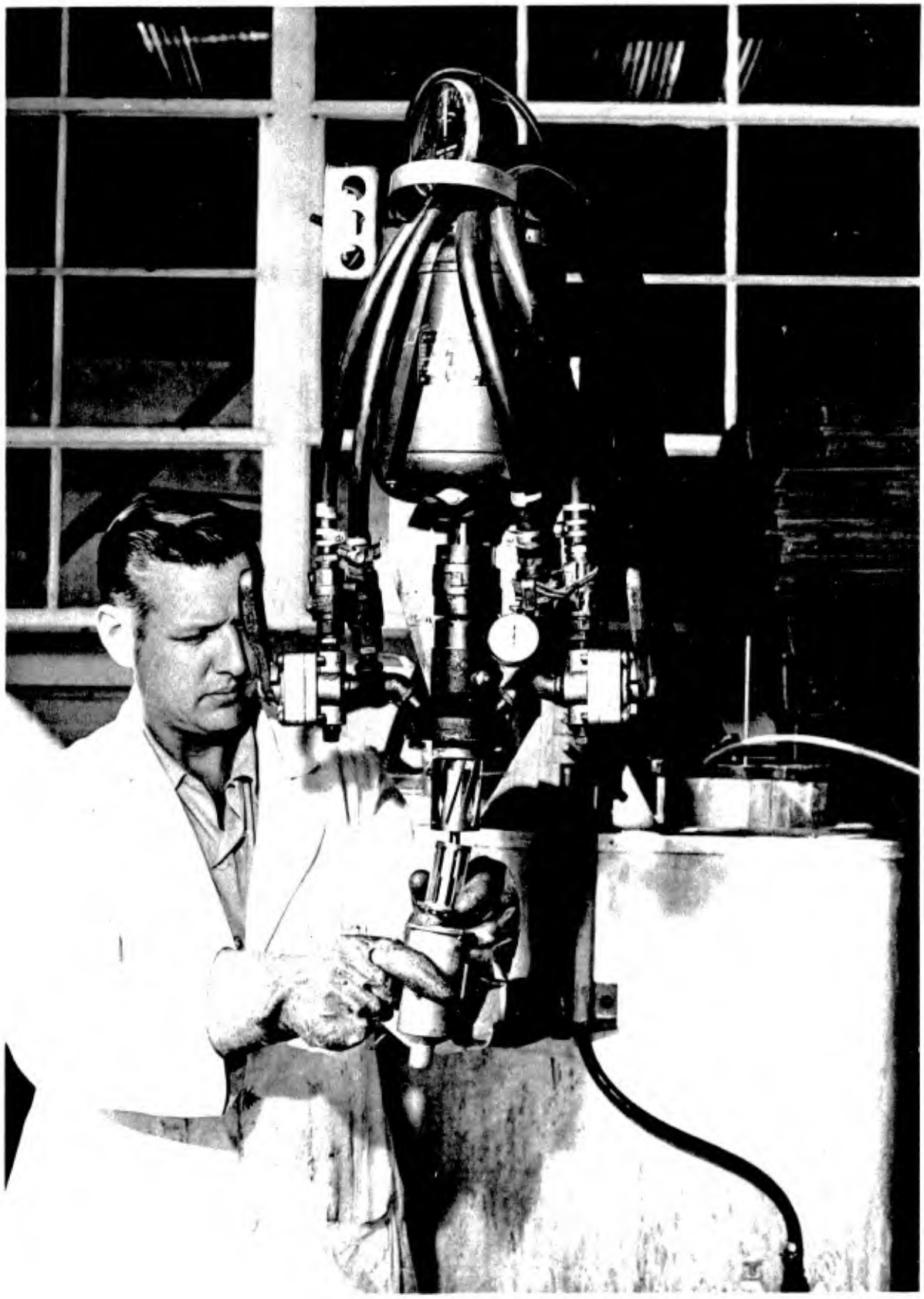

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Figure 9. Dissembled Foam Mixing Head after Cleaning.

and order of their addition for a modified 100C formulation were as shown in Table XLIX.

Table XLIX

Modified 100C Formulation for Machine Mixing

Ingredient	Content (lb)
Diallyl phthalate	60
Castor oil, AA	120
Quadrol	180
Petromix #9	6
Witco 77/86	6

Thirty pounds of this stock mixture were weighed into a 5-gallon container and just before a run began 680 grams (1.5 pounds) of ethyl cellulose N-100 were added. Water, the last component to be added, was variable in amount. A hand paddle was used to blend the composition to a homogeneous mixture before adding it to the feed tank.

(1) Calibration of Machine for the Modified 100C Formulation

With a mixing head speed of 2100 rpm and a resin temperature of 23°C, the machine was calibrated as follows.

For the 100C resin (140 grams of water/30 pounds of stock resin mixture) the variable meter-pump dial was set at 5 and readings of pump rpm taken several times at intervals of 5 seconds. This same procedure was repeated at dial settings of 10, 15, 20, 25, and 30. The amount of resin delivered was measured by collecting samples directly at the mixing head and weighing (Table L). Results are shown in Figure 10.

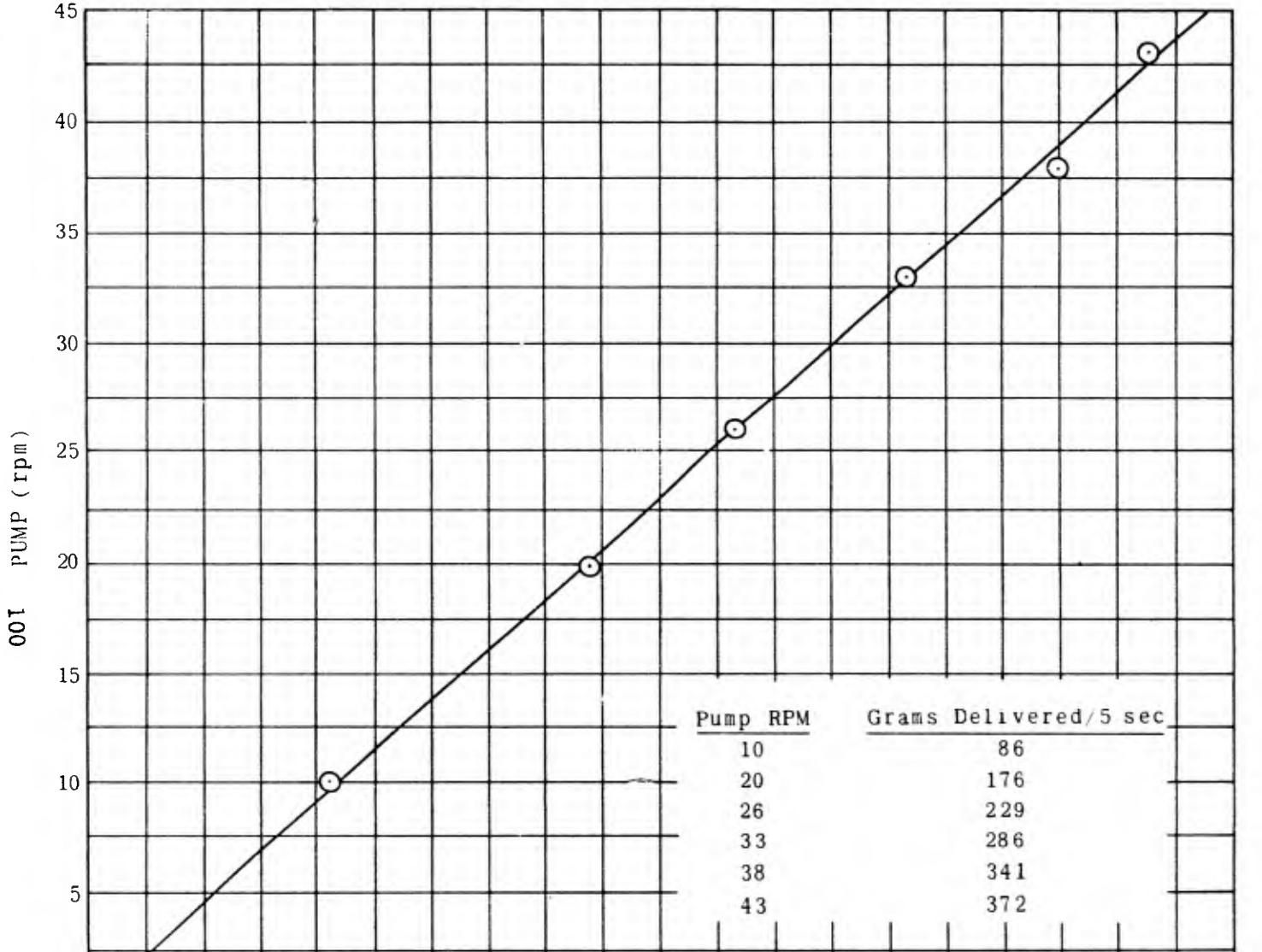

Figure 10. Flow of Resin of Formulation 100C at 5-Second Intervals at 32°C.

Table L

Calibration Mixing Data for Resin of Formulation 100C

Dial Setting of Variable Meter Pump	Average Pump rpm/5 Seconds	Average Weight (gm) Delivered in 5 Seconds
5	10	86
11	20	176
15	26	229
20	33	286
25	38	341
30	43	372

The amount delivered was independent of the speed of the mixing head whether at 0 or 2100 rpm.

For the TDI (Nacconate 80) the calibration of the machine for the modified 100C formula (1:1.36 ratio of TDI/Resin) was the same as for the modified 108 formula (See Figure 6).

Varying amounts of water were added to 30 pounds of the stock resin mixture of the modified 100C formulation to obtain information on control of density. Corrugated paper boxes, 24 × 24 × 3 inches, were used as molds. Several boxes were used in order to get the average density (Table LI).

Table LI

Measured Densities of Modified 100C Formulation Using Various Amounts of Water

Grams of Water per 30 Pounds of Resin	Average Density (16 lb/cu ft)	Toluene Diisocyanate Temperature (°C)	Resin Temperature (°C)	Ambient Temperature (°C)
105	4.83	21	18	18
140	4.26	17	23	18
140	3.82	18	23.5	21
145	4.01	18	23	20
150	3.55	20	18.5	19.5

(2) Cleaning

Cleaning procedures were similar to those used with the 108C foam.

(3) Maintenance

The maintenance of the Klauder-Williams machine occasioned some difficulty. Valves and hose which had been in contact with diisocyanates became brittle and had to be replaced. Diisocyanate fumes which penetrated the shaft of the mixing head had reacted with moisture in the grease with consequent loss of lubricating properties. The mixing head and shaft were cleaned and relubricated. The Hoover ball bearings (WC 8016), located at both ends of the shaft housing, became inoperable and had to be removed and replaced.

Although the diisocyanate metering system, after the lines were blown out with dry pressurized nitrogen, was washed three times with circulating acetone after each period of use, there was sufficient diisocyanate for reaction with water vapor to form a minute coating of reaction product. This interferes with lubrication (diisocyanate fumes also react with grease to form hard solids). The shaft of the Viking metering pump for diisocyanate broke on starting after a period of disuse and had to be replaced.

C. HAND-MIXING AND HAND-POURING OF BATCHES OF PFR-6 (NATIONAL ANILINE)

Mixing effected by kneading of material poured into plastic films held in the shape of a bag proved efficient and simple. An 18- × 18- × 18-inch block of foam was prepared by mixing the ingredients in a polyethylene film held in the shape of a bag by kneading and dumping the contents into a mold as foaming began. This formulation, PFR-6 (National Aniline), was relatively cool, and was self-curing when poured at room temperature. It had the composition shown in Table LII.

Table LII

Formulation PFR-6

Ingredient	Content (gm)
Polyester (National Aniline PFR-6)	4000
Hexane triol-diisocyanate adduct (National Aniline 1080-H)	5600
Water	80
Emulsifier EL-719	40
N-methyl morpholine	40

D. HAND-MIXING AND HAND-POURING OF BATCHES OF MODIFIED 108C

The feasibility of hand-pouring and mixing was investigated. Mixing could be accomplished either by (1) the resin mixture being poured directly into the mold and then the toluene diisocyanate added and mixed with a paddle; or (2) the resin mixture could be placed in a polyethylene bag, toluene diisocyanate added, and the bag kneaded, slashed, and the contents forced into a mold.

It was necessary to determine the minimum number of pours necessary to fill the cardboard containers without formation of bulges and fissures. For these tests the molds were corrugated paper boxes, 24 by 24 by 3 inches. The ratio of 140 grams of water to 30 pounds of resin was held constant, and an interval of 5 minutes was allowed between pours. The results are shown in Table LIII.

Table LIII

Results for Hand-Pouring of Modified Formulation 108C

Number of Pours to Fill Box	Total Toluene Diisocyanate and Resin per Batch (gm)	Average Density (lb/cu ft)	Remarks
7-8	295	5.25	Slight bulging, no burning of fissures, excellent.
4-5	590	5.75	Bulging, few fissures, no burning.
1	5900	-	Marked bulging and fissuring.

It may be noted that the observed average density was higher than had been obtained by the tests given in Table LI.

The average temperature of foaming, with 5-minute intervals between pours and 4 to 8 pours per box, was 165°C. If less than 4 pours per 24- × 24- × 3-inch cardboard box are used, confining frames for the boxes are needed to avoid excessive bulging.

A 48- × 48- × 6-inch plywood mold, with hinged-fasteners for quick breakdown, was used for experiments to determine the maximum weight of material that could be mixed, poured, and foamed by hand, and to determine the effect of interval between pours on uniformity and degradation of foams prepared at 15 to 20°C. The mold was lined with wrapping paper treated with lubricating oil for ready release of foam. This was a highly satisfactory release agent.

Formulation 108C was used. Thirty-pound batches of resin were blended with the Lightning mixer. The sequence of addition of resin components was as follows:

(1) Quadrol
(2) Castor oil
(3) Vinyl toluene
(4) Petromix #9
(5) Witco 77/86
(6) Ethyl cellulose N-100
(7) Water (35 grams to 30 pounds of above mix)

Resin mix and Nacconate 80 were placed in their respective pots over the metering pumps of the Klauder-Williams machine.

The mixing head of the Klauder-Williams machine was removed, and resin and Nacconate 80 were metered out separately at constant ratio into containers. Batch quantities, i.e., total weight of both resin and Nacconate 80 for mixing, were varied: 1, 2, 3, and 4 pounds. The containers for final mixing were either 1-gallon paper cartons (ice cream containers) or polyethylene bags. In the case of the paper cartons mixing was effected with a wooden paddle. Mixing in polyethylene bags was done by kneading the components by hand.

After a mixing period of 25 to 30 seconds the mixtures were poured into the mold*. The intervals between pours were 5, 10, 15, and 20 minutes.

Temperature of resin and Nacconate at the time of mixing ranged from 15 to 20°C. Temperature of the molds ranged from 2 to 4°C. Density of these foams averaged 7 lb/cu ft.

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*The polyethylene bags were slit with a knife and the contents squeezed into the mold.

The following conclusions were drawn from these experiments.

(1) The minimum temperature for mixing and pouring the components of formulation 108C, packaged separately, is about 15°C. The 2,4-isomer of the 80:20 2,4-2,6 toluene diisocyanate begins to precipitate at 14°C. Further development should be done on (1) foaming systems based on the 65:35 (2,4-isomer:2,6-isomer) toluene diisocyanate blend, such as Nacconate 65 which is liquid at temperatures above 5°C, and on (2) monomer-diisocyanate mixtures blended on the spot, with subsequent mixing with resin components and foaming at temperatures of 32°F and above.

(2) The maximum quantity of material (formulation 108C) which could be mixed and poured by hand was about 3.5 pounds (1575 grams), using an interval between pours of 5 minutes. Larger pours at this interval yield foams slightly discolored by excessive heat buildup. Increasing the interval between pours reduces "legging" at the foam interface of successive pours. The cooler the surface of foam for successive pours the greater the uniformity of foam. A 20-minute interval between pours resulted in a much more uniform foam than a 5- or 10-minute interval.

(3) Four men could pour by hand approximately 1000 pounds of 6-lb/cu ft foam a day. One man would be needed for blending the resin components (using a paddle and metal drum), one for volumetric dispensing of resin and diisocyanate into containers, one for mixing and pouring, and one for manipulating of molds. Water, to control density of foam, could be added at time of mixing of resin. Premixing of castor oil and Quadrol would reduce mixing time required for homogeneity of resin mix.

Prepackaging of measured quantities to expedite processing would be somewhat more expensive. They would require the following equipment:

(1) Fifty-five-gallon drum and wooden paddle for mixing resin components.

(2) Drying tube, hand pump, and appropriate fittings for dispersing diisocyanate.

(3) Fittings for dispersing castor oil and Quadrol or castor oil-Quadrol mixtures.

(4) Confining frames for the cardboard boxes used as molds for the foam (at least 20 to get the desired interval between pours).

(5) Cardboard boxes with tape for assembly in the field.

(6) Containers for hand-mixing of resin and diisocyanate.

(7) Aluminum coasters or other device for moving the boxes downwind for protection of personnel against inhalation of diisocyanate fumes. (This equipment could be dispensed with: the boxes could be aligned, assuming no shift of wind, in such a manner that personnel would not be exposed to fumes.)

(8) Face masks for personnel. (However, men on this project did not find it necessary to wear masks while working in the open.)

E. DESIGN OF MACHINE FOR THE PRODUCTION OF FOAM IN THE FIELD

An inexpensive foam mixer that could be used by unskilled personnel in the field was required. The foam delivered by the unit was to be used primarily for shock protection of supplies air-dropped to troops.

A requirement of 1.5 cu ft of 6-lb/cu ft-density foam (from 1 gallon of liquid mix) per minute was specified for the mixer. This foam mix was to be composed of equal parts of liquid-resin mixture and toluene diisocyanate. Further design objectives were simple construction, simple maintenance, low cost, operation by unskilled labor, lightweight, and simple logistics. To be included with the mixer were storage tanks for the components, means of conducting the components to the mixer, and metering pumps. In some applications, it would be desirable to include means of isolating the catalyst from contact with moist air.

1. Flow Calculation

The problem of friction loss in the supply lines to the mixer needs careful consideration. The TDI presents little or no problem as its viscosity is quite low; however, the viscosity of the liquid-resin mixture is about 3000 cps.

The Hagen Poiseuille law for low Reynolds numbers can be stated as:

$$\Delta P = \frac{128 \mu LQ}{\pi D^4}$$

where: ΔP = pressure loss in lines in psi

μ = viscosity

L = length

Q = quantity of flow

D = diameter of lines

From this equation we can plot the pressure drop in the resin hose as shown in Figure 11. This curve shows the pressure drop for 10- and 20-foot lengths of hose. Considering these curves, a hose of 1-inch, internal diameter and 10-foot length is chosen for the supply lines from storage drums of other reservoirs, to the mixer unit, which will be discussed later. This gives a pressure drop of 4 psi between the reservoir and mixer.

The metering pump is designed as a U-shaped tube alternately compressed by rollers and, as such, an approximation for flow rate can be calculated. Flow rate versus rpm can be plotted as shown in Figure 12 for various sizes of pump tubing. The best compromise seems to be a 0.75-inch internal-diameter hose with the metering pump rotor turning at 40 rpm.

2. Pump-Mixer Design

The design shown in Figure 13 was selected as the most promising pump-mixer design to meet the requirements mentioned above. This pump mixer unit is designed to be held by one man on either a unipod or an arm support such as used in breast drills.

The two components are fed to the metering pumps through the two hoses from the left side of the pump. These hoses are attached to the metering pumps by two-way shut-off, quick-disconnect fittings. The components enter flexible tubes which form the conducting lines through the pumps.

The metering pumps consist of this flexible tubing laid against the inside of a drum and pinched off every sixty degrees by a roller located toward the center of the drum. As a roller passes the inlet port, it traps a measured quantity of resin or catalyst between the pinch and the next preceding pinch of the tube. The pinch is then moved along the tube by the action of the roller moving in a circular direction until a roller crosses the outlet part. The succeeding roller then forces the trapped liquid through the outlet and into the mixing chamber. This pumping principle is well known in the chemical industry for pumping corrosive liquids.

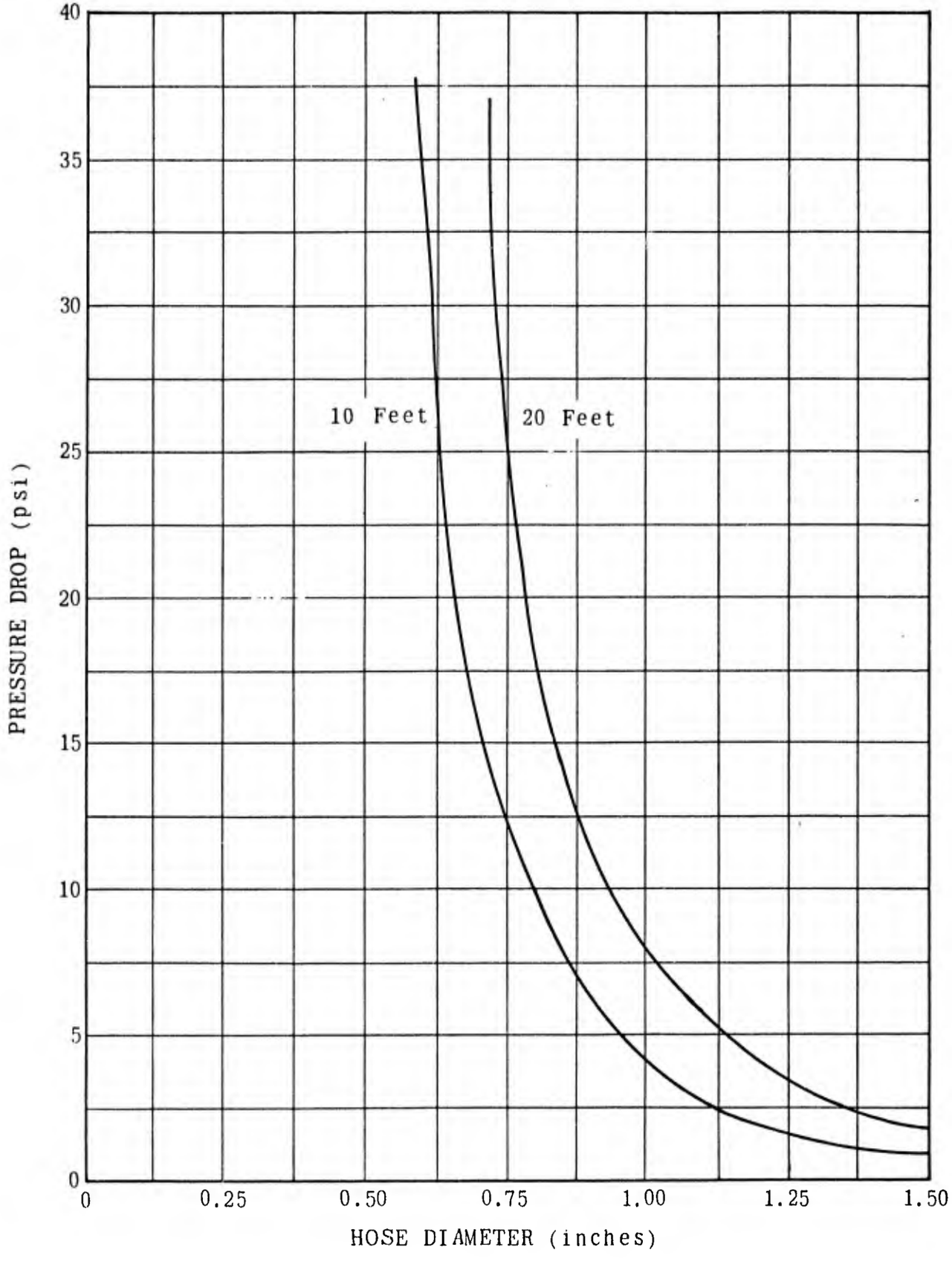

Figure 11. Field Foam Mixer: Friction Head Pressure Drop Correlated with Various Diameters Delivering 0.5 gpm of Resin.

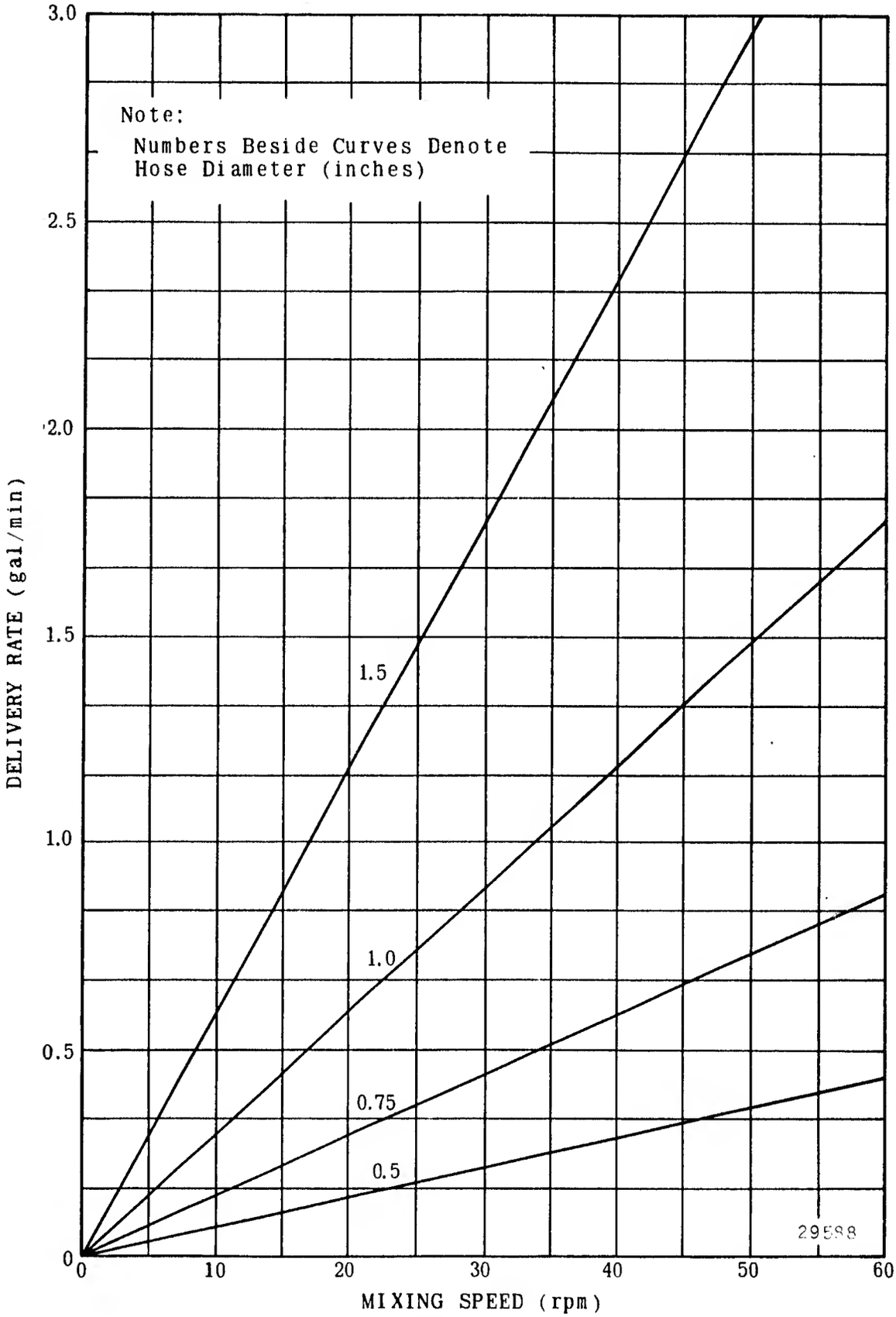

Figure 12. Field Foam Mixer: Delivery Rate Correlated with Mixing Speed.

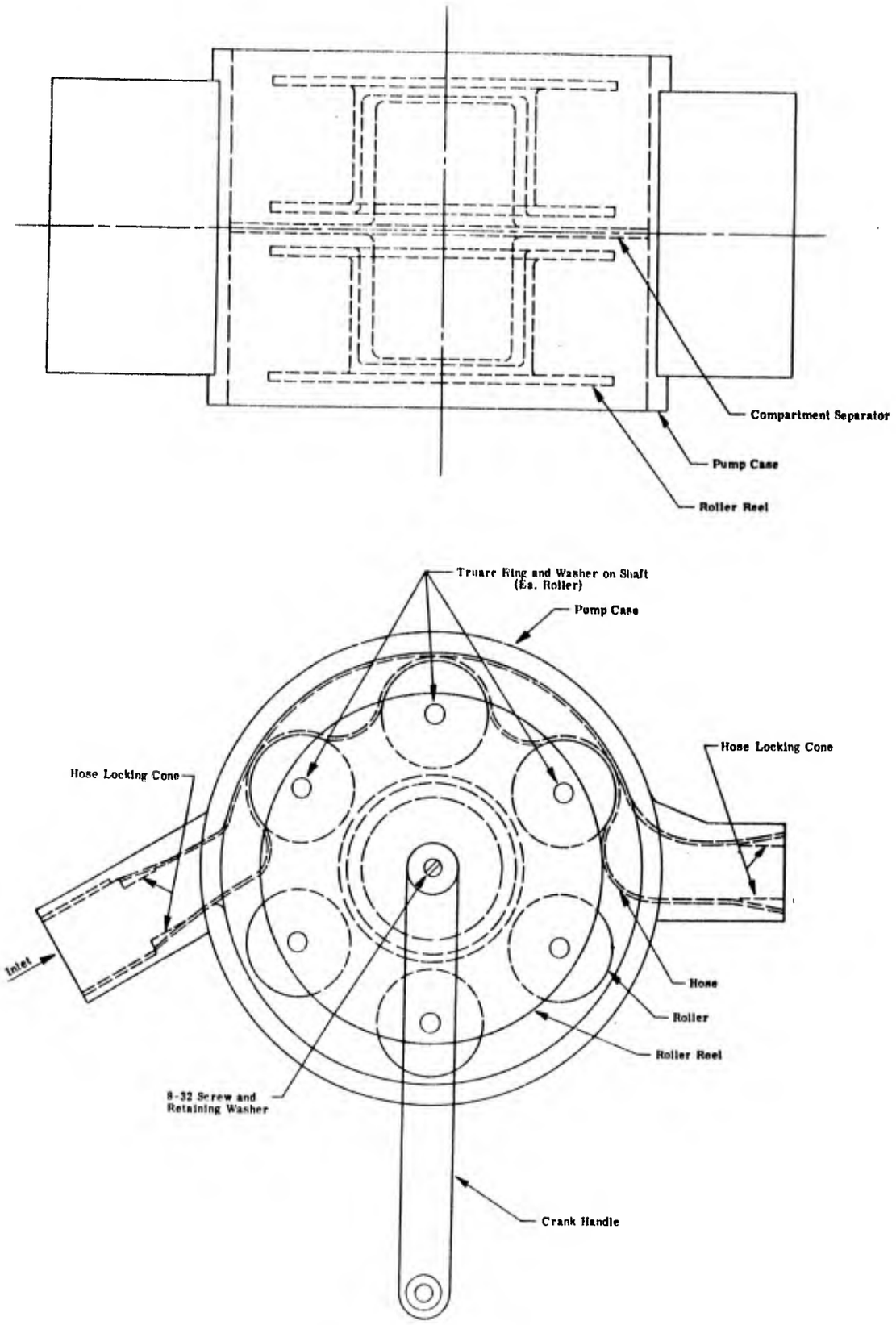

Figure 13. Design for Hand-Operated Foam Machine for Use in the Field by Unskilled Personnel.

As a liquid resin mixture and TDI enter the mixing chamber they are given a helical motion by a fixed helical insert in the mixing tube and will be completely intermixed by the time they leave the outward extremity (right in Figure 13) of the nozzle.

The mixing chamber and nozzle are designed for easy removal from the metering-pump unit for cleaning or disposal. In Figure 13, check valves are shown separating the pumps from the mixing chamber. These may not be required, and the first tests of the unit will be made without them.

The reservoirs proposed for the field foam mixer are the original steel-drum shipping containers used for the castor oil and the TDI. A bladder can be attached to the TDI drum and, when filled with dry air, will serve as a barrier to prevent contact between the TDI and moist air. An alternate design would be the use of a desiccator tube attached to one of the parts of the TDI drum. If required, a pressure connection can be added to the liquid-resin-mixture drum to help overcome the pressure drop in the supply line.

Construction of a simple, hand-operated foam mixer was completed, and a testing program was conducted to determine suitability of the mixer for the production of foams, using the 100C formulation. It was found that an orifice plate gave better mixing than the original helical spring mixer in the mixing chamber, and the design was so modified.

The mixer was demonstrated to the Quartermaster Corps at Natick, and these suggestions for improvement in design were discussed.

(1) Make all hose entries and exits tangential to the pumping circle.

(2) Select hose-sizes that will give desired metering.

(3) Use hose couplings to connect the supply hoses to the pump thereby eliminating all hose-to-pipe connection.

(4) Pressurize the oil-component feed tank.

(5) Use a special expendable mixing-tee in the pump instead of present fitting.

(6) Eliminate the segregation-diaphragm between the two tubes in the pump and use one set of wide rolls for both tubes.

(7) Install a combination throttle-shut-off valve in the TDI supply line and a shut-off valve in the liquid-resin-mixture line at the entries to the pump.

(8) Install air blow-off connections near the pump entry to clear both lines after the shut-off valves are closed.

A new mixer incorporating these changes would be a great improvement over the existing model. Designing and constructing a hand mixer of this type is recommended.

3. Viscosity of the Liquid Resin Mixture of Modified 100C Formulation as a Function of Temperature

Viscosity data on the liquid resin component as a function of temperature were needed for the computation of flow rates. Viscosities were measured at different temperatures of resin mixture, with and without diallyl phthalate. Silicone L-520, instead of ethyl cellulose, was used as the foam stabilizer. Water (0.91 ml per 124 grams of liquid-resin mixture) was added. The viscosities are shown in Table LIV.

Table LIV

Viscosity-Temperature Data for Formulation 100C

Temperature (°C)	Viscosity (Centipoises)[a]	
	100C Resin Mixture	100C Without Diallyl Phthalate
25	1340	3600
17	2250	9600
13	2580	14,400
11	3550	----
10	----	22,600
9	----	31,500
8	6160	----
7	7550	----
5	----	39,500
-5	26,000	----
-27	100,000	----

[a]Brookfield Viscometer

F. SPRAY APPLICATIONS

Spray-application of foams, both rigid and flexible, on tents, shelters, or inflated bags, is well suited for the preparation of insulated structures.

1. Alteration of the Klauder-Williams Machine for Sprayed-on Applications

The SP-100 formulation (a modification of 100C to enhance rate of foam rise and set) proved to be an excellent system for the production of foam structures (Table LV).

TABLE LV

Formulation SP-100[a]

Ingredient	Content (lb)
Quadrol	60
Castor oil, AA	40
Diallyl phthalate	20

a. To 30 pounds of above mix add 100 grams of water, 20 grams of Silicone L-520, 40 grams of N-methyl morpholine. This final batch is subsequently mixed with TDI (80:20 isomers) in the ratio, batch:TDI, of 80 grams:69 grams.

The valves controlling the flow of diisocyanate and resin from the metering pumps, which had been attached to the mixing head, were removed and mounted onto an aluminum plate that was secured by bolts to the side of the machine housing. The arrangement is shown in Figure 14. This enabled the operator to utilize the recycling hoses and control the flow of components to the spray gun. Seventy-foot lengths of 3/8-inch inside diameter, two-ply Neoprene hose, attached to the valve heads from the metering pumps for diisocyanate and resin, were used as feed lines to the spray gun. All connections were made with Breco Pulomatic quick-disconnect couplings; difficulty was experienced in securing tight closures on the diisocyanate lines. The couplings were thoroughly rinsed with acetone after use.

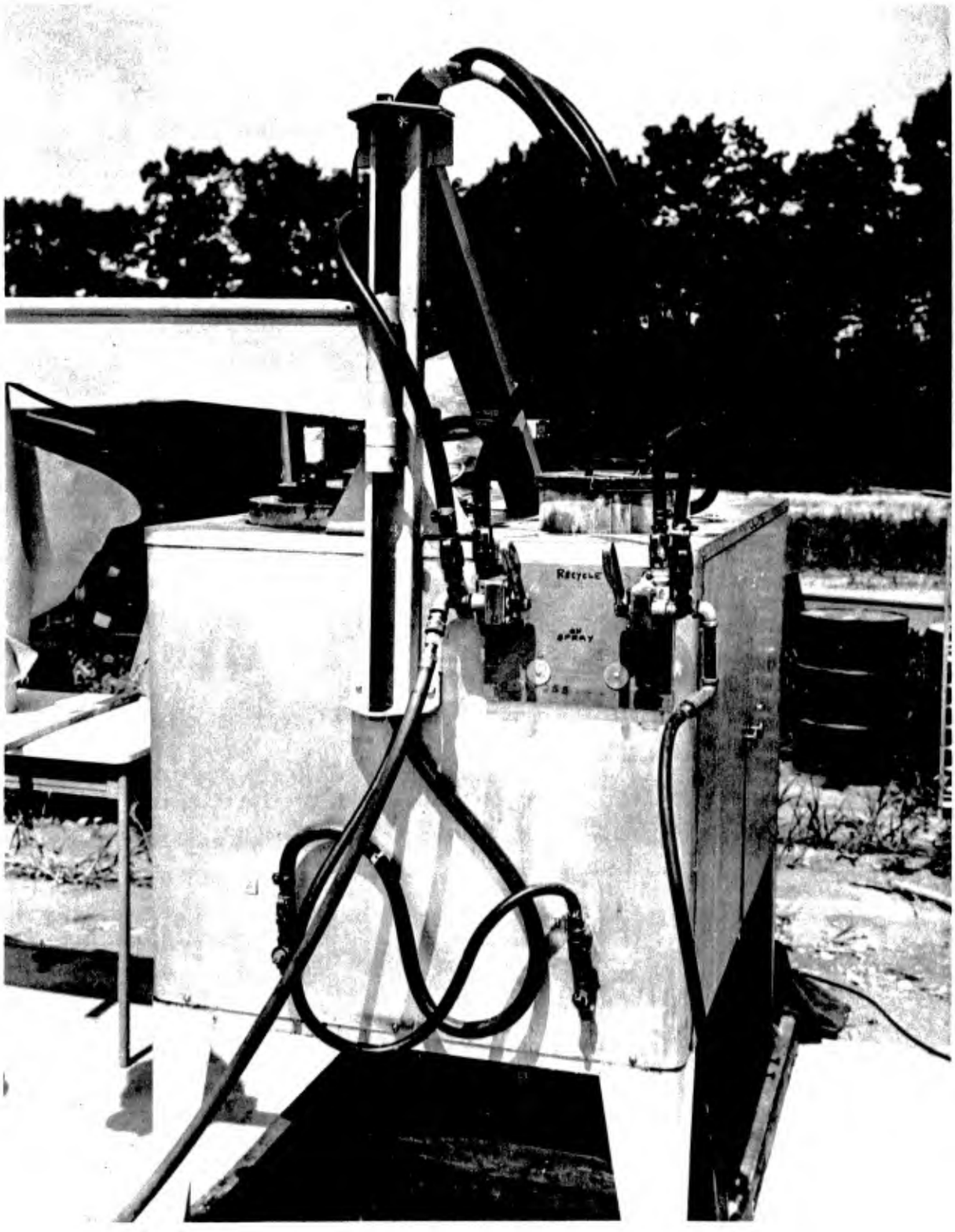

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Figure 14. Flow Valves Mounted on Side of Klauder-Williams Machine for Spraying.

2. Spray Gun

The spray gun was a modified National Aniline spray device, as shown in Figure 15. It could be dissembled readily for quick cleaning. It was a stationary gun. Diisocyanate and resin are mixed and dispersed with compressed air. The diisocyanate hose is attached at the rear orifice of the gun, the compressed air line at the center inlet, and the resin hose at the inlet nearest the nozzle. When the gun is in use, the valves for the hose lines carrying diisocyanate and resin to the gun are turned off before closing the compressed air line. This permits the air to clear the gun before it is dissembled and immersed in acetone for cleaning.

3. Air Compressor

A Schraum compressor mounted on a truck capable of delivering 105 cu ft/min of air, over a pressure range of 50 to 150 psi, was used for the tests. The air-output gauge was operated manually. This compressor has an automatic device for maintaining a constant flow of oil-vapor into the air stream. The presence of oil in the air stream did not appear to interfere with foaming.

4. Operating Variables

Formulation 100C was selected for the initial trials. Foam rise and set of this mix when sprayed onto vertical surfaces was not sufficiently rapid to avoid flow on contact. This was corrected by the addition of catalysts, such as N-methyl morpholine. The resulting modification, formulation SP-100 (Table LV), proved to be an excellent mix for spray applications.

All ingredients except the TDI were blended and poured into the resin pot and the dial of the variable-meter pump set at 5.5 for a delivery rate of 80 grams per 5 seconds. Nacconate 80, pressurized with dry nitrogen, was forced into the pot above the pump metering TDI, and the dial set at 7.5 to give a delivery rate of 69 grams per 5 seconds. These rates of delivery to the gun were found to be optimum. The optimum air pressure for operating the gun was 90 to 95 psi. Lower pressures were not adequate for thorough mixing and dispersion; higher pressures produced fine "mists" which were difficult to apply without excessive waste..

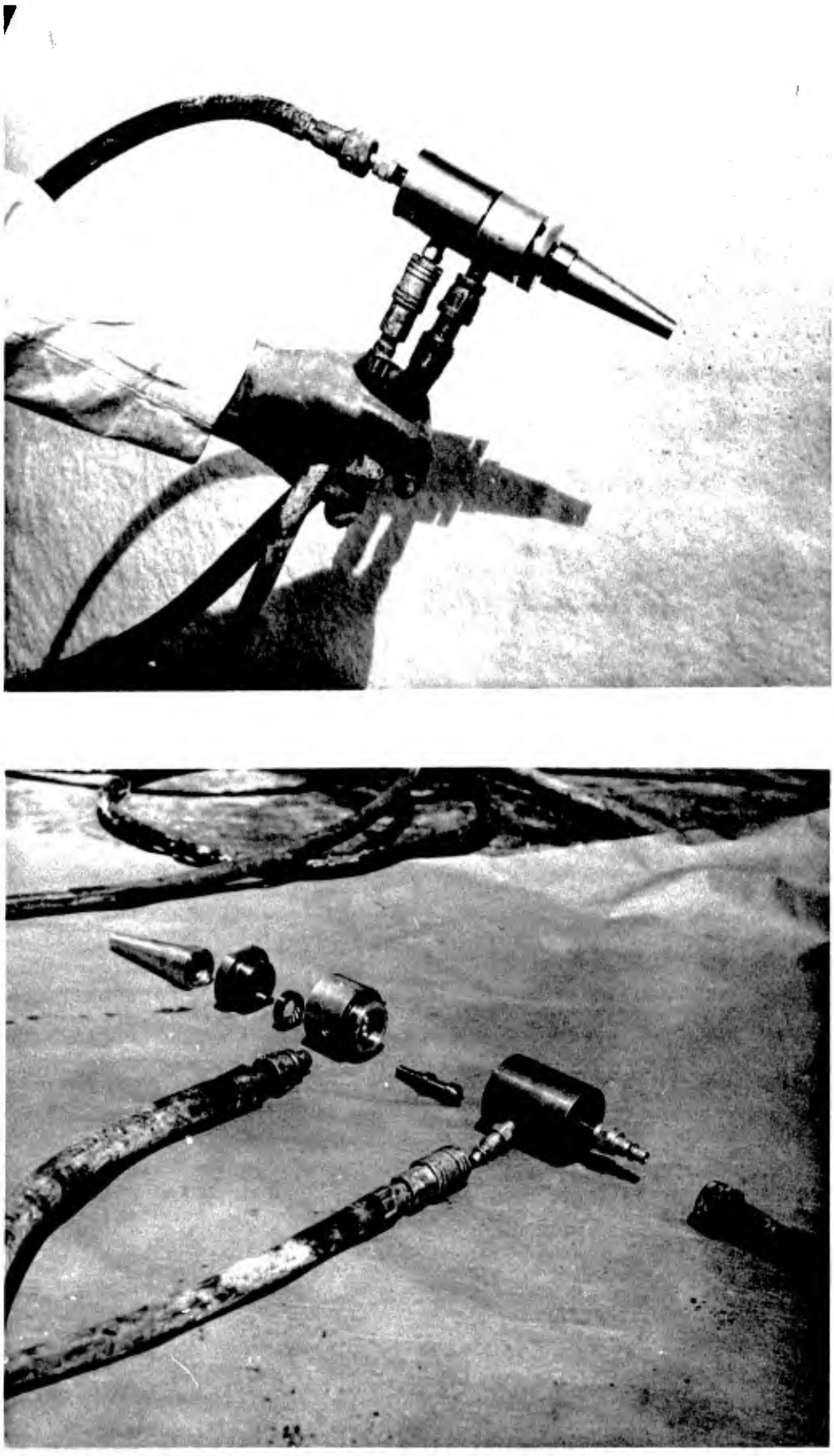

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Figure 15. Spray Gun for Foams.

5. Sprayed-on Shelter

A sprayed-on shelter was made by spraying an inflated canvas bag, and subsequently deflating and removing the bag from the rigid, foamed structure. Figure 16 shows the foam being sprayed. The dome was approximately 6 feet in diameter. Foam thickness was approximately 1 inch. Density of the foam, using the modified 100C formulation above, was 5.2 lb/cu ft. A furnace blower was used to inflate the canvas hemisphere while foam was sprayed. After spraying of the foam was complete, the panel was cut out and canvas hemisphere removed. Figure 17 shows a completed shelter.

6. Mixing of Foam Ingredients at Low Temperatures for Spraying

Temperatures near the solidification point of the 80:20 mixture of the 2,4- and 2,6-isomers of toluene diisocyanate (59 to 60°F), were investigated. Formulation SP-100 foams can be applied by spraying at ambient temperatures of 59 to 60°F, using the Klauder-Williams machine, at delivery rates as high as 8 lb/min. The foams set up and become non-tacky to the touch in less than 30 minutes. They are self-curing in less than 12 hours at this temperature. The density of foams, using the same formulation, is much higher when sprayed on at 60°F than when sprayed at 85°F: 12 and 5.5 lb/cu ft, respectively. Details of the experimental work follow.

The high-speed mixing head was removed from the Klauder-Williams foam machine and the hose lines from the metering pumps attached to an Atlantic Research spray gun (a modification of the National Aniline model). An air compressor operating at 90 to 95 psi (optimum pressure for the type of spray desired) was used for mixing and dispersion of the diisocyanate (Nacconate 80) and resin.

The spray formulation used was a modified SP-100 formula containing more N-methyl morpholine, and had the composition shown in Table LVI.

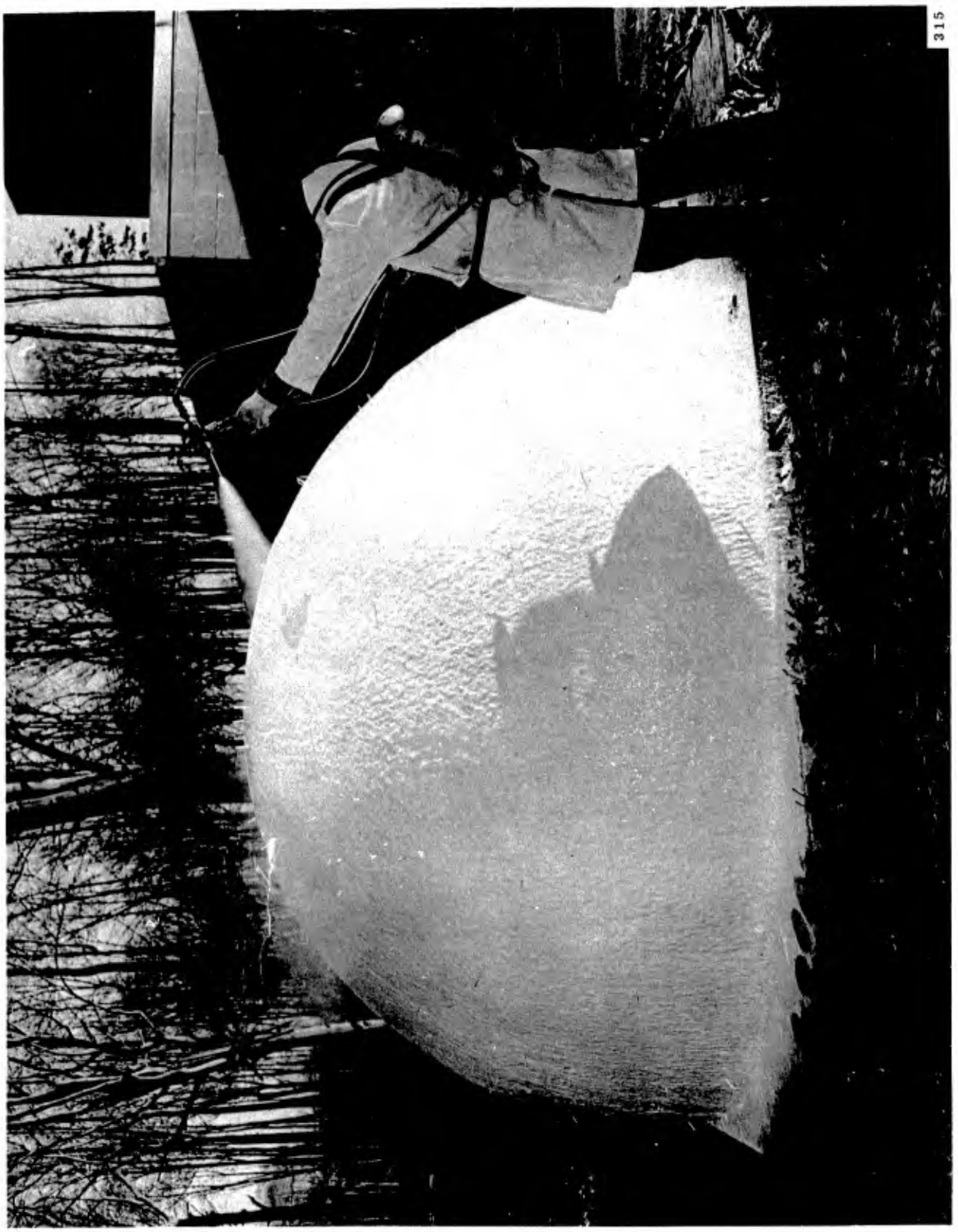

Figure 16. Spraying Foam on an Inflated Bag.

Figure 17. Completed Foam Shelter.

TABLE LVI

Modified Formulation SP-100 for Spraying

Ingredient	Content (parts by weight)
Quadrol	60
Castor oil, AA	40
Diallyl phthalate	20

Thirty-pound batches of this mix were blended with 100 grams of water, 20 grams of Union Carbide's Silicone L-520, and 80 grams of N-methyl morpholine. The meter-pump dial for the resulting liquid resin was set at 5.5 for a delivery rate of 80 grams per 5 seconds. The meter-pump dial for the toluene diisocyanate (Nacconate 80) was set at 7.5 to give a delivery rate of 69 grams per 5 seconds.

The material was sprayed against paper, plywood, and an inflated canvas dome (a hemisphere 6 feet in diameter and 3 feet high). The temperature of the mix was 60°F. The temperature of the room was 58°F. Set time (non-tacky to touch) for the foams was 25 to 30 minutes. Adherence of foam to paper and plywood was excellent. Adherence of foam to the wax-coated canvas bag was poor enough that the bag was readily stripped without damage to the shell of foam.

7. Production of Foams by Mixing and Spraying under Outdoor Conditions at Low Temperatures

A hemispherical canvas bag, 12 feet in diameter at the base and 6 feet high, fitted with a zippered slit (3 feet long) and a blower sleeve (6.5 inches in diameter) was placed on a wooden platform and inflated with a furnace blower. Cardboard strips, 2 inches in height, were applied at intervals over the surface of the inflated bag. These markers serve as indicators for determining the depth of sprayed-on foam.

The inflated bag was then sprayed, with repeated spray applications over the entire surface of the bag, with the modified 100C spray formulation. The temperature of the spray mixture was 60°F. Ambient temperatures during the spraying period ranged from 58 to 42°F. Wind velocity was

7 to 10 knots. The temperature for cure at the end of the spraying period, overnight (12 hours), was below the freezing point for water (30 to 31°F). The sprayed-on foams under these conditions required approximately 2 hours to set up (non-tacky to the touch). They cured to form rigid, non-tacky structures after 12 hours at 30 to 31°F. The density was approximately 15 lb/cu ft. To avoid the possibility of heterogeneity of foam structure during spray buildup on large surfaces, such as 6- by 12-foot hemisphere, type and concentration of catalyst were not altered to accelerate rate of foam set up. If the interval between spray applications is sufficiently long for surface hardening--and this interval is short for highly catalyzed systems--the foam layers form a noncoherent laminar structure.

Three hours were required for the application of a foam layer 2 to 2.5 inches deep. Spray deposit lost to the wind was high. The foamed structure was of uniform texture but it was not as strong as a foam of lower density prepared previously indoors with an overnight cure at 58 to 60°F.

In accordance with instructions, both movie and still pictures were taken of the spray demonstration.

The relationship between weight and density of foam of varied thickness for a hemisphere, 6 × 12 feet was computed. The data are presented in Table LVII.

TABLE LVII

Relationship Between Weight and Density of Foam for a Hemisphere 12 Feet in Diameter and 6 Feet High

Density (lb/cu ft)	5	7	9	10	12	13	14	15
Thickness (in)	Total Foam Weight (lb)							
0.5	47.13	65.98	84.83	94.26	113.11	122.53	131.96	141.38
1.0	94.24	131.94	169.64	188.49	226.19	245.03	263.88	282.73
1.5	141.37	197.92	254.47	282.74	339.29	367.57	395.84	424.11
2.0	188.50	263.90	339.30	377.00	452.40	490.10	527.80	565.50

$$\text{Weight} = 1/2\ \pi\ D^2\ t\ p$$

$$S = 1/2\ \pi\ D^2$$

$$\text{Volume} = S\ t = \text{Surface} \times \text{Thickness}$$

$$W = S\ t\ \rho$$

t = Thickness of shell

ρ = Foam density

G. TESTS FOR FIELD USE

1. Storage Stability

Tests were made on storage stability of components and component mixtures, as it affects packaging, handling, and foaming under field conditions, of the five best formulations: 108C, 100C, 99B, 113B, 121A.

Results indicate that where components are packaged separately for storage, and later mixed in the field at time of foaming, the stability on storage is limited to temperatures of about 60°F (15°C +) and above when the 80:20 mixture of the 2,4-:2,6-toluene diisocyanate (Nacconate 80) is used. One of the isomers, the 2,4-toluene diisocyanate, begins to solidify and separate out on storage below 60°F. Mixing for foaming at 60°F and above may be effected by hand or by machine. Stability on storage at over 40°F for the components of the formulations containing vinyl toluene or diallyl phthalate, 108C and 100C, was obtained by substituting Nacconate 1080-H, a hexane triol adduct with toluene diisocyanate, Nacconate 80. Hand mixing for foaming at 40°F is preferred to machine mixing because of high viscosity of some of the components. Mixing is effected by first kneading the resin mix in flexible bags (polyethylene) until well-blended. The diisocyanate is then added and kneading continued until foaming begins. The bag is slashed and the contents are dumped into the mold.

In two-component systems, comprising (1) the castor oil-polyololefinic monomer; and (2) the diisocyanate, packaged separately for storage, the oil-polyol mixtures containing vinyl toluene (formulation 108C) lost stability within two weeks at room temperature and the foaming characteristics changed. The mix became very viscous. The marked increase in viscosity is attributed to insufficient inhibitor for preventing polymerization of the vinyl toluene (only 10-20 ppm of a butylated cresol is normally added to avoid having to remove it preceding polymerization at the factory). Shelf-life of these monomers

at room temperature, as received, is about three months. The monomer used was three months old. Higher concentrations of inhibitor would be required for the two-year storage period desired for this application. Castor oil-polyol mixes containing diallyl phthalate (100C) and those containing diallyl succinate (99B) remained stable over a period of four months and their foaming characteristics did not change. The inhibitor used in these cases appeared to be well-suited for storage stability. Castor oil-polyol systems containing N,N'-diallyl melamine (121A) became unstable after two months storage at room temperature. The mix separated quickly on standing; homogeneous blends were difficult to obtain because of incompatibility of the aged components. Castor oil-polyol systems containing vinyl stearate (113B) retained their appearance after two months' storage at room temperature, but they no longer gave satisfactory foams. These changes may have been due to slow polymerization during storage.

In the two-component systems, comprising (1) castor oil-polyol and (2) diisocyanate-olefinic monomer, packaged separately for storage, the five olefinic monomers used were mixed in one series of tests with the appropriate amount of Nacconate 80, and in another series with an equivalent amount of the hexane triol adduct (Nacconate 1080-H). These samples stored three weeks at 0°C. Vinyl toluene was the only monomer of the group which maintained the fluidity of both the Nacconate 80 and the Nacconate 1080-H for three weeks at 0°C. Diallyl phthalate permitted about one-half of the Nacconate 80 to precipitate, but gave clear solutions with Nacconate 1080-H that remained fluid after three weeks at 0°C. Diallyl succinate precipitated about three-fourths of the Nacconate 80, but only a slight amount of the 1080-H. Diallyl melamine permitted both mixes to solidify completely. Vinyl stearate, tested only with Nacconate 80, permitted it to solidify.

The two-component systems of formulations 108C (vinyl toluene), 100C (diallyl phthalate), 113B (vinyl stearate), and 121A (N,N'-diallyl melamine), were prepared using the castor oil-Quadrol additives as one phase and the Nacconate 80-olefinic monomer as the second phase. These

were stored separately overnight at 0°C. The following day the castor oil-Quadrol component was placed in polyethylene bags, followed by the Nacconate 80-olefinic monomer mixtures, and the contents were mixed at 1°C by kneading until foaming began. Some of these mixtures were pasty solids at 1°C. The density of foams produced and the exotherm obtained at 1°C, relative to that of the same foams prepared at 25°C, are shown in Table LVIII.

Table LVIII

Exotherms at 25 and 1°C for Various Foams

	Foamed at 25°C		Foamed at 1°C	
Formulation	Density (lb/cu ft)	Maximum Temperature (°C)	Density (lb/cu ft)	Maximum Temperature (°C)
108C	5.34	170	6.22	153
100C	5.56	176	8.58	150
113B	5.96	170	10.17	Tacky (poorly mixed)
121A	6.13	168	7.84	138

Foams prepared at 1°C by formulations 108C and 100C, using approximately 200-gram batches, set up rapidly with some increase in density over foams made at room temperature. The exotherm, starting at 1°C, was adequate for cure.

2. Compressive and Flexural Strength

The relationship between foam density and compressive strength was determined. Foams based on formulation 100C, modified by reduction of isocyanate to lower the exotherm, were prepared over a density range of 6.4 lb/cu ft to 38.1 lb/cu ft. Samples of 1-inch cubes were submitted for an evaluation of compressive strength, using the Tinius-Olsen machine at a loading rate of 0.1 in/min. All samples had aged 26 days at the time of the compressive strength tests. The formulations used and the results of the tests are included in Table LIX.

Table LIX

Density and Compressive Strength of Modified 100C

HP-78 Sample	Water Added[a] (gm)	Density (lb/cu ft)	Compressive Strength (psi)
A_1	0.0	38.1	2000
A_2	0.0	36.3	1746
B_1	0.5	11.3	226.5
B_2	0.5	10.6	218.5
C_1	0.85	6.4	79.8
C_2	0.85	6.4	90.4
D_1	0.2	20.8	626
D_2	0.2	18.8	552

a. These foams were all made using a modified 100C formulation. A reduced NCO:OH ratio was used, and the density was controlled by addition of various amounts of water to the following formulation:

Ingredient	Content (gm)
Quadrol	60
Castor oil, AA	40
Diallyl phthalate	20
Ethyl cellulose N-100	3
Nacconate 80	57.3

Samples of these foams were then submitted to the Bridge Branch of the U. S. Army Engineering Research and Development Laboratories, Fort Belvoir, for measurements of flexural strength. The Tate-Emery load-maintainer machine was used for these tests, and calculations were made according to the A.S.T.M. method, Designation D-790-45T (Flexural Test of Plastics).

Beams 24 X 1 X 1.5 inches were cut and supports were loaded midway between two supports 12 inches apart. The 1.5-inch dimension was vertical, so that the breadth of the beam was 1 inch, and depth was 1.5 inches. Speed of loading was 0.2 in/min. The load and the deflection were recorded. Results appear in Table LX.

Table LX

Flexural Strength Data for Modified 100C

Beam	Density (lb/cu ft)	Maximum Load[a] (lb)	Maximum Deflection[a] (in)
A_1[b]	38.1	265	0.60
A_2	36.3	207	0.46
D_1	20.8	103.8	0.73
D_2	18.8	85.3	0.65
B_1	11.3	38.8	0.71
B_2	10.6	35.0	0.74
C_2	6.4	14.8	0.83

a. Average of two measurements.

b. Code used in Table LIX.

The data of Table LX give straight lines on log-log plots. The ultimate load appears to vary as the 3/2 power of the foam density. The ultimate deflection decreases slightly as the density increases. The results were consistent enough that the data could be used for design purposes.

These foams might be much improved without introducing too much of a weight penalty, if they were reinforced on the tension side with a light metal framework. Foam is probably weaker in tension than in compression. A beam of variable density, more dense on the tension side might prove useful.

3. Dimensional Stability

Four-inch cubes were checked for dimensional stability by placing them in controlled temperature chambers of -65 and 160°F, and subjecting them to three cycles of 16 hours at each temperature. Dimensional stability was measured by the percentage of change in the longest dimension of the cube when measured at room temperature before and after the test. Specimens for the compression test were cut to 1

× 1 × 2 inches, three from each cube. By testing in three directions, any anisotropy of compressive properties due to the direction of foaming could be detected. Compression measurements were conducted on an Instron machine.

For the determination of cell structure, 1-inch cubes were used. The cubes were bonded to an aluminum plate with liquid, colored epoxy. The aluminum plate with the cubes was placed in a vacuum chamber and a vacuum of 29 inches of water applied. As soon as the vacuum pressure attained this value the vacuum was released and the epoxy allowed to cure. The cell structure, open and closed cells, was determined by sawing the cubes through the center and noting the penetration of colored epoxy into the open cells of the foam, using counts of colored and noncolored cells.

Results of these tests are listed in Table LXI. Dimensional stability of foams made by formulations 100C and 108C was excellent. Styrofoam at a density of about 2 lb/cu ft with a value of -0.27 per cent (shrinkage) was not as good. The 100C and 108C foams proved to be predominantly open-celled. Compressive strength values differed little from the expected values.

4. Drop Tests

Drop-testing* of foams prepared by formulations 108C and 100C, indicated that energy-dissipation of the 108C foams varied with density, as expected. However, energy-dissipation of the 100C foams appeared to be independent of density. No explanation of the anomalous behavior of the 100C was apparent.

Because other drop-test data disagreed with this result, the problem was examined. Sources of disagreement might include (1) instrumentation and calculation errors; (2) change in properties of the 100C foams due to aging; and (3) variation in calculated density of foams cast into cardboard boxes, 24 × 24 × 3 inches, because of bulging of the container at the time of casting and voids formed at the interface between pours.

*Performed by Dr. Turnbow, of the University of Texas.

Table LXI

Evaluation of Foam Properties

Density (lb/cu ft)	Dimensional Stability 3 Cycles (-65 to 160°F)	Ultimate Compressive Strength in 3 Perpendicular Directions (psi)			Compressive Yield Point for 0.2 per cent Elongation (psi)			Modulus of Elasticity (psi)			Cell Structure (per cent open celled)
		1	2	3	1	2	3	1	2	3	
2.74	-0.14[a]	23	23	22	10	14	18	480	470	740	95
2.08	-1.2	20	14	13	16	9	10	716	215	350	0
2.48	-0.11	21	21	20	16	14	14	841	710	651	98
5.04	+0.11	109	100	99	82	66	74	3860	3020	2750	70
5.37	-0.17	95	81	77	74	53	53	3090	2020	1810	90
7.25	+0.4	128	114	112	105	87	84	5100	3770	4160	60

a. Denotes shrinkage; + denotes swelling.

Change in properties due to aging during storage was investigated. Blocks of foam of formulation 100C, 24 × 24 × 3 inches, of the same age as those tested were removed from storage. The foamed blocks, which had been mixed by machine and cast into cardboard cartons, ranged in density from 2.25 to 5.0 lb/cu ft. The blocks were marked at intervals of 2 inches and cut into units, 2 × 2 × 3 inches. The cardboard was then cut away to give 2-inch cubes of foam. Similar blocks of foam at densities greater than 5.0 lb/cu ft were freshly prepared.

These foams were subjected to drop-tests, with the results shown in Figure 18. The energy absorption after a storage period of approximately one year, appears to be a function of the 2.5 power of the density on a log-log plot. Confirmation of the energy-dissipating characteristics of foams of the 100C type by repetition of the drop tests on the aged foams led to the conclusion that neither instrumentation and calculation errors at Atlantic Research nor change in properties of foam due to aging are responsible for the anomalous behavior of the 100C foams in the drop tests.

Variation in measured density from the calculated density, which was based on the weight of the foam and an assumed volume of 1 cu ft for the 24- × 24- × 3-inch cardboard molds, was investigated. A large number of boxes of 100C and 108C foams were pulled from storage and variation in dimensions and density measured. Dimensional change for the 100C foams was less than that for the 108C foams. The reason for the discrepancy in test results remained unexplained.

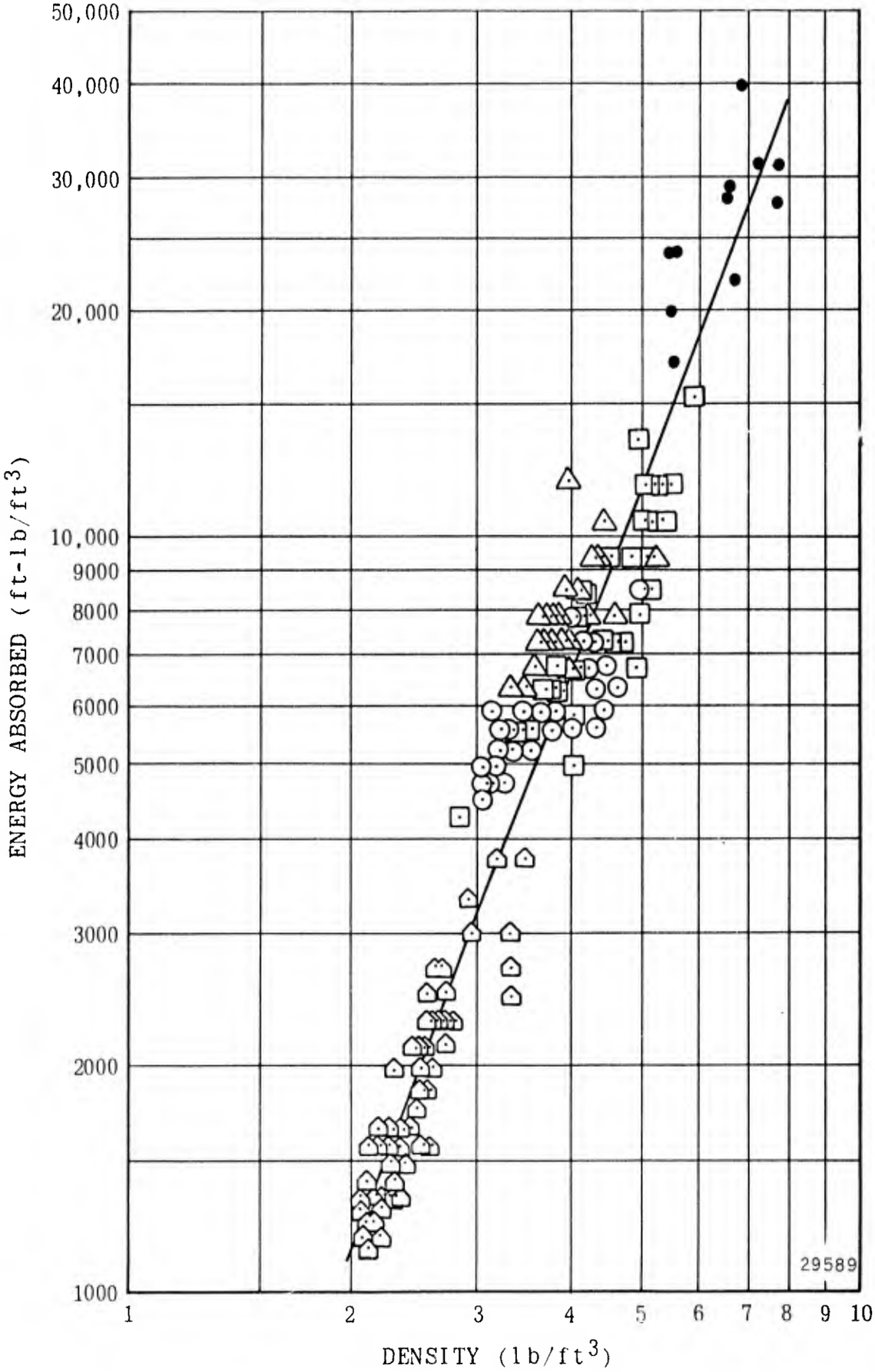

Figure 18. Correlation of Energy Absorption and Density for Formulation 100C.

IV. CONCLUSIONS AND RECOMMENDATIONS

Results obtained in the course of this program have uncovered several approaches to the problem of developing processes suitable for the production of foamed-in-place, energy-dissipating, and insulating materials under field conditions. Research is recommended in several areas because of high probability of success:

(1) Investigations of castor oil-monomer systems based on polyols other than Quadrol should be carried out. Less basic tetrols characterized by carbon chains between -OH groups larger than those of Quadrol are now available and should be tried as cross-linking agent with polyether-polyol blends.

(2) Polyols other than castor oil which contain unsaturated groups should be copolymerized with various monomers during the foaming-in-place reaction to alter properties of foamed structures. Alkyd polyester polyols, e.g., maleic anhydride-phthalic anhydride condensed with an excess of some triol or mixtures of diols and polyols are examples. Reaction rates and exotherm could be controlled more readily than with castor oil.

(3) Stabilizers are needed for vinyl and diene monomers, which will not react with diisocyanates. These are necessary if monomers are to be used as solvents to prevent solidification of the diisocyanates at low temperatures.

(4) Studies on catalysis, both negative and positive, for urethane condensations in anhydrous systems, as well as for those containing water, are required for process control over the temperature range anticipated under field conditions.

(5) Diisocyanates and adducts of low volatility which are fluid at temperatures below the solidification points of the currently available toluene diisocyanates would simplify foaming at low temperature. The hexane triol-diisocyanate adduct is an example.

(6) Anhydrous, one-shot, foamed-in-place polyurethane-monomer systems, utilizing organic acids, certain lactones (e.g., beta-propiolactone), and acid anhydrides instead of water as the source of gas for foaming, are feasible. Dinitrosopentamethylene tetramine may also be used as the source of gas for blowing. Stannic

chloride, aluminum chloride, etc., may be used to initiate the polymerization of the vinyl or diene component whose heat of reaction induces urethane condensation and liberation of CO_2 from the diisocyanate-acid adduct. The same catalysts promote decomposition of dinitrosopentamethylene tetramine with liberation of nitrogen gas. Alkali metal and metal alkyls could be substituted in systems with the dinitroso compound as the source. Research along this line should be profitable for producing foams at sub-zero temperatures.

(7) Studies on foaming-in-place at very low temperatures (-30 to -65°F) based on the use of vinyl and diene monomers should be extended. Feasibility was demonstrated. Both cationic and anionic catalysts are suitable initiators.

(8) The development of a simple, high-speed laboratory tester for evaluating the behavior of experimental energy-dissipating structures at high velocities of impact would be of great value.

V. BIBLIOGRAPHY

Some references of interest that are not available in Dombrow's book* on polyurethanes are listed below:

Abbott, J. A., "How Low-Density Solids are Made," Chemical Engineering, July 1952.

Bailey, M. E., "New Surface Coatings Based on Diisocyanates," Society of Plastic Engineers Journal, 14, No. 2, February 1958.

Boye, F. C., N. E. Wahl, A. F. Reilly, "Development of Foamed Core Material for Radomes," Cornell Aeronautical Laboratory, Inc., Report No. UB-691-M-11, September 19, 1952.

Brenner, W., "Foam Plastics," Materials & Methods, June 1956.

Cassias, G., R. E. Christensen, D. S. Trifan, "Castor Oil-m-Tolylene Diisocyanate Polyurethane Resins and Related Modifications as Potting Compounds," Plastics Laboratory, Princeton University, Technical Report No. 26C, Signal Corps Contract DA-36-039-sc-133, July 25, 1952.

Chiola, V., S. Bonotto, G. Cassias, N. Vasileff, "Castor Oil-Tolylene Diisocyanate Polyurethane as Impregnating, Encapsulating, and Potting Compound," Plastics Laboratory, Princeton University, Technical Report 21B, Signal Corps Contract DA-36-039-sc-133, July 21, 1951.

Christensen, R. E., D. S. Trifan, "Plasticized Modifications of Dipropylene Glycol-Castor Oil-m-Tolylene Diisocyanate Polyurethane as Potting Resins," Plastics Laboratory, Princeton University, Technical Report 31A, Signal Corps Contract DA-36-039-sc-133, November 30, 1953.

Colodny, P. C., V. A. Tobolsky, "Chemorheological Study of Polyurethane Elastomers," Frick Chemical Laboratory, Princeton University, RLT Technical Report No. 22, Contract NOnr-185807, April 12, 1957.

Cornwell, A. C., D. B. V. Parker, L. N. Phillips, "Foamed-in-Place Techniques with Sebalkyd and Flexalkyd Resins," Royal Aircraft Establishment (Great Britain), Technical Note No. 1295, February 1957.

Edwards, J. T., "Investigation of Diisocyanate Resins for Filling Hollow Propeller Blades," Aeroproducts Division, General Motors Corporation, Final Progress Report, July-August 1952, Engineering Report No. 699, Contract AF 33(038)11286, November 4, 1952.

---

* Dombrow, Bernard, Polyurethanes, Reinhold Publishing Company, New York (1956).

Ephraim, S., A. E. Woodward, R. B. Mesrobian, "Kinetic Studies of the Reaction of Phenyl Isocyanate with Alcohols in Various Solvents," Journal of the American Chemical Society, March 20, 1958.

Forbes, R. S., "Polyurethane Casting Resins," Components and Systems Laboratory, Wright Air Development Center, Technical Note No. WCLC 52-3, December 1952.

Glickman, M., L. C. Ritter, "Foam-in-Place Application of Polyurethane Foam in Buoyancy Compartments of Small Boats," Industrial Test Laboratory, Philadelphia Naval Shipyard, Final Report, Report Nos. 2804B, Part 2, and 2968, August 1956.

Graham, D. C., "Self-Expanding Thermoplastic Foam," Materials & Methods, April 1957.

Hopkins, R. P., "Polyester-Urethane Foams," Resin Review, July 1955.

Leidigh, E. T., R. D. McLeod, J. M. Wrightson, "Improvement of Inert Sealer in Bombs," Aerojet-General Corporation, Informal Progress Report No. 11, Report No. L1911/12-11, Contract DA(I)28-017-501-ORD(P)-2115.

Mason, T. D., "Polyurethane Base Enamelled Winding Wire," Royal Aircraft Establishment, Technical Note No. EL 102, JSRP No. 560017, September 1955.

Merriman, P., "Isocyanate-Based Polymers," Research, 9, 254-259, July 1956.

Phillips, L. N., "The Chemistry and Technology of Flexible Polyurethane (Flexalkyd) Foams," Royal Aircraft Establishment, ASTIA 22-56, December 1955.

Reilly, C. B., "The Chemistry of the Cross-Linking of Polyurethanes," Applied Science Research Laboratory, University of Cincinnati, Progress Report No. 2, Contract AF 33(616)-3162, November 1, 1955-January 21, 1956.

Reynolds, H. E., "Summary of Static Tests Performed to Evaluate 'Armofoam' as a Filler in a Ribless F40-198-18M2 Thrust Member Type Propeller Blade," Aeroproducts Division, General Motors Corporation, Engineering Report No. 682, Contract AF 33(038)11286, June 24, 1952.

Rogers, T. H., "Elastomeric Cellular Materials I", Rubber World, August and September 1955 issues.

Walsh, R. H., "Automotive Engineering with Urethane Foams," Rubber World, June 1957.

Wrightson, J. M., "Development of an Improved Bomb Sealant," Aerojet-General Corporation, Informal Progress Report No. 1, Report No. L 1911-1, Contract DA-28-017-501-ORD-2115, June 21, 1956.