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TECHNICAL REPORT

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DEVELOPMENT OF LOW-DENSITY HIGH-STRENGTH FOAMED PLASTICS VIA IONIC POLYMERIZATION

CLOTHING & ORGANIC MATERIALS DIVISION

MARCH 1964 NATICK, MASSACHUSETTS

U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

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DEVELOPMENT OF LOW-DENSITY HIGH-STRENGTH FOAMED PLASTICS VIA IONIC POLYMERIZATION

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FOREWORD

There has been a considerable amount of interest by the military in a method to produce foamed plastics under field conditions over a wide range of ambient temperatures without requiring special equipment or highly-trained personnel. Foamed plastics would be valuable as an energy dissipator, as flotation material, as protection for cached items, and, particularly under arctic conditions, for the rapid production of small, temporary insulated shelters for a small group of men.

The work covered in this report, performed by the Atlantic Research Corporation under Contract No. DA19-129-AMC-9 (X), represents a preliminary investigation of one possible approach to the problem, namely the use of ionic catalyzed vinyl monomers as a foam-forming system.

The U. S. Army Natick Laboratories Project Officer was Dr. G. E. Murray, and the Alternate Project Officer was Mr. J. F. Furrer, both of the Plastics Section, Clothing & Organic Materials Division.

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ABSTRACT

Equimolecular mixtures of mono- or di-allyl ethers of trimethylolpropane and sulfur monochloride gave tough, spongy foams when reacted in a halogenated solvent, which also acted as a blowing agent. Reaction was rapid at room temperature, but quite slow at 0°F.

A number of vinyl alkyl and divinyl ethers were evaluated using cationic catalysts and chlorinated solvents as blowing agents at room temperature. Foams were obtained in a number of cases, and the flexibility of the foams was related to the ratio of the mono-vinyl to the divinyl ether. The foams were quite spongy and friable.

Use of 3,4-dihydro-2H-pyran-2-methanol as a co-monomer with vinyl ethers gave moderately strong, lightweight foams. ( )

DEVELOPMENT OF LOW-DENSITY HIGH-STRENGTH FOAMED PLASTICS VIA IONIC POLYMERIZATION

I. INTRODUCTION

A. GENERAL

Under Contract DA 19-129-AMC-9(X) with the U. S. Army Quartermaster Research and Engineering Command,*Atlantic Research Corporation successfully has demonstrated the feasibility of foamed plastics preparation via ionically catalyzed polymerization. This work was initiated as the first step in the development of a reliable, inexpensive, portable foamed plastic dispenser for the generation of foams under field conditions over a broad (-40°F to +110°F) temperature range.

Foamed-in-place plastics are now most commonly generated by condensation polymerization to yield polyurethanes, phenolics, epoxies or silicones.** However, these are not readily adaptable to low operating temperatures because of the marked dependence of monomer viscosities and reaction rates on temperature.

Ionically catalyzed polymerizations proceed rapidly at extremely low temperatures to yield high molecular weight products and were therefore designated as the method of choice for the field production of foamed plastics over a much broader temperature range.

B. BACKGROUND

The ultimate program objectives were (a) the development of a low-density high-strength, rigid to semi-rigid, non-friable foamed plastic, capable of being produced over the temperature range of -40°F to +110°F; and (b) the design and construction of an operational 10-lb prototype kit intended to permit the reactants for the selected foaming precursors to be blended as required for the production of foam. The acceptable system could consist of not more than two liquids, each with

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* Now U.S. Army Natick Laboratories

** Resnick, I., Rigid Foam Plastics Information Manual, Materials Laboratory, New York Naval Shipyard, Brooklyn 1, N. Y., Final Report, SR-007-03-04, Dec. 1960; Tanner, William C., Plastic Foam Primer, Picatinny Arsenal, Dover, N. J., Tech. Report 2671, March 1960.

a viscosity low enough to be handled, metered and/or pumped over the specified temperature range, and the reaction must produce enough heat to foam and cure even at low ambient temperature, without an auxiliary heat source. Furthermore, the system must be capable of withstanding repeated thermal cycling over the range of -65°F to +160°F for a period of 1 year and the foam should exhibit the following characteristics:

compressive strength	$\geq$ 25 lb/sq in
strain	$\leq$ 0.2
density	$\leq$ 1.3 lb/cu ft

To achieve this goal the major effort would be devoted to a study of ionically catalyzed polymerization of vinyl monomers and a much smaller effort would be made to develop urethane and/or epoxy liquid systems capable of producing foams over the range of +40°F to +110°F.

With these objectives in mind, a comprehensive bibliography of government-sponsored work was obtained from the ASTIA* library and candidate materials were selected for laboratory evaluation.

Styrene, the allyl ethers of trimethylol propane, acrylate esters of polyethylene glycol, and vinyl ethers were screened. Based on the observed results and on the known properties of these materials, vinyl ethers were selected for intensive study.

Because of the limited availability of vinyl ethers and the time required for our own synthesis and purification of the divinyl ethers of polyglycols, the ultimate program objectives were not achieved during the contract year. However, the feasibility of the preparation of foamed plastics via ionically catalyzed polymerization was demonstrated conclusively.

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*ASTIA (Armed Services Technical Information Agency), now DDC (Defense Documentation Center, Department of Defense).

II TECHNICAL DISCUSSION

The generation of a field-foamed plastic involves the formation of gas bubbles in a polymerizing liquid system and the subsequent growth and stabilization of these bubbles as the polymerization proceeds to completion. Hence, the development of a field-foamed plastic requires an understanding not only of the physics and chemistry of polymer formation, but also an awareness of the behavior and properties of colloidal systems.

Because of their commercial value, the formation of polyurethane foams has been examined in considerable detail. From these studies, it has become evident that the foam-forming process is extremely complex although a fairly reliable qualitiative understanding has been developed.*

Little or no attention seems to have been directed to the development of foamed-in-place plastics by vinyl addition type polymerizations, whether free-radical or ionically catalyzed, apparently because of the sensitivity of these reactions to subtle environmental changes.**

A. IONIC POLYMERIZATIONS

Ionically catalyzed vinyl polymerizations are reactions initiated by either cations or anions and involve the addition of monomer to electrically charged growing molecules or ions. Ionic polymerizations have received much less attention than either free radical polymerizations or the numerous condensation polymerizations and are therefore, less well

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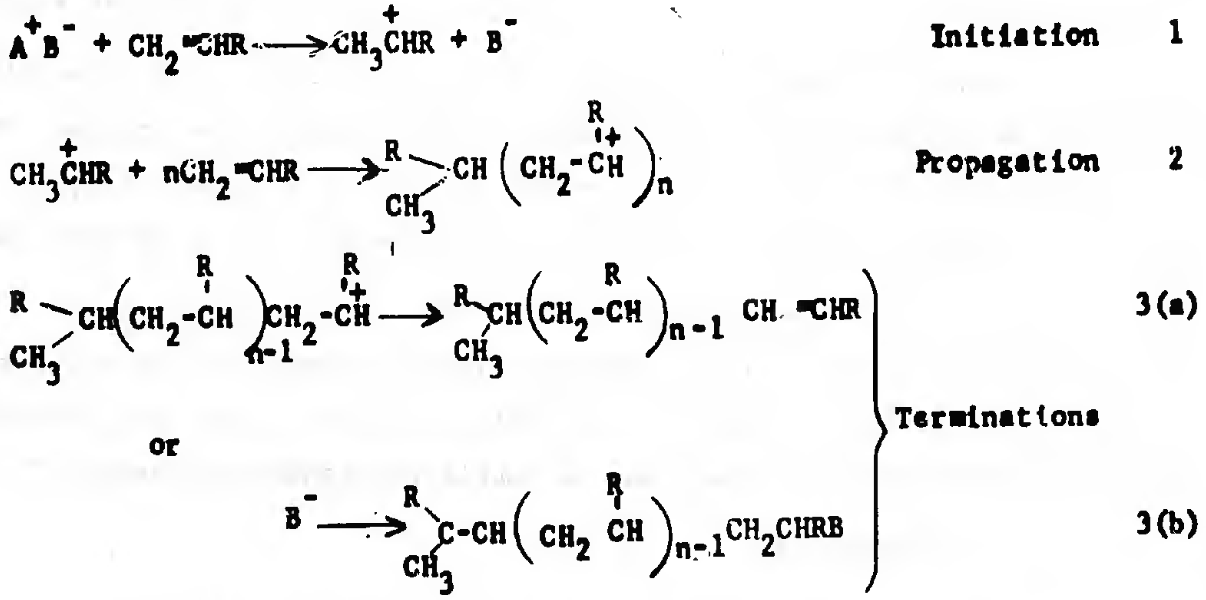
* Saunders, J. H., and K. C. Frish, Polyurethane, Chemistry and Technology, Part I, Chemistry, Chapter 5, Interscience Publishers, New York, 1962. (b) J. H. Saunders, The Formation of Urethane Foams, Rubber Chemistry and Technology, 33, 1293 (1960)

** See for example, P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N. Y., 1953 understood. This is probably due to the fact that these reactions are in general experimentally difficult to control and to reproduce, and are extremely sensitive to subtle changes in reaction conditions.*

The ionically catalyzed polymerization process is analogous to the free radical process, proceeding by an initiation, propagation and termination. The steps in the cationically catalyzed process may be described as follows:



$$A^+B^- + CH_2{=}CHR \longrightarrow CH_3\overset{+}{C}HR + B^- \qquad \text{Initiation} \quad 1$$

$$CH_3\overset{+}{C}HR + nCH_2{=}CHR \longrightarrow \underset{CH_3}{R}{>}CH\left(CH_2-\overset{R}{\overset{+}{C}H}\right)_n \qquad \text{Propagation} \quad 2$$

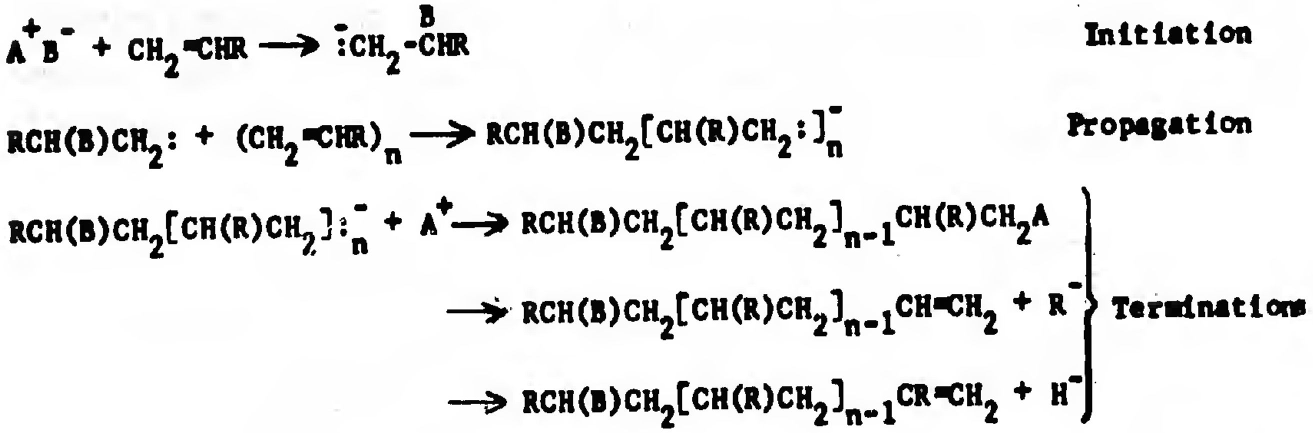
$$\underset{CH_3}{R}{>}CH\left(CH_2-\overset{R}{C}H\right)_{n-1}CH_2-\overset{R}{\overset{+}{C}H} \longrightarrow \underset{CH_3}{R}{>}CH\left(CH_2-\overset{R}{C}H\right)_{n-1}CH{=}CHR \qquad 3(a)$$

or

$$B^- \longrightarrow \underset{CH_3}{R}{>}C-CH\left(CH_2\ \overset{R}{C}H\right)_{n-1}CH_2CHRB \qquad 3(b)$$

Terminations

The anionically catalyzed mechanism is described below;



$$A^+B^- + CH_2{=}CHR \longrightarrow \overset{-}{:}CH_2-\overset{B}{C}HR \qquad \text{Initiation}$$

$$RCH(B)CH_2: + (CH_2{=}CHR)_n \longrightarrow RCH(B)CH_2[CH(R)CH_2:]^-_n \qquad \text{Propagation}$$

$$RCH(B)CH_2[CH(R)CH_2]:^-_n + A^+ \longrightarrow RCH(B)CH_2[CH(R)CH_2]_{n-1}CH(R)CH_2A$$

$$\longrightarrow RCH(B)CH_2[CH(R)CH_2]_{n-1}CH{=}CH_2 + R^- \qquad \text{Terminations}$$

$$\longrightarrow RCH(B)CH_2[CH(R)CH_2]_{n-1}CR{=}CH_2 + H^-$$

The reactivity of vinyl monomers towards either anionic (Lewis base) or cationic (Lewis acid) catalysts is dependent on the electronegativity of the substituents adjacent to the double bond. A strongly

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* Schildknecht, Calvin E., Chapter 6, in Polymer Processes, Vol. X of High Polymer Series, Intersciences Publishers Inc. N.Y., 1956.

electrophilic monomer is readily polymerized by basic catalysts but not by acidic catalysts and vice versa. The relationship between substituents and susceptibility of vinyl monomers, $CH_2{=}CHR$, to different catalysts is shown in the following list:*

$$R = \overbrace{\underbrace{\mathrm{CN,\ CO_2Me,\ OAc,\ \mathrlap{\underbrace{\phantom{CH{=}CH_2,\ pClC_6H_4,\ C_6H_5,\ CH_3,\ OAlkyl,\ -C_6H_4OMe(p)}}_{\text{Acidic}}}CH{=}CH_2,\ pClC_6H_4,\ C_6H_5}}_{\text{Basic}}}^{\text{Free Radical}},\ \mathrm{CH_3,\ OAlkyl,\ -C_6H_4OMe(p)}$$

The requirement that the system withstand storage for 1 year over the range -65°F to +160°F eliminated from consideration those monomers which are sensitive to free-radical polymerization.

Since most anonically catalyzed monomers are also sensitive to free-radical catalysis, we directed our attention to those monomers which respond only to acid catalysis. The vinyl ethers, especially of polyalkylene glycols, were specifically selected for the following reasons:

(a) The structural features of polymerized vinyl ethers will be similar to those of polyurethanes, viz., long polyalkylene oxide chains. This should facilitate the preparation of foamed plastics with predictable physical properties, by comparison with related polyurethane foams of known compositions.

(b) The use of relatively high molecular weight monomers should permit some degree of control over the rate and heat of reaction as well as viscosity of the polymerizing mixture. The entrapment of gas bubbles is at least in part dependent on the viscosity of the system.

(c) These compounds can be expected to have low freezing points. A polypropylene glycol of molecular weight 2000 (n=35) has a freezing point of -30°C. The corresponding divinyl ether should have an even lower freezing point since the hydroxyl groups, which are responsible for hydrogen bonding, are replaced by the less polar vinyl ether groups. Copolymers of ethylene oxide and propylene oxide should yield mixtures of even lower freezing points.

(d) Greater flexibility in formulation should be possible. Monovinyl ethers can be prepared in great variety to be used as modifying co-monomers. Polyfunctional vinyl ethers synthesized from glycerol or pentaerythritol can be used to give a higher degree of cross-linking. Functional vinyl ethers, such as the monovinyl ethers of the polyalkylene glycols can be used to provide sites for cross-linking or chain extension by alternate mechanisms.

(e) Vinyl ethers polymerize quite rapidly at low temperatures to yield fairly high molecular weight polymers. In fact the degree of polymerization (DP) is an inverse function of the reaction temperature.

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*Pepper, D.C., Ionic Polymerization, Quart Rev., 8, 88 (1954)

B. CATIONIC POLYMERIZATION

Cationic polymerization reactions proceed through highly unstable carbonium ions, unstable in the sense that they have a high probability of self-destruction by combination with anions or anionic fragments from potentially ionizable substances. In the case of primary and secondary carbonium ions, the destruction occurs by loss of proton. Hence, their lifetimes are quite short and to a certain extent are influenced by the polarity of the surrounding medium.

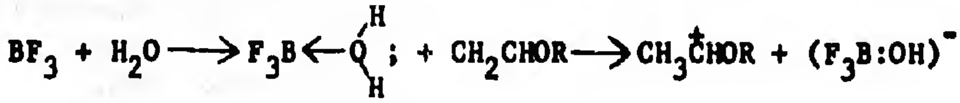
This type of polymerization is initiated by reaction between monomer and a catalyst to form a carbonium ion. When the catalyst is a protic acid, e.g., H_2SO_4, HF, the carbonium ion intermediate is undoubtedly formed by addition of a proton as follows:

$$HX + CH_2{=}CH\overset{..}{\underset{..}{O}}R \longrightarrow CH_3\overset{+}{C}H\ OR\ X^-$$

It is generally believed that Friedel-Crafts catalysts, e.g., $AlCl_3$, $SnCl_4$, $TiCl_4$, BF_3, etc., are not readily capable of initiating polymerization alone; these catalysts usually require the presence of a co-catalyst such as water, alcohol (proton-releasing substances) or an alkyl halide (a carbonium-ion forming substance). This belief is supported by numerous experimental observations as well as by theoretical considerations. Thus, the reaction described in the equation below

$$(BF_3 + CH_2{=}CHOR \longrightarrow F_3\bar{B}CH_2\overset{+}{C}H_2OR)$$

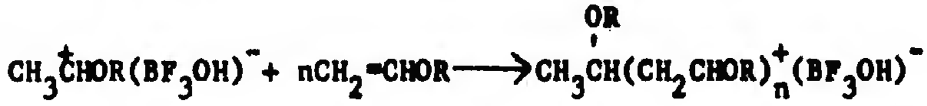
to produce an intermediate with the indicated charge separation would require an excessive amount of energy. The addition of either water or tert-butyl chloride immediately facilitates the conversion of the vinyl monomer to the carbonium ion as indicated below:



$$BF_3 + H_2O \longrightarrow F_3B \leftarrow \overset{H}{\underset{H}{O}}\,; + CH_2CHOR \longrightarrow CH_3\overset{+}{C}HOR + (F_3B{:}OH)^-$$

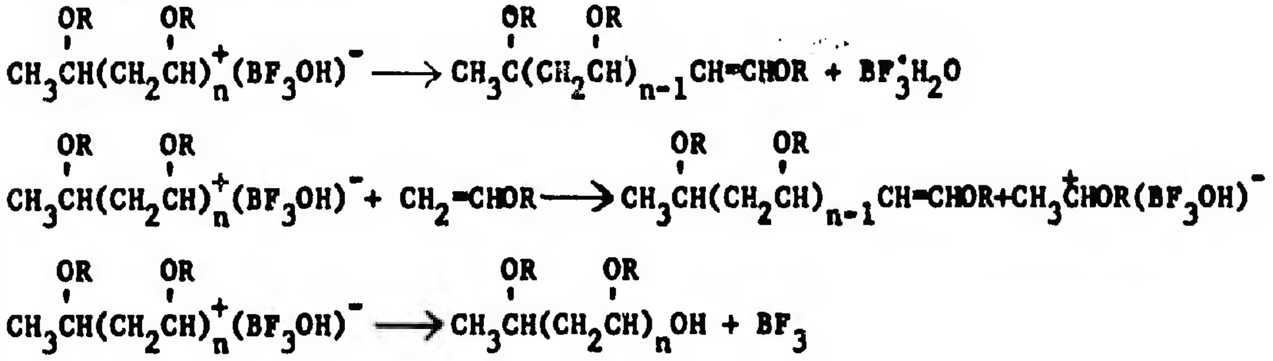
$$(CH_3)_3CCl + SnCl_4 \longrightarrow (CH_3)_3C^+SnCl_5^-; + CH_2{=}CHOR \longrightarrow (CH_3)_3CCH_2\overset{+}{C}HOR + SnCl_5^-$$

The carbonium ion thus produced grows rapidly by repeated addition to new monomer:



$$CH_3\overset{+}{C}HOR(BF_3OH)^- + nCH_2{=}CHOR \longrightarrow CH_3\overset{OR}{C}H(CH_2CHOR)_n^+(BF_3OH)^-$$

until it either loses a proton or combines firmly with an anion to destroy the positive charge.



$$CH_3\overset{OR}{C}H(CH_2\overset{OR}{C}H)_n^+(BF_3OH)^- \longrightarrow CH_3\overset{OR}{C}(CH_2\overset{OR}{C}H)_{n-1}CH{=}CHOR + BF_3{\cdot}H_2O$$

$$CH_3\overset{OR}{C}H(CH_2\overset{OR}{C}H)_n^+(BF_3OH)^- + CH_2{=}CHOR \longrightarrow CH_3\overset{OR}{C}H(CH_2\overset{OR}{C}H)_{n-1}CH{=}CHOR + CH_3\overset{+}{C}HOR(BF_3OH)^-$$

$$CH_3\overset{OR}{C}H(CH_2\overset{OR}{C}H)_n^+(BF_3OH)^- \longrightarrow CH_3\overset{OR}{C}H(CH_2\overset{OR}{C}H)_nOH + BF_3$$

C. VINYL ETHERS

The vinyl ethers are pleasant smelling, colorless liquids or solids, insoluble in water and soluble in most organic solvents. They do not readily polymerize by heating or by treatment with peroxides, although prolonged exposure to these environments will result in small quantities of low molecular weight polymers. These ethers react rapidly in the presence of cationic catalysts to yield polymers ranging from viscous liquids to pliable or rigid solids, depending on reaction conditions, the choice of catalyst and reactive monomer. Thus, Reppe* observed that the addition of catalysts such as $SnCl_4$, $AlCl_3$, $ZnCl_2$, $FeCl_3$, BF_3, $SiCl_4$, H_2SO_4, H_3PO_4, SO_2 and certain acid silicates to a variety of vinyl ethers at room temperature and above, resulted in violent reactions with the production of low molecular weight polymers. Under more carefully controlled conditions high molecular weight rubber- and wax-like polymers have been obtained.

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*Reppe, W., See Schildknecht, C. E., Vinyl and Related Polymers, Chapter XI, John Wiley and Sons, Inc., New York, 1952.

Schildknecht and co-workers have extensively studied the polymerizations of vinyl ethers and have noted the effects of various techniques on the nature of the products obtained.*

D. METHODS OF IONIC POLYMERIZATION OF VINYL ETHERS

1. Bulk Polymerization

Bulk polymerizations are those reactions which are conducted in the absence of a solvent. This technique has been used commercially over the temperature range of 0°C to 100°C for the preparation of syrupy, balsamlike polymers from the lower molecular weight alkyl vinyl ethers. The rate of heat evolution is frequently quite high and these reactions may become quite violent. The reactions can be moderated to a degree by use of mild catalysts and by controlled rate of mixing of monomer with catalyst. As the polymer is formed, it usually remains dissolved in the monomer.

2. Solution Polymerization

Polymerizations in solutions generally produce higher molecular weight polymers than do those conducted in bulk. This is probably due not only to better temperature control, but also to the influence of solvents on the course and rate of reaction. Thus, solid polyvinyl isopropyl ethers have been prepared at 0° to 5°C in solutions of halogen-containing solvents by the addition of small amounts of a diluted catalyst solution to highly purified monomers over a period of several hours. Higher molecular weight materials may be obtained at temperatures in the range -70°C to -30°C.

3. Flash-Type Polymerization

Flash polymerization is a low-temperature instantaneous reaction which produces high molecular weight rubberlike polymers. In a typical experiment a mixture of about 0.01 per cent BF_3 in liquid -

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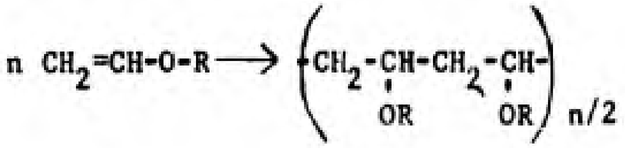
*Schildknecht, C. E., A. O. Zoss and F. Grossen, Ionic Polymerization of Some Vinyl Compounds, Ind. and Eng. Chem., 41, 2891 (1949) propane at -70°C is rapidly mixed with a 30 to 50 per cent solution of isobutyl vinyl ether. The reaction proceeds instantly to completion with a great evolution of heat to yield a tacky rubberlike white solid.

4. Polyphase or Proliferous Polymerization

This type of ionic polymerization is one in which the polymer grows slowly as a solid phase about an insoluble catalyst such as boron trifluoride etherate. By this technique, solid, high molecular weight polymers possessing a high degree of crystallinity and chain regularity may be prepared.

In a typical experiment freshly distilled boron trifluoride etherate is added, a few drops at a time, to a well stirred 20 per cent solution of vinyl isobutyl ether cooled in a -70°C bath. The polymerization occurs in a heterogeneous manner around the insoluble catalyst droplets. The reaction product is a white solid, crystalline by X-ray.

Although the products obtained from each of these methods differ in physical properties, in each instance the reaction proceeds via cationic initiation, propagation and termination stages to yield a hydrocarbon chain with pendant ether groups formed by head-to-tail linkage.



$$n\ CH_2{=}CH{-}O{-}R \longrightarrow \left(CH_2{-}\underset{OR}{CH}{-}CH_2{-}\underset{OR}{CH}{-} \right)_{n/2}$$

E. REACTION KINETICS

Eley* and co-workers have studied the kinetics of the polymerization of vinyl alkyl ethers initiated by iodine, stannic chloride, silver perchlorate and m-cresol solutions of triphenylmethyl chloride, and have noted the effects of variations of temperature and dielectric constant on the reaction rate and on the molecular weight of the polymer product. They found the rate expression for the iodine catalyzed polymerizations of vinyl octyl ether in 1,2-dichloroethane,

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*Eley, D.D. & A.W. Richards, The Kinetics of Ionic Polymerization, PtI., Trans. Faraday Soc., <u>43</u>, 425 (1949); PtII, Ibid, <u>43</u>, 436 (1949); D.D. Eley & J. Saunders, PtIII, J. Chem. Soc., p 4167 (1952) petroleum ether and diethyl ether to be $-dM/dt = k[M][C]^2$ where $[M]$ is the concentration of monomer and $[C]$ is the concentration of catalyst. Variations in monomers or catalyst concentrations had no systematic effect on the molecular weight of the polymer at 20 per cent polymerization in these solvents, the molecular weight remained uniform throughout the reaction to 100 per cent polymerization and a large rise in molecular weight was observed after 100 per cent polymerization if the catalyst remained intact in the mixture.

The reaction rate constant is markedly affected by the dielectric constant (ε) of the solvent, increasing exponentially with increasing ε. However, the molecular weight of the polymer is slightly lower in the higher dielectric solvent.

The increase in rate with an increase in dielectric constant is not due to a decreased activation energy, as one might first expect. The over-all measured activation energy in petroleum ether is 10 Kcal whereas in 1,2-dichloroethane it is 16 Kcal. The rate dependance is probably due to a combination of solvation and electronic effects complicated by interactions between ion pairs.

In all solvents an increase in temperature produced a very slight decrease in molecular weight over the range of 25°C to 50°C.

The rate data obtained for the iodine catalyzed polymerization of the monovinyl ether fits the following kinetic scheme:

$$\left.\begin{array}{rl} 2I_2 \longrightarrow I^+ + I_3^- & k_1 \\ I^+ + M \longrightarrow I^+ M \equiv M^* & k_2 \end{array}\right\} \quad \text{Initiation}$$

$$\left.\begin{array}{r} M^* + M \longrightarrow M^*_2 \\ M^*_{n-1} + M \longrightarrow M^*_n \end{array}\right\} \quad k_3 \quad \text{Propagation}$$

$$\left.\begin{array}{rl} M^*_n \longrightarrow M_n + H^+ & k_4 \\ M^*_n + M \longrightarrow M_n + M^* & k_5 \end{array}\right\} \quad \text{Termination}$$

Assuming stationary concentrations of I^+ and M^*, we can write:

$$k_1[I_2]^2 - k_2[I^+][M] = 0;\ [I^+] = \frac{k_1[I_2]^2}{k_2[M]} \qquad (1)$$

$$k_2[I^+][M]-k_4[M^*]=\frac{k_2}{k_4}[I^+][M] \qquad (2)$$

or

$$[M^*]=\frac{k_1}{k_4}[I_2]^2$$

and

$$-\frac{d[M]}{dt}=k_3[M^*][M]$$

$$=\frac{k_1k_2}{k_4}[I_2]^2[M]$$

The average degree of polymerization (D P.) is directly proportional to the rate of propagation and inversely proportional to the transfer and termination rates:

$$D.P. = \frac{k_3[M^*][M]}{k_4[M^*]+k_5[M^*][M]} = \frac{k_3[M]}{k_4+k_5[M]}$$

Since the molecular weight is essentially independant of monomer concentration the transfer process is the most important termination mechanism and $k_5[M]>>>k_4$.

The rate equation for the polymerization of vinyl octyl ether catalyzed by stannic chloride, silver perchlorate or triphenylmethyl chloride was observed to be $-\frac{dM}{dt}=k[C][M]^2$.

The molecular weight of the polymer obtained by stannic chloride catalysis was indepentant of catalyst concentration except at very low values of [C], but varied directly with monomer concentration up to high concentrations (ca. 1.0 mole/ℓ) where it became constant (i.e., independant of concentration). The same trends, but not as pronounced, were observed with the silver perchlorate catalyst.

The rate data for these three catalysts are in agreement with the scheme previously described for the iodine catalyzed polymerizations:

$$\begin{aligned}
C + M &\longrightarrow CM \equiv M^* && k_2\\
\left.\begin{aligned} M^* + M &\longrightarrow M^*_2 \\ M^*_{n-1} + M &\longrightarrow M^*_n \end{aligned}\right\} & && k_3\\
M^*_n &\longrightarrow M_n + C && k_4\\
M^*_n + M &\longrightarrow M_n + M^* && k_5
\end{aligned}$$

therefore

$$-\frac{d[M]}{dt} = \frac{k_2k_3}{k_4}[C][M]^2$$

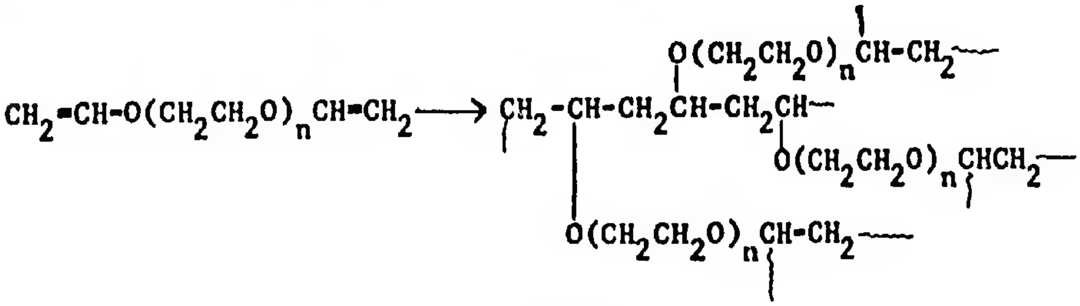
and

$$D.P. = \frac{k_3[M]}{k_4 + k_5[M]}$$

These data emphasize the importance of evaluating catalysts over a range of concentrations, and solvents of various dielectric constants for the more promising candidate monomer system, in an effort to obtain a polymer or copolymer with the optimum desired characteristics.

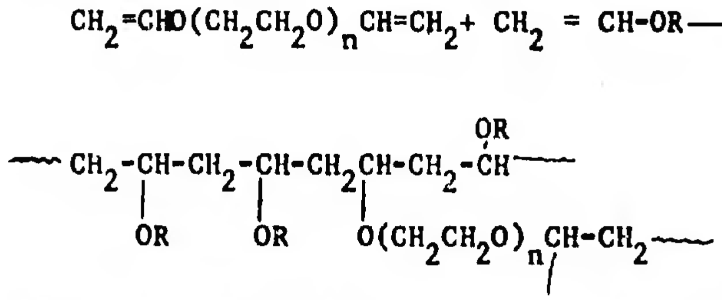
F. COPOLYMERIZATION

Since relatively low molecular weight polymers are generally obtained by cationic polymerization of vinyl alkyl ethers over the temperature range of 0° to 50°C (32° to 122°F), these materials are not by themselves suited to the preparation of foamed-in-place plastics. However, by polymerization of divinyl ethers of moderately high molecular weight polyglycols alone or by co-polymerization with other vinyl ethers, it should be possible to obtain solid polymers with the desired physical properties. Thus, although the degree of polymerization of a divinyl ether may be low, the product will have a high molecular weight (dependent on the choice of starting materials) and will be crosslinked to improve rigidity.



$$CH_2{=}CH{-}O(CH_2CH_2O)_nCH{=}CH_2 \longrightarrow CH_2{-}CH{-}CH_2CH{-}CH_2CH{-}$$

The degree of cross-linking can be controlled by copolymerization with monovinyl ethers. A typical copolymer of divinyl and monovinyl ethers may be represented as follows:



$$CH_2{=}CHO(CH_2CH_2O)_nCH{=}CH_2 + CH_2 = CH{-}OR \longrightarrow$$

$$\sim CH_2{-}\underset{OR}{\underset{|}{CH}}{-}CH_2{-}\underset{OR}{\underset{|}{CH}}{-}CH_2\underset{O(CH_2CH_2O)_nCH{-}CH_2\sim}{\underset{|}{CH}}{-}CH_2{-}\overset{OR}{\overset{|}{CH}}\sim$$

It is readily apparent that polymers with a wide range of physical properties should be capable of preparation by the careful selection of monomer ratios.

The reaction process may be complicated in copolymerizations wherein two or more monomers are competing for the catalyst in the initiation stage and for the carbonium ion during propagation. The ability of various monomers to compete in these steps is a measure of their relative reactivities, and may usually be estimated, at least qualitatively, from electronegativity data. Fortunately, in the development of polyvinyl ether polymers the study has been confined to the use of straight- and branched-chain alkyl vinyl ethers and to a limited number of structurally simple divinyl ethers, none of which differ sufficiently in reactivity to present a serious problem. In those instances where marked differences in reactivity may occur, the procedure could be modified by varying addition rates, monomer ratios or catalysts.

G. FOAMS

Foams consist of a network of very thin laminae whose kinetic stability is dependent on the surface characteristics of the parent liquid system. These surface characteristics are often markedly influenced by the presence of a class of solutes known as surface-active agents, which alter the surface tension and hence, the surface-free energy of the system.

1. Classification of Foams*

Pure liquids do not foam, and mixtures of liquids of similar chemical type and surface tension as well as aqueous solutions of highly hydrophilic solutes such as glycerol or sucrose do not readily foam. On the other hand, such a great variety of chemical substances promote the formation of foams (of widely differing kinetic stabilities) that the chemistry of these materials is not a useful criterion for a classification as foam producers.

It is necessary to distinguish between thermodynamic and kinetic stability because, although a disperse system contains a higher surface area, and therefore, higher surface free-energy than the segregated gas and liquid, and is subsequently thermodynamically less stable than the segregated system, it may frequently exhibit an indefinitely long lifetime, i.e., be kinetically stable for reasons described below. The variation in the lifetimes of foams has resulted in the somewhat arbitrary classification of foams as unstable or metastable.

Unstable foams, exemplified by dilute solutions of short-chain aliphatic acids and alcohols, constantly collapse as the liquid drains from between the bubbles. The life time for this class of foams, although generally dependant on the concentration of solute in solution, seldom exceeds 20 seconds for aqueous solution at ambient temperatures.

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* Kitchner, J.A. and C.F. Cooper, Current Concepts in the Theory of Foaming, Quarterly Rev., 13, 71-97 (1959).

Metastable foams, examples of which are solutions of soaps, proteins, saponin, anionic, cationic and nonionic detergents, maintain their integrity for some indefinitely longer period because the drainage of liquid from between the bubbles eventually stops. Thus, in this class of foams, a potential energy barrier exists which is dependent on the structure of the surface layers. This barrier prevents excessive localized thinning of the liquid membrane without interfering with controlled general thinning and hence permits the formulation of metastable foams.

Liquid systems demonstrating this unique behavior have the ability to oppose and counterbalance applied stresses which tend to cause local thinning. The restoration of opposing forces increases with displacement, as occurs in a stretched rubber sheet. Pure liquids cannot exhibit this elasticity because their surface tension is independent of surface extension. However, surface-active agents, when added to pure liquids, tend to concentrate at the liquid-air interface, destroying the independance of surface tension on extension and also increasing the surface viscosity. This latter effect delays liquid drainage from between the bubbles and further increases the kinetic stability of the foam. The fact that each solute-solvent system has an optimum concentration of solute for maximum foaming supports the surface elasticity theory summarized above.

2. Foamed-in-Place Plastics

The conversion of a polymerizing system to a foam requires the generation of a gas dissolved in a liquid phase to yield a supersaturated solution with subsequent dissolution and formation of bubbles. The bubble-forming process (nucleation) is aided by the presence of finely divided solids and irregular solid surfaces. The gas is obtained from a "blowing agent", which may be either a solid which readily decomposes to produce a gas (usually nitrogen or carbon dioxide), or a low boiling liquid. As polymerization begins, the gas must be generated quickly to produce an enormous number of tiny bubbles throughout the liquid medium. Ideally, the viscosity of the polymerizing system should be increasing rapidly enough to retain the bubbles and ultimately yield a solid foam.

In the preparation of polyurethane foams, selected silicone oils are added in concentrations of about 1 per cent as stabilizers during foam formation. These materials generally serve two purposes, viz., they lower the surface tension of the polymerizing system which reduces the thermodynamic instability, and they frequently function as nucleating agents, promoting the formulation of a myriad of tiny bubbles. These foam stabilizers govern the cell structure and hence the over-all integrity of the foamed plastic. When used properly, as defined by experiment, they prevent the formation of voids, fissures and collapse of the foam during the polymerization process. Our investigations did not proceed to the stage wherein an examination of surface active agents merited consideration.

H. KIT DESIGN

The Kit Intended for Use in Field Foaming

For optimum efficiency a kit intended for use in field foaming should have as high a ratio of foam to container as possible, should contain its own power source for activation and should be relatively inexpensive. In keeping with these requirements a design has been formulated which provides for the isolated storage of reactive ingredients, a mixing chamber and a nozzle to direct the foam to its destination. In an effort to eliminate a heavy gas bottle as a power source to expel the foam, we have conceived the use of a small solid propellant charge as a power source. The gaseous combustion products may be used to transfer the materials to the mixing chamber and to discharge the foam. This concept is illustrated in Figure 1.

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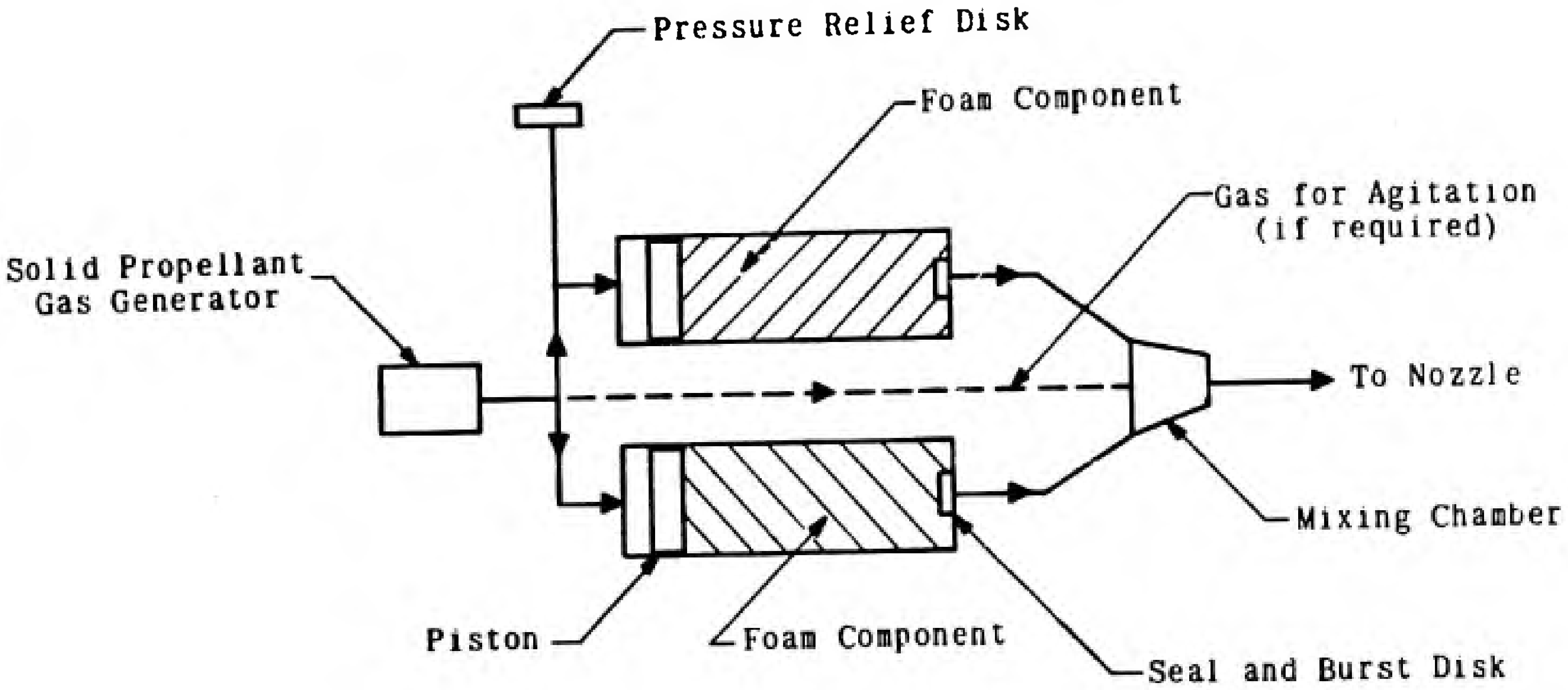

Figure 1. Schematic of Proposed Expendable Pre-Packaged Foam Kit.

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These experiments were conducted only in an effort to verify the earlier reported observations and were not pursued further.

C. POLYGLYCOL ACRYLATES

Several brief attempts were made to prepare acrylate esters of polyglycols as functional monomers but each attempted esterification was accompanied by polymerization. This approach was discontinued because of the susceptibility of acrylates to free-radical catalyzed polymerization.

D. TRIMETHYLOLPROPANE ALLYL ETHERS

The reactions of sulfur monochloride with the mono- and di-allyl ethers of trimethylolpropane to prepare tough polymeric materials was recently described.* An equimolar mixture of the two reactants in dioxane or carbon tetrachloride very quickly became quite hot and reacted to produce a tough polymer insoluble in most common solvents. We prepared extremely tough, spongy foams by mixing these reagents in halogenated solvents which also served as the blowing agents. Although the reaction proceeded rapidly at or above room temperature, the reaction rate was severly depressed at low temperatures and foams could not be prepared from the cooled mixtures. These results are summarized in Table I.

E. VINYL ETHERS

Most of the commercially available vinyl ethers, which included isopropyl, isobutyl, isoctyl, 2-ethylhexyl and octadecyl vinyl ethers and the divinyl ethers of butanediol and diethyleneglycol, were evaluated in candidate formulations. In addition, a generous sample of the divinylether of 1,6-hexanediol, as yet not commercially available, was provided by the Antara Division of General Anline and Film Corporation and a small amount of impure divinyl ether of carbowax 400 was obtained from the high pressure laboratories of Rohm and Haas. Several vinyl ethers of polyglycols were synthesized in our laboratory.

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* Celanese Chemical Co., New Product Bulletins N-97 NB2-3, and N-98 NB2-4, June 5, 1962; also personal communication from Dr. J. J. Cahill, Celanese, N. Y.

TABLE I

Trimethylol Propane Allyl Ether Foam Systems

1.	8.90 cc TMP diallyl ether + 3.22 cc S_2Cl_2	Porous and jelly-like foam was produced after a 20-second induction period. The interior of the foam charred.
2.	Same as 1 + 8 cc CH_2Cl_2 (blowing agent)	Foam was formed after a one-minute induction period. Physical properties were similar to test 1.
3.	Same as 1 + 4 cc CH_2Cl_2 + 8 cc octyl vinyl ether	An exothermic reaction occurred with the formation of a dark viscous material which became rigid overnight. No foam was formed.
4.	Same as 1 + 2 cc CH_2Cl_2	Foam formed within a few seconds.
5.	6.80 cc TMP monoallyl ether 3.22 cc S_2Cl_2	Quick vigorous boiling resulted, with large deposits of sulfur on the sides of the container. A yellowish-brown viscous liquid was finally formed.
6.	6.80 cc TMP monoallyl ether 3.22 cc S_2Cl_2 4.00 cc CH_2Cl_2	Vigorous boiling and splashing occurred initially with a yellowish-brown viscous material being formed.
7.	8.95 cc TMP diallyl ether + 6.44 cc S_2Cl_2 + 6.80 cc TMP monoallyl ether + 4.00 cc $2CH_2Cl_2$	Violent exotherm. Most of the material boiled vigorously and bumped out of the container.
8.	Same as 7 except 3.22 cc S_2Cl_2 were used and 8.00 cc trichloroethylene replaced CH_2Cl_2 (2:1 mole ratio)	Violent boiling, but no foam was formed.
9.	8.95 cc TMP diallyl ether 2 4.83 cc S_2Cl_2 (50% molar excess) + 4.00 cc TCE	A good foam was formed, but it was tacky and spongy. Its density was quite high.
10.	8.95 cc TMP diallyl ether + 4.83 cc S_2Cl_2 + 2.20 cc Styrene + 4.00 cc TCE	Boiling occurred, but no foam was formed.
11.	Same as 10 except the volumes of styrene and TCE were doubled. $TiCl_4$ was used to initiate the polymerization of the styrene.	Same as 10.

TABLE I (Cont'd)

Trimethylol Propane Allyl Ether Foam Systems (Cont'd)

2.	Same as 10. $TiCl_4$ was used as the catalyst for the styrene.	A foam was formed but excessive heat charred the interior.
3.	Same as 12 + 8 cc TCE	Same as 12, but there was less charring. The cell structure was fairly uniform, but the foam was spongy and tacky.
4.	Same as 12 + 15 cc TCE	Very good, vigorous foaming occurred, but the foam collapsed.
5.	8.95 cc diallyl ether + 1.80 cc S_2Cl_2 + 4.00 cc TCE (approx. 2:1 mole ratio)	No foam was formed, though boiling did occur.
6.	18.0 cc TMP diallyl ether + 6.5 cc S_2Cl_2 + 8.0 cc TCE + L-520 silicone foam stabilizer	A foam was formed with no charring. It was tacky and very resilient.
7.	Same as 16 with 4.4 cc styrene	Much vigorous boiling occurred, but no foam was formed.
8.	Same as 17. Reactants were cooled to 0°C and mixed.	While in an ice bath, little or no reaction occurred for several minutes. When the ingredients were taken out of the ice bath, the temperature began to rise slowly to about 75°C within 5 minutes and then quickly boiled, forming a foam which collapsed partially. The apparent density of the foam was approximately 10 lb/cu ft.
9.	18.0 cc TMP diallyl ether + 6.5 cc S_2Cl_2 + 8.0 cc TCE + 10.0 cc octyl vinyl ether (OVE) + L-520	Violent boiling began immediately and much material overflowed the container. Within a minute, a second reaction began which produced a foam that was not satisfactory.
0.	Same as 19, but 16 cc of TCE were used and $TiCl_4$ was needed to initiate the reaction of the OVE. No L-520 was used.	Very vigorous boiling resulted, but no foam was formed. A viscous dark brown liquid formed.

1. Synthesis of Vinyl Ethers

a. Vinylation

The equipment for our vinylation experiments consisted of a two-liter stainless steel pressure vessel (in which the mixture of polyglycol, base catalyst and solvent (either N-methylpyrrolidone or diglyme) was saturated with acetone-free acetylene, a Lapp Process Equipment Division Model LS-30 Pulsfeeder pump, a coiled length of 1/8 inch I.D. high pressure stainless steel tubing (the reactor), a Grove Company Model S-91-XW Mity-Mite back pressure regulator with a No. 100-00801 loading cross for pressure control. The arrangement of this equipment is diagramed is Figure 2.

In a typical experiment, the reaction mixture was circulated through the heated reactor at a pressure of 1500-2000 psi and a temperature of 150°-200°C for from 3 to 5 minutes and was then transferred to a receiver maintained at ambient temperature and atmospheric pressure. The solvent was generally removed by a rapid 1-plate vacuum distillation and the high boiling residue was slowly distilled in a high-vacuum falling film still. Although preliminary efforts to vinylate polypropylene glycols were not successful, polyethylene glycols -200, -300, -400 and -600 yielded products containing both monovinyl and divinyl ethers. We were unable to achieve completely satisfactory separations of these high molecular weight products using the falling film still, primarily because of its relatively low efficiency per pass for these materials. A more efficient molecular still could possibly provide the desired separations of the high molecular weight monomers.

b. Chugaev Reaction

During the later stages of the contract year, we considered the possibility of preparing the divinyl ethers of polyglycols via a cis β elimination process. The Chugaev Reaction, an example of this class of reactions, reportedly proceeds rapidly under relatively mild conditions with no significant side reactions to form unrearranged olefins in high yields. The steps in this reaction with a polyglycol should be as follows:

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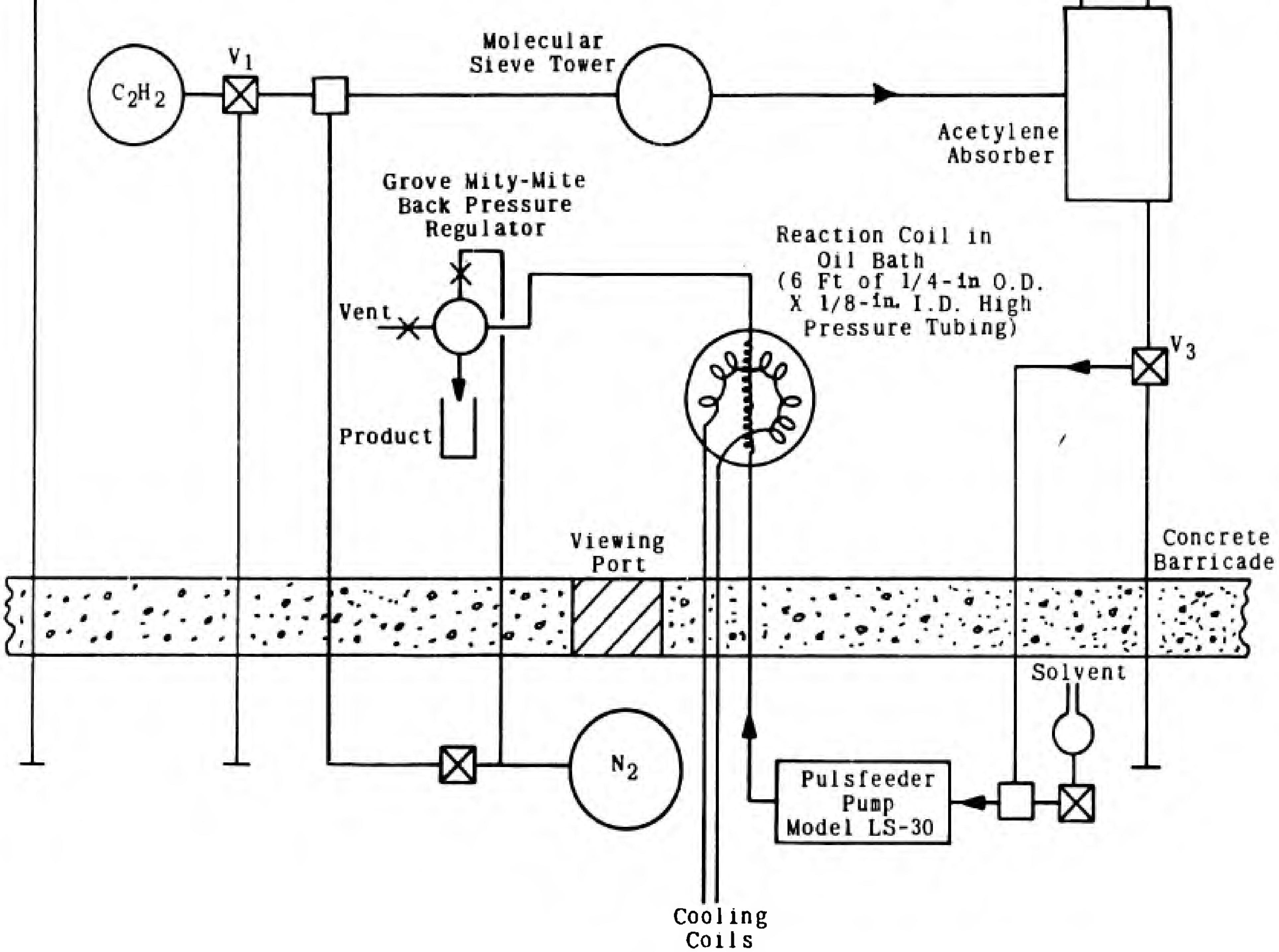
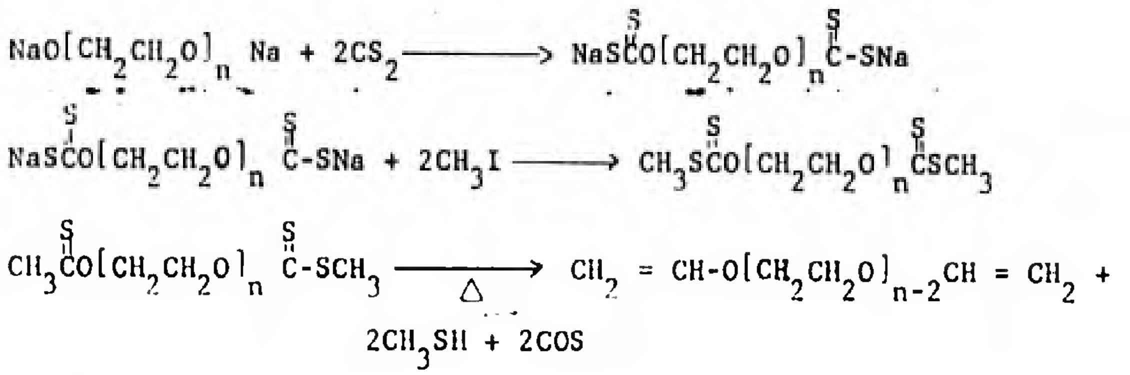


Figure 2. Divinyl Ether Synthesis Equipment.

$$HO-[CH_2CH_2-O]_nH + 2Na \xrightarrow{Et_2O} NaO[CH_2CH_2O]_n Na + H_2 \qquad (1)$$



$$NaO[CH_2CH_2O]_n Na + 2CS_2 \longrightarrow NaS\overset{S}{\overset{\|}{C}}O[CH_2CH_2O]_n\overset{S}{\overset{\|}{C}}-SNa \qquad (2)$$

$$NaS\overset{S}{\overset{\|}{C}}O[CH_2CH_2O]_n \overset{S}{\overset{\|}{C}}-SNa + 2CH_3I \longrightarrow CH_3S\overset{S}{\overset{\|}{C}}O[CH_2CH_2O]_n\overset{S}{\overset{\|}{C}}SCH_3 \qquad (3)$$

$$CH_3\overset{S}{\overset{\|}{C}}O[CH_2CH_2O]_n \overset{S}{\overset{\|}{C}}-SCH_3 \xrightarrow[\Delta]{} CH_2 = CH-O[CH_2CH_2O]_{n-2}CH = CH_2 + 2CH_3SH + 2COS \qquad (4)$$

The dimethyl xanthate of polyethyleneglycol -400 was prepared according to equations 1 and 2 above, and was pyrolyzed by slowly dropping it through a column of glass beads heated to 450-480°C. A small quantity of vile-smelling, yellow liquid was the only product obtained, presumably because of the high pyrolysis temperature. Lower reaction temperatures should result in the production of the desired monomers.

2. Evaluation of Polyglycol Vinyl Ethers

The mixtures of vinylated products partially purified by falling-film vacuum distillation were blended with vinyl alkyl and, in some cases, with other divinyl ethers and these formulations were examined as candidate foam systems. Although several of the formulations produced foams with poor physical properties, many of the formulations did not produce solid polymers. These results may be due to the presence of a large proportion of unreacted polyglycol or they may be attributed to the use of too mild a catalyst or improper blending with comonomers. This phase of the investigation requires a more detailed examination of the divinyl ethers of polyglycols. Typical formulations and results are outlined in Table II.

3. Commercially Available Vinyl Ethers

A large number of formulations consisting only of commercially available vinyl alkyl and divinyl ethers was evaluated. Foams were obtained from many of these experiments. The flexibility of the foams could be controlled by adjusting the ratio of monovinyl to divinyl ethers; increasing the proportion of divinyl ether increased the rigidity or brittleness of the product. Unfortunately, all of the foams produced with

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TABLE II

Foam Formulations Containing Vinyl Ethers of Polyethylene Glycols

	Monomer	Catalyst	Volume Ratio Monomer/Blowing Agent	Remarks
1.	$(ViO)_2$ PEG-200 (1)[a] $(ViO)C_8$ (1) $(ViO)_2C_4$ (1)	$I_2/CHCl_3$	1/1 $CHCl_3$	Vigorous exothermic reaction. Brown liquid, no foam.
2.	$(ViO)_2C_4$[b] $(ViO)_2$ PEG-600[c] $(ViO)_2$ PEG-200	2% wt/vol $VI_2/CHCl_3$	1/1 $CHCl_3$	Vigorous exothermic reaction. No foam.
3.	$(ViO)_2C_4$ $(ViO)_2$ PEG-600 $(ViO)_2$ PEG-200	2% wt/vol $VI_2/CHCl_3$	1/2 $CHCl_3$	Vigorous exothermic reaction. Black semi-solid to solid product.
4.	$(ViO)_2$ PEG-600 $(ViO)_2$ PEG-200	2% wt/vol $VI_2/CHCl_3$	1/3 $CHCl_3$	No reaction.
5.	$(ViO)_2$ PEG-600 $(ViO)_2$ PEG-200	$SOCl_2$	1/3 $CHCl_3$	Mild heat evolution; no foaming.
6.	$(ViO)_2C_4$ $(ViO)_2$ PEG-200	$I_2/CHCl_3$	1/1 $CHCl_3$	Vigorous exothermic reaction. Black solid.
7.	$(ViO)_2$ PEG-200 $(ViO)C_8$[d]	$I_2/CHCl_3$	1/1 $CHCl_3$	Vigorous exothermic reaction. Brown liquid; no foam.
8.	$(ViO)_2$ PEG-200 $(ViO)C_8$	$I_2/CHCl_3$	1.25/1 $CHCl_3$	Vigorous exothermic reaction. Brown liquid; no foam.
9.	$(ViO)_2$ PEG-200 $(ViO)C_8$ $(ViO)_2C_4$	$I_2/CHCl_3$	2.4/1 $CHCl_3$	Vigorous exothermic reaction. Brown liquid; no foam.
10.	$(ViO)_2$ PEG-200 (5) $(ViO)C_8$ (3) $(ViO)_2C_4$ (2)	$I_2/CHCl_3$	1/1 $CHCl_3$	Brown foam which collapsed.

Footnotes are at end of Table.

TABLE II (Cont'd)

Foam Formulations Containing Vinyl Ethers of Polyethylene Glycols (Cont'd)

	Monomer	Catalyst	Volume Ratio Monomer/Blowing Agent	Remarks
18.	(ViO PEG-300)$_2$ TDI (10) (ViO PEG-300)$_2$ M-MR (10)	Saturated solution I_2/CCl_4	-	Very slight temperature increase. No visible change in appearance.
19.	(ViO PEG-300)$_2$ TDI (7) (ViO)$_2$C$_4$ (4) ViOiC$_4$ (7)	Saturated solution I_2/CCl_4	-	Dark precipitate formed at once. Mixture became hot; final product was a friable black gel.
20.	(ViO PEG-300)$_2$ TDI (4)	Saturated solution I_2/CCl_4	-	A tough, rubbery, black solid was formed.

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a. Numbers in ( ) represent volume of ether in mixtures.
b. (ViO)$_2$C$_4$ = divinylether of butane-1,4-diol.
c. (ViO)$_2$ PEG-600 = divinyl ether of PEG-600.
d. (ViO)C$_8$ = vinyl 2-ethylhexyl ether.

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TABLE III

Foam Formulations Containing Commercially Available Vinyl Ethers

Volume	Formulation	Catalyst	Remarks
7.5 cc 2.5 cc 5.5 cc	$ViOiC_4$ $(ViO)_2C_4$ CCl_4	3% v/v PCl_3/CCl_4	No apparent reaction; when several drops of 100% PCl_3 were added, mixture became hot, and turned green.
33 cc 10 cc	Green liquid product from Formulation 1. $ViOiC_4$	PCl_3	Vigorous, exothermic reaction to yield crumbling wax-like product; then brief induction period followed by extremely rapid reaction to yield a dense, tough, charred foam.
8 cc 4 cc 2 cc 10 cc	$ViOiC_4$ $ViOiC_8$ $(ViO)_2C_4$ CCl_4	$BF_3 \cdot Et_2O$	Black solid particles formed almost instantly at points of contact between $BF_3 \cdot Et_2O$ and formulation, followed by brief induction period and then exothermic reaction to yield a white, resilient foam with good compressive strength but very poor tear resistance.
9 cc 4 cc 4 cc	$ViOiC_4$ $ViOiC_8$ ViO_2C_4	5% v/v $BF_3 \cdot Et_2O/CCl_4$	Approximately 20-second induction period followed by vigorous reaction. Product was brittle, yellow solid.
8 cc 4 cc 3 cc 10 cc	$ViOiC_4$ $ViOiC_8$ $(ViO)_2C_4$ CCl_4	5% v/v $BF_3 \cdot Et_2O/CCl_4$	One experiment produced a gel-like material which easily crumbled when handled; in another experiment, a black precipitate was first observed, then the reaction rate increased and the mixture foamed. Most of the foam collapsed, possibly due to incomplete polymerization.
10 cc 10 cc	$ViOiC_8$ CCl_4	9% v/v $BF_3 \cdot Et_2O/Et_2O$	Mixture became slightly warm. Product was a viscous yellow liquid.
10 cc 2 cc 10 cc	$ViOiC_8$ $(ViO)_2C_4$ CCl_4	9% v/v $BF_3 \cdot Et_2O/Et_2O$	After about 5-second induction period, reaction became vigorous. Product was a brittle white solid.
10 cc	$ViOiC_8$	9% v/v $BF_3 \cdot Et_2O/Et_2O$	Exothermic reaction. Product was a white foam which had good compressive strength, but very poor tear resistance. Formulations containing 1.2 and 1.5 cc $(ViO)_2C_4$ yielded crumbling solids instead of foams.

TABLE III (Cont'd)

Foam Formulations Containing Commercially Available Vinyl Ethers (Cont'd)

	Volume	Formulation	Catalyst	Remarks
9.	10 cc 1 cc 10 cc	$\mathrm{ViOiC_3}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	9% v/v $\mathrm{BF_3 \cdot Et_2O}$	Exothermic reaction. Product was a brittle solid.
10.	5 cc 10 cc 10 cc	$\mathrm{ViOiC_3}$ $\mathrm{ViOiC_8}$ $\mathrm{CCl_4}$	5% v/v $\mathrm{BF_3 \cdot Et_2O/Bu_2O}$	Exothermic reaction. Product was a viscous yellow liquid.
11.	5.0 cc 5.0 cc 1.5 cc 10.0 cc	$\mathrm{ViOiC_3}$ $\mathrm{ViOiC_8}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	5% v/v $\mathrm{BF_3 \cdot Et_2O/Bu_2O}$	Exothermic reaction. Product was a white foam with large pores. Foam crumbled when handled.
12.	10 cc 1 cc 10 cc	$\mathrm{ViOiC_8}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	8 drops 1 $\mathrm{BF_3 \cdot Et_2O}$/ 2 $\mathrm{Bu_2O}$	Vigorous exothermic reaction. Solid product had cheese-like consistency.
13.	10 cc 1 cc 10 cc	$\mathrm{ViOiC_8}$ $\mathrm{(ViO)_2C_6}$ $\mathrm{CCl_4}$	8 drops 1 $\mathrm{BF_3 \cdot Et_2O}$/ 2 $\mathrm{Bu_2O}$	Vigorous exothermic reaction. Solid product had cheese-like consistency.
14.	10 cc 1 cc 10 cc	$\mathrm{ViOiC_4}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	8 drops 1 $\mathrm{BF_3 \cdot Et_2O}$/ 2 $\mathrm{Bu_2O}$	Vigorous exothermic reaction. Solid product had cheese-like consistency.
15.	10 cc 5 cc 1 cc 10 cc	$\mathrm{ViOC_{10}}$ $\mathrm{ViOiC_4}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	8 drops 1 $\mathrm{BF_3 \cdot Et_2O}$/ 2 $\mathrm{Bu_2O}$	Vigorous exothermic reaction. Solid product had cheese-like consistency.
16.	10.0 cc 5.0 cc 1.5 cc 10.0 cc	$\mathrm{ViOC_{10}}$ $\mathrm{ViOiC_4}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	8 drops 1 $\mathrm{BF_3 \cdot Et_2O}$/ 2 $\mathrm{Bu_2O}$	Vigorous exothermic reaction. Solid product had cheese-like consistency.
17.	10 cc 10 cc	$\mathrm{ViOiC_8}$ $\mathrm{CCl_4}$	15 drops 1 $\mathrm{BF_3Et_2O}$/ 2 $\mathrm{Bu_2O}$	Mixture became hot in about 2 minutes. Product was a viscous liquid.
18.	15.0 cc 1.5 cc 10.0 cc	$\mathrm{ViOiC_8}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	5 cu cm 2.5% $\mathrm{BF_3}$ in $\mathrm{Bu_2O}$	Qualitatively a very satisfactory foam Exhibited a density gradient, bottom being much heavier than top.

TABLE III (Cont'd)

Foam Formulations Containing Commercially Available Vinyl Ethers (Cont'd)

Volume	Formulation	Catalyst	Remarks
15.2 cc 1.0 cc 9.0 cc	$\mathrm{ViOiC_8}$ $\mathrm{(ViO)_2C_4}$ $\mathrm{CCl_4}$	5 cu cm 2.5% $\mathrm{BF_3}$ in $\mathrm{Bu_2O}$	Mixture foamed, with increasing density from top to bottom. Foam crumbled when handled.
15.0 cc 8.0 cc 0.5 cc 7.5 cc	$\mathrm{ViOiC_4}$ (polymer) $\mathrm{ViOiC_4}$ $\mathrm{(ViO)_2C_6}$ $\mathrm{CCl_4}$	0.6 cu cm 2.5% $\mathrm{BF_3}$ in ether	Exothermic reaction to produce moderately strong, dense, white foam.
2.0 cc 8.0 cc 4.0 cc 10.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{(ViO)C_8}$ $\mathrm{CCl_4}$	Saturated $\mathrm{I_2}$ in $\mathrm{CCl_4}$	18 ml catalyst solution added before reaction commenced. The foam was brittle near the bottom of the container and was spongy near the top.
3.0 cc 7.0 cc 5.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Exothermic reaction with frothing. Product was dark brown viscous liquid.
2.5 cc 7.5 cc 5.5 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Vigorous, exothermic reaction to yield brittle, charred foam.
2.0 cc 8.0 cc 7.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Exothermic reaction; soft, crumbling foam.
2.0 cc 8.0 cc 4.0 cc 10.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{(ViO)C_8}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Exothermic reaction; flexible, rubbery foam which readily crumbled.
3.0 cc 8.0 cc 4.0 cc 10.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{(ViO)C_8}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Exothermic reaction; flexible, rubbery foam which readily crumbled.
1.5 cc 4.0 cc 2.0 cc 10.0 cc	$\mathrm{(ViO)_2C_4}$ $\mathrm{(ViO)iC_4}$ $\mathrm{(ViO)C_8}$ $\mathrm{CCl_4}$	1:1000 $\mathrm{SnCl_4/CCl_4}$	Slightly blown foam; soft, flexible, but readily crumbled.

TABLE IV

Foam Formulations Containing 3,4-Dihydro-2H-Pyran-2-Methanol

	Volume	Formulation	Catalyst	Remarks
1.	15 cc	Pyran[a]	PCl_3	Vigorous boiling to yield viscous liquid.
2.	15 cc	Pyran	I_2/CH_2Cl_2 saturated solution	Vigorous boiling to yield viscous liquid.
3.	15 cc	Pyran	2.5% BF_3 in Bu_2O	Vigorous boiling to yield viscous liquid.
4.	6 cc 6 cc 6 cc 9 cc	Pyran $(ViO)_2C_6$[b] $ViOiC_4$[c] CCl_4	10 cc 2.5% BF_3 in Bu_2O	Vigorous reaction to yield a white, moderately tough, light foam in some experiments and a hard brittle foam in others.
5.	6 cc 2 cc 6 cc 10 cc	Pyran $(ViO)_2C_4$[d] $ViOiC_4$ CCl_4	3 cc 2.5% BF_3 in Bu_2O	Exothermic reaction to yield a viscous yellow liquid.
6.	6 cc 6 cc 3 cc 10 cc	Pyran $(ViO)_2C_4$ $ViOiC_4$ CCl_4	5 cc 2.5% BF_3 in Bu_2O	Vigorous exothermic reaction to yield a tough, spongy, light foam.
7.	15 cc	Pyran	0.5 ml PCl_3	Exothermic reaction to yield viscous liquid.
8.	10 cc	Pyran	0.5 ml I_2/CCl_4 saturated solution	Exothermic reaction to yield viscous liquid.
9.	6 cc 6 cc 6 cc 9 cc	Pyran $(ViO)_2C_6$ $ViOiC_4$ CCl_4	6 cu cm 2.5% BF_3 in ether	Vigorous exothermic reaction to yield moderately strong, lightweight foam. Density was approximately 2 lb/cu ft. Product gradually deteriorated over several days to a much denser solid.

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a. 3,4-dihydro-2H-Pyran-2-methanol
b. 1,6-divinyloxyhexane
c. Vinyl isobutyl ether
d. 1,4-divinyloxybutane

In a very few experiments, the effect of carbon black as a nucleating agent was examined. No improvement in the quality of the foams obtained could be observed in these limited experiments. These miscellaneous experiments are summarized in Table VI.

TABLE VI

Miscellaneous Formulations

	Volume	Formulation	Catalyst	Remarks
1.	15 cc 0.5 gm 5 cc	ViOiC$_4$ ORF #4 * CCl$_4$	5 cc 2.5% BF$_3$/Bu$_2$O	About 5-minute induction period, then rapid reaction. Mixture became hot; product was red liquid. Solids did not foam.
2.	25 cc 1 gm 10 cc	ViOiC$_4$ ORF #4 CCl$_4$	5 cc 2.5% BF$_3$/Bu$_2$O	About 5-minute induction period, then rapid reaction. Mixture became hot; product was red liquid. Solids did not foam.
3.	15 cc 2 cc 1 gm	ViOiC$_4$ (ViO)$_2$C$_4$ ORF #4	5 cc 2.5% BF$_3$/Bu$_2$O	Vigorous exothermic reaction to yield jelly-like product. Solids did not foam.
4.	15.2 cc 1.0 cc Variable 9.0 cc	ViOiC$_8$ (ViO)$_2$C$_4$ Carbon black CCl$_4$	5 cc 2.5% BF$_3$/Bu$_2$O	Carbon black did not contribute to physical properties of foam.

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* See Table V

IV CONCLUSIONS

(1) The feasibility of preparing foamed-in-place plastics via ionically catalyzed addition polymerization has been conclusively demonstrated.

(2) Foams ranging in consistency from soft, pliable materials to rigid or brittle materials, but with no appreciable tear resistance have been obtained by copolymerization of commercially available vinyl ether monomers. The rigidity of the foams is proportional to the ratio of divinyl ether present in the starting material.

(3) The addition of 3,4-dihydro-2H-pyran-2-methanol to formulations containing the commercially available vinyl ethers resulted in foamed plastics with slightly improved tear resistance.

(4) It should be possible to prepare materials with the desired physical properties by using the divinyl ethers of polyglycols in conjunction with lower molecular weight monovinyl ethers.

(5) A detailed kinetic study, including an investigation of the role of the catalyst, solvent, and reaction temperature are essential to the satisfactory development of a system which will reproducibly generate a foamed plastic over the range of specified conditions.

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U. S. Army Natick Laboratories, Natick, Mass. DEVELOPMENT OF LOW-DENSITY HIGH-STRENGTH FOAMED PLASTICS BY IONIC POLYMERIZATION, by Robert J. F. Palchak, Carl H. Hassis and Joseph A. Terek. March 1964. 37 pp., illus. (Technical Report C&OM 2)

Equimolecular mixtures of mono- or di-allyl ethers of trimethylolpropane and sulfur monochloride gave tough, spongy foams when reacted in a halogenated solvent, which also acted as a blowing agent. Reaction was rapid at room temperature, but quite slow at 0° F.

A number of vinyl alkyl and divinyl ethers were evaluated using cationic catalysts and chlorinated solvents as blowing agents at room temperature. Foams were obtained in a number of cases, and the flexibility of the foams was related to the ratio of the mono-vinyl to the divinyl ether. The foams were quite spongy and friable.

Use of 3,4-dihydro-2H-pyran-2-methanol as a co-monomer with vinyl ethers gave moderately strong, lightweight foams.

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2. Vinyl plastics
3. Polymerization
4. Catalysts
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