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TECHNICAL REPORT AFATL-TR-74-163

**DEVELOPMENT OF LOW VISCOSITY,
HIGH OXYGEN CONTENT, CURABLE PREPOLYMERS
FOR USE AS PYROTECHNIC BINDERS**

ADB000950

MUNITIONS DIVISION

OCTOBER 1974

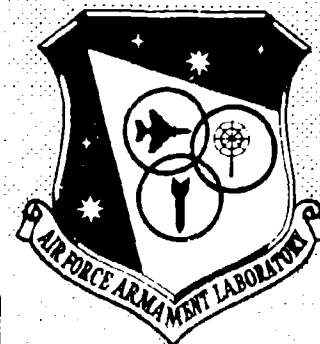
FINAL REPORT: January 1972 to September 1973

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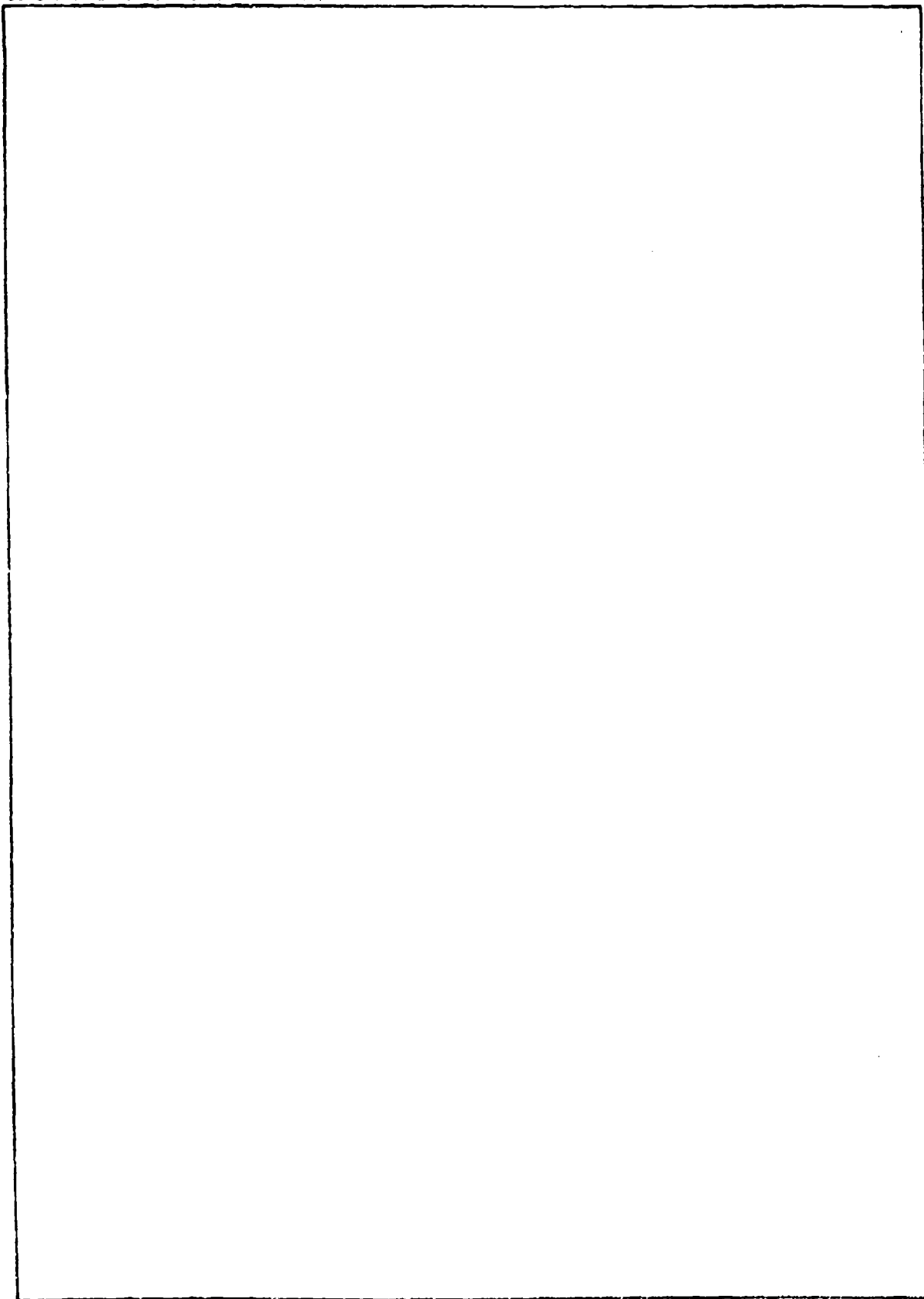
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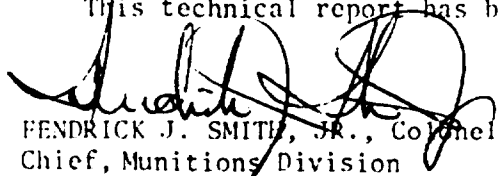
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PREFACE

The work discussed in this technical report was performed at the Air Force Armament Laboratory in support of Project 25630603 "Pyrotechnic Binder Study" between January 1972 and September 1973.

This technical report has been reviewed and is approved.



FENDRICK J. SMITH, JR., Colonel, USAF
Chief, Munitions Division

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SECTION I

INTRODUCTION

A program was initiated to develop a binder system yielding a pour castable pyrotechnic composition that could be cured to a solid without using high pressure consolidation. The advantages of pour casting flare grains are stated in Reference 1 (Page 3) as follows:

- a. Simplified, rapid production leading to lower item cost.
- b. Increased handling safety of a pyrotechnic composition during production due to "wetting" by liquid binder.
- c. Ease of manufacture of flare grains in a variety of shapes.
- d. More efficient burning due to homogeneous grain structure.

Development programs for cast flares have been undertaken by the three services at various times (see Bibliography).

The first attempts at formulating castable pyrotechnic compositions for illuminating flares involved increasing the binder content to decrease the viscosity of the mixture; however, as binder content increased, light output efficiency was significantly reduced (Reference 1, Pages 10 to 13, and Reference 2, Pages 5 to 7). Many binder formulations and various additives have been tested in pyrotechnic compositions to improve efficiency, with the result that high oxygen content in the binder improves efficiency with oxygen bound to nitrogen being the most effective (Reference 1, Pages 10 to 13). Experiments conducted by a contractor demonstrated a pour castable illuminating pyrotechnic composition with efficiency approaching compositions used in Navy and Air Force standard illumination flares (References 3 and 4). The major drawback to this formulation was

Reference:

1. S. C. Dollman, S. M. Kaye, and F. R. Taylor: Parameters Affecting Performance Characteristics of Cast Flare Systems. Picatinny Arsenal-TR-3839, March 1969.
2. G. A. Lane and W. A. Smith (Dow Chemical Co.): Research and Development for a Castable Magnesium Containing Illuminant. Dow Report No. CM-8-69, Picatinny Arsenal, September 1969.
3. G. A. Lane, E. M. Jankowiak, and D. Girardin (Dow Chemical Co.): Research and Development of Flow-Cast Magnesium Flares. Air Force Armament Laboratory TR-71-C-120, September 1971.
4. G. A. Lane, E. M. Jankowiak, and K. Roberson (Dow Chemical Co.): Development and Optimization of Flow-Cast Magnesium Flare Compositions. Air Force Armament Laboratory TR-72-105, June 1972.

the use of a nitrated plasticizer, triethylene glycol dinitrate, to decrease viscosity and to raise light output efficiency. High temperature storage of a similar flare composition containing this plasticizer resulted in decreased performance of the item (Reference 5).

The Pyrotechnic Binder Development Team was established at the Air Force Armament Laboratory (AFATL) to conduct an in-house program that was planned to proceed in three stages:

- a. Stage 1: Develop prepolymer synthesis, develop cure reaction, and test compatibility of binder with pyrotechnic substances.
- b. Stage 2: Develop illuminating flare compositions using new binder.
- c. Stage 3: Measure light output efficiency of compositions from Stage 2, and compare with illuminating compositions in current inventory.

Work in Stage 1 and limited work in Stage 2 were underway when the exploratory development work in pyrotechnics was discontinued by AFATL. This report describes several prepolymer syntheses and cure reactions studied by the Pyrotechnic Binder Development Team.

Reference:

5. J. A. Carrazza Jr., S. M. Kaye, and F. R. Taylor: Evaluation of Castable Illuminant Formulations in Flare, Surface, Trip, M49A1. Picatinny Arsenal TR-4295, April 1972.

SECTION II

SUMMARY

Six liquid polyester prepolymers were prepared and given preliminary evaluations for use as pyrotechnic binders. The six prepolymers were:

a. Five polyesters from diethylene glycol or triethylene glycol and the following acids, anhydrides, and carbonates:

- (1) tartaric acid (polytartrate prepolymer)
- (2) succinic anhydride (polysuccinate prepolymer)
- (3) diglycolic acid (polydiglycolate prepolymer)
- (4) dimethyl carbonate (polycarbonate prepolymer)
- (5) oxalic acid (polyoxalate prepolymer)

b. One polyester from triethylene glycol and succinic anhydride post-reacted with maleic anhydride to provide an unsaturated polysuccinate prepolymer.

The polytartrate prepolymer was not suitable for use as a pyrotechnic binder because it had excessive viscosity (>50,000 centipoises) and poor cured properties. The polyoxalate prepolymer was low in viscosity and high in oxygen content but was not stable when cured as a polyurethane and exposed to air and humidity. Four prepolymers (polysuccinate, polydiglycolate, polycarbonate, and unsaturated polysuccinate) were cured to give products with acceptable strength, flexibility, and stability. These prepolymers were incorporated in a limited number of experimental pyrotechnic compositions before the project was terminated.

In a period of 18 months, more than 500 separate syntheses and cure reactions were conducted on five separate binder systems. Several prepolymer materials were examined to determine their possible potential use in pyrotechnic compositions. No final determination of the potential of these materials as pyrotechnic binders was possible because no experimental determination of flare performance using these binder materials was completed.

SECTION III

TECHNICAL DISCUSSION

1. SELECTION OF POLYESTER SYSTEMS

High oxygen content liquid polyester prepolymers were the first systems investigated. This synthetic route was chosen for the following reasons:

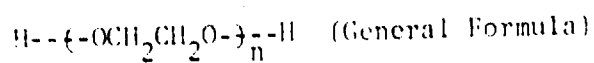
- a. Polyester synthesis reactions are simple and give high yields.
- b. Several high oxygen content monomers are available for polyester prepolymer synthesis in sufficient quantity to be used for large scale production of a pyrotechnic binder.
- c. A polyester prepolymer is one component of the LUU-2B illuminating flare.
- d. Polyester prepolymers were examined by one contractor for use as pour castable binders; however, this company chose to develop epoxy resins in further work and stopped all efforts with polyester systems (Reference 2, pages 5 to 8).

Previous experience at AFATL with the binder used in the LUU-2B flare indicated that the carboxyl terminated polyester was reacting with some types of magnesium powder used in production of the flare composition. The reaction was believed to occur between the terminal carboxyl group of the binder and residues from processing of the magnesium powder, resulting in gas formation during mixing and curing of the composition. Hydroxyl terminated prepolymers allow a cure mechanism different than the epoxide cure used for the LUU-2B binder. The hydroxyl terminated prepolymers were cured with commercially available polyfunctional isocyanate compounds to produce a polyurethane as the final solid binder.

2. SATURATED POLYESTER PREPOLYMER STRUCTURES

Variations on five basic prepolymer structures were synthesized and evaluated for use as pyrotechnic binder materials. All five basic structures involved condensation polymerization of a diester precursor with a dialcohol.

a. Dialcohol Structures



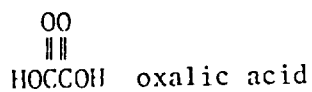
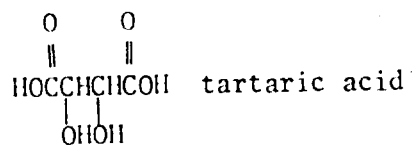
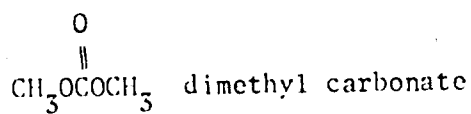
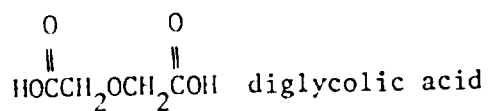
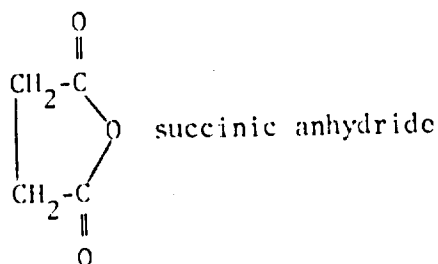
$n = 1$ ethylene glycol

$n = 2$ diethylene glycol

$n = 3$ triethylene glycol

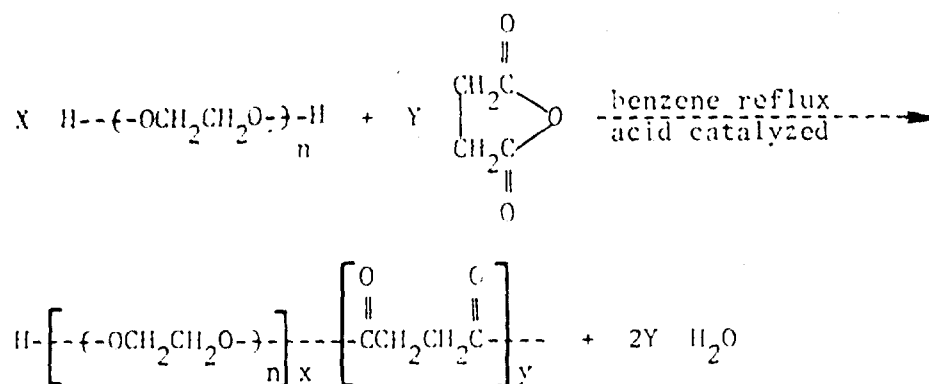
$n = 4$ tetraethylene glycol

b. Diester Precursor Structures

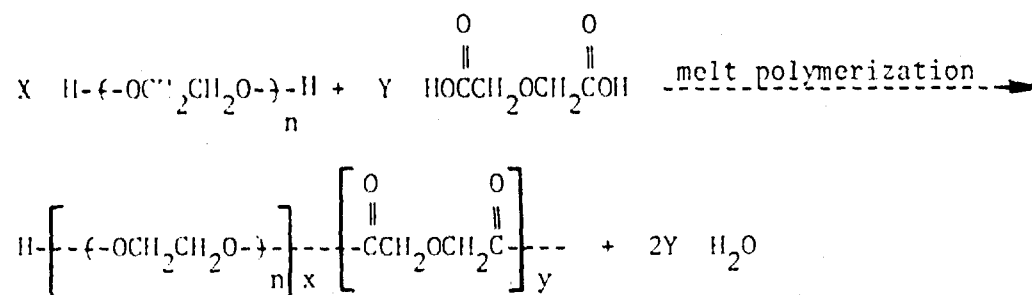


The five prepolymer structures are produced by the following generalized reactions:

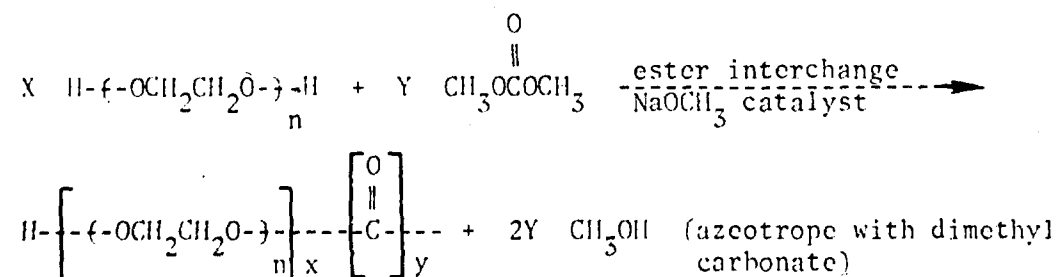
a. Polysuccinate Prepolymer



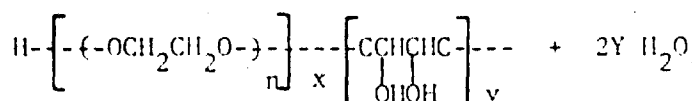
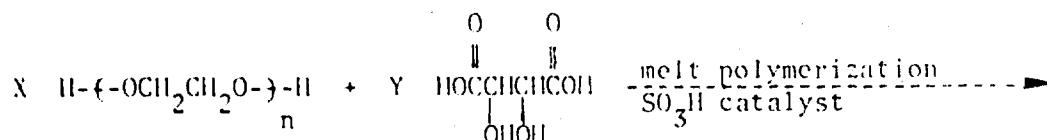
b. Polydiglycolate Prepolymer



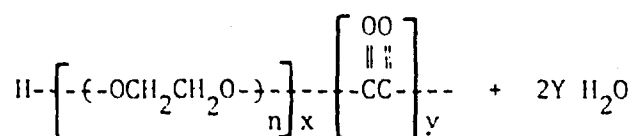
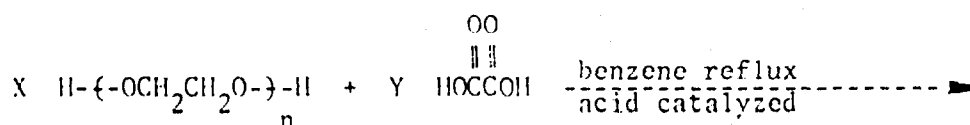
c. Polycarbonate Prepolymer



d. Polytartrate Prepolymer.



c. Polyoxalate Prepolymer



3. SATURATED POLYESTER PREPOLYMER SYNTHESIS PROCEDURES

The synthesis methods used to prepare small batches (50 to 500 ml) of liquid prepolymers are outlined in this section. Each reaction description gives the apparatus and procedures that resulted in the most consistent and usable products.

a. Melt Polymerization

In melt polymerization, the reactants are added to a reaction vessel and heated under a constant flow of dry nitrogen until the reaction is complete.

A 500 ml, round bottom, two-neck flask was charged with Y moles triethylene glycol and X moles succinic anhydride and the vessel plus contents was weighed to the nearest 10 mg. Nitrogen gas was admitted through one neck of the flask, after passing through a CaCO_3 drying tube, and exited through the other neck. Nitrogen gas flow was monitored by placing the exit tube under water, and the flow was maintained at 2 to 4 bubbles per minute throughout the heating of the reactants. Heat was supplied by an oil bath maintained at 180°C , and both the bath and

reaction vessel were stirred magnetically. Progress of the reaction was determined by removing a small aliquot (2 ml) of reaction mixture, titrating it with a standardized solution of 0.5N potassium hydroxide (KOH) in anhydrous ethanol to a phenolphthalein end point, and then determining the weight loss of the reaction mixture. Heating was stopped when less than 1% of the titratable acid remained and when the measured weight loss equalled or exceeded the weight of water calculated from the reaction. The final product was transferred to a glass container and stored.

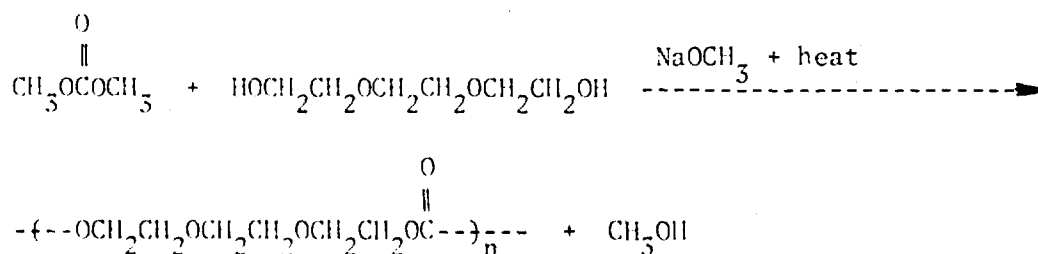
b. Benzene Reflux

The benzene reflux method allows the polymerization reaction to proceed at lower temperatures than does the melt method and eliminates the water byproduct as the benzene-water azeotrope.

A 500 ml, one neck, round bottom flask fitted with a Dean-Stark tube and reflux condenser was charged with Y moles diethylene glycol, X moles succinic anhydride, and 300 ml of dry benzene. Acid catalyst for the reaction was a strong acid cation exchanger resin, CGC 240 in the acid form. The mixture was stirred magnetically, and heat was applied slowly from an electric resistance heating mantle until the benzene-water azeotrope was refluxing in the condenser. During reflux, the mixture temperature remained close to 90°C. The reaction was considered complete when the amount of water calculated to be lost from the reactants was collected in the Dean-Stark tube. The reaction mixture was filtered while still warm to remove the ion exchange resin. Benzene was removed from the filtrate with a rotary evaporator and dry ice-acetone trap. During evaporation, the mixture was rotated in a water bath at 50° to 60° C, and drying was continued until the pressure in the flask was 0.2 to 0.7 mm Hg. The resulting prepolymer was transferred to a glass container.

c. Dimethyl Carbonate/Methanol Azeotrope

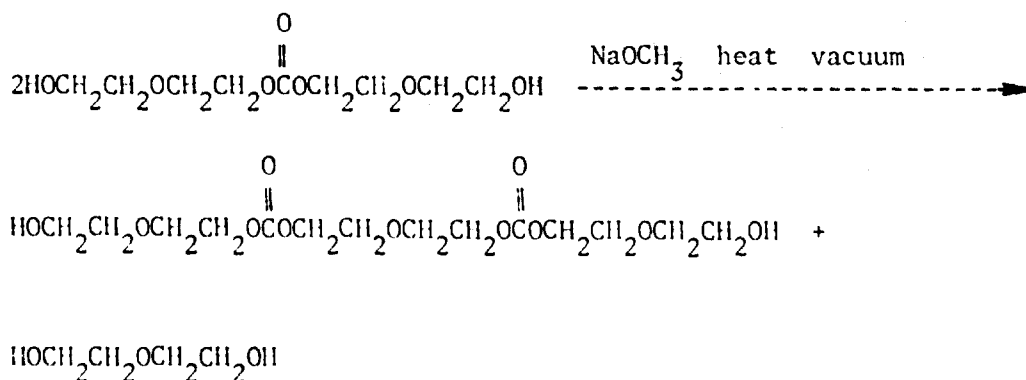
The dimethyl carbonate/methanol azeotrope was used to make only the polycarbonate liquid polyester. The reaction of dimethyl carbonate and triethylene glycol proceeds as an ester interchange using sodium methoxide as a catalyst according to the following equation:



Methanol must be removed from the reaction mixture to allow the polymerization to continue; therefore, excess dimethyl carbonate is added to the reaction to remove methanol as an azeotrope. The reaction stoichiometry is complicated by the fact that the azeotroping material is also one of the reactants. The required stoichiometry was established with dimethyl carbonate and triethylene glycol as reactants, and the amount of methanol expected to be produced was calculated. Finally enough excess dimethyl carbonate was added to azeotrope the calculated methanol.

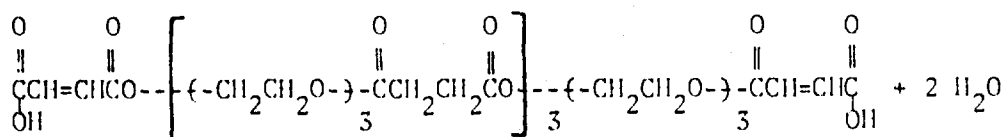
A 500 ml, two neck, round bottom flask fitted with a magnetic stirrer, a nitrogen inlet valve, distilling head, straight condenser, and collection flask was charged with X moles dimethyl carbonate, Y moles diethylene glycol, and 0.01% sodium methoxide catalyst and was then weighed to the nearest 0.01 gram. Heat was supplied by an oil bath, and both bath and reactants were stirred magnetically.

The reaction mixture was heated under a dry nitrogen flow at an oil bath temperature of 85° to 90° C for 29 hours; during this time, the temperature of the distilling head remained near 50° C. Near the end of the 29 hour period, no further distillate was produced, and the head temperature declined. The second stage of reaction was conducted under vacuum at a pressure of 0.6 mm Hg. Heating was continued for 18 hours, and the head temperature remained close to 35° C. During the total reaction, the material lost from the mixture was more than the weight of dimethyl carbonate and methanol calculated to be lost; the extra weight loss was assumed to be due to further polymerization, with diethylene glycol being reformed instead of methanol, as follows:



The final product was taken up in chloroform and allowed to stand over strong acid cation exchange resin in the acid form to remove the catalyst. The resulting solution was then evaporated in a rotary evaporator under 0.6 mm Hg pressure to remove the chloroform, and was stored in a glass container.

h. Structure

$$\text{H}-\left[(-\text{OCH}_2\text{CH}_2\text{O}-)_3\right]_4-\left[\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\right]_3-\text{H} + 2 \text{ } \begin{array}{c} \text{O} \\ \parallel \\ \text{CHC} \\ \parallel \quad \diagup \quad \diagdown \\ \text{CHC} \quad \text{O} \\ \parallel \\ \text{O} \end{array} \xrightarrow{\text{melt polymerization}}$$

$$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CCH}=\text{CHCO}-\left[\text{--}\left(\text{--CH}_2\text{CH}_2\text{O--} \right)_3 \text{--}\left(\text{--}\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CO--} \right)_3 \text{--}\left(\text{--CH}_2\text{CH}_2\text{O--} \right)_3 \text{--}\overset{\text{O}}{\parallel}\text{CCH}=\text{CHC} \overset{\text{O}}{\parallel} \\ \text{OH} \end{array} \xrightarrow[\text{XS CH}_3\text{OH}]{\text{reflux with}} \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CCH}=\text{CHCO}-\left[\text{--}\left(\text{--CH}_2\text{CH}_2\text{O--} \right)_3 \text{--}\left(\text{--}\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CO--} \right)_3 \text{--}\left(\text{--CH}_2\text{CH}_2\text{O--} \right)_3 \text{--}\overset{\text{O}}{\parallel}\text{CCH}=\text{CHC} \overset{\text{O}}{\parallel} \\ \text{OCH}_3 \end{array} + 2 \text{H}_2\text{O}$$

b. Synthesis Procedure

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5. CURE REACTIONS

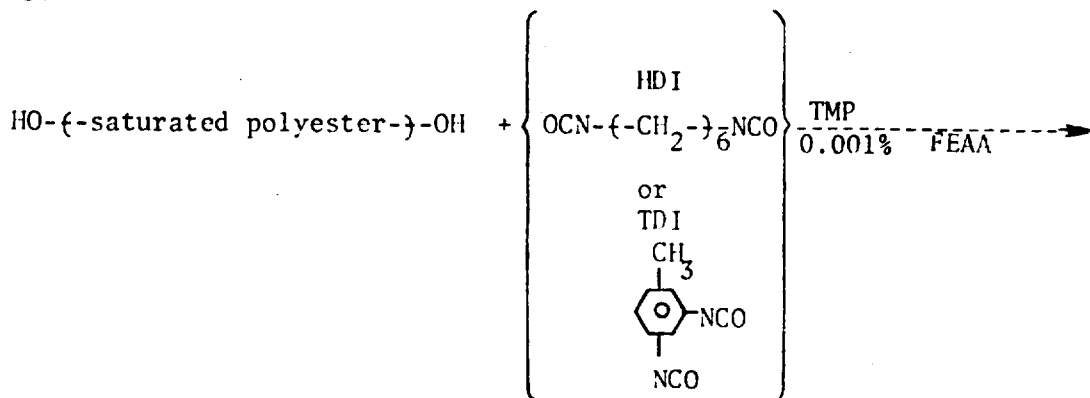
The following paragraphs outline the cure reactions used to crosslink the liquid polyester prepolymers and form a solid. Initial cure reactions were performed with prepolymers in the absence of pyrotechnic solids.

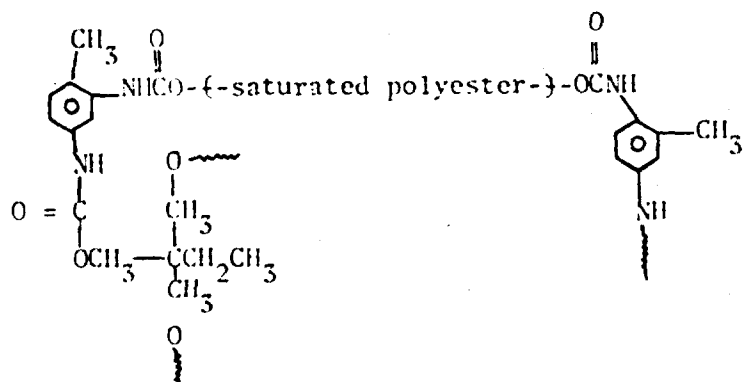
a. Selection of Polyisocyanate Curing Agents

Polyhydroxyl functional compounds reacted with polyisocyanates form the basis of commercial polyurethane foams, adhesives, coatings, and elastomers. The value of polyurethane products has led to the development of a wide variety of polyisocyanate materials, and these commercial polyisocyanates were used as curing agents for the hydroxyl functional polyester prepolymers.

Tolylene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) were selected as the curing agents for two reasons. First, high oxygen content of the binder was a design goal of the project; however, the oxygen content of commercial polyisocyanate curing agents was low. TDI and HDI have oxygen contents around 20%, but they also have low equivalent weight so that only a small amount of curing agents was required to cure the polyester prepolymers. The low equivalent weights of TDI and HDI minimized the reduction of total binder oxygen content when they were used to cure the polyester prepolymers. Second, other investigators had found that aromatic groups in experimental binders for illuminating flares were a possible source of degradation of flare performance. To investigate the hypothesis that aromatic groups in the binder degraded flare light output, tests were to be performed using illuminating flare compositions that were identical except for the choice of curing agent. The use of TDI as a curing agent would have incorporated an aromatic group into the binder of a flare compositions, and the performance of this composition could have been measured against a composition cured with HDI and containing no aromatic group.

The generalized cure reactions of TDI and HDI can be presented as follows:





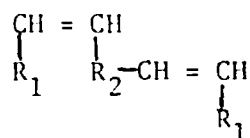
The function of trimethylolpropane (TMP) is to provide a crosslinking agent for forming a three dimensional solid polymer structure. Elimination of the TMP would yield as a product long chains of alternating prepolymer and TDI and HDI units with no interconnecting links between chains. Ferric acetyl acetate (FEAA) was used as the catalyst.

b. Procedure for Curing Saturated Polyester Prepolymers

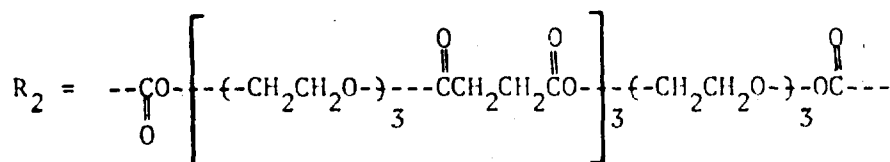
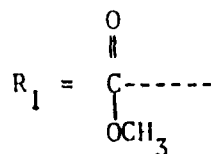
The polyester prepolymer was dried before cure by placing it in a rotary evaporator at a pressure of 0.7 mm Hg and heating the flask in a water bath at 55° to 60° C. After a minimum of 2 hours drying time, TMP (2.3 moles TMP to 1 mole polyester) and FEAA (0.001% by weight) were added to the flask, and vacuum and heat were applied until the TMP and FEAA dissolved. The mixture (prepolymer, TMP, and FEAA) was poured into curing containers placed on a top loading balance inside a fume hood, and TDI or HDI curing agent was added until the calculated total weight of cure reactants was reached. The curing container was placed in an oven at 75° to 80° C and was observed and timed until the cure was complete.

c. Free Radical Initiated Cure Reaction

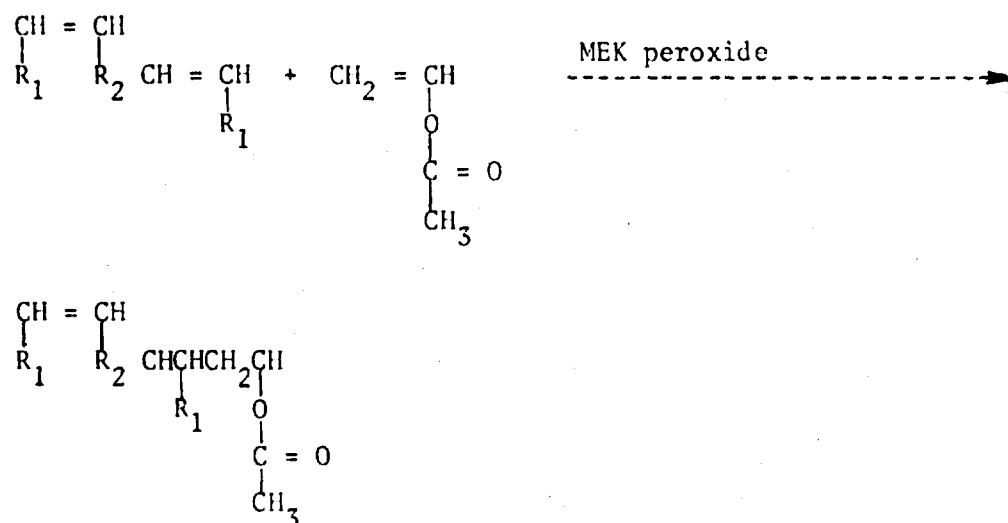
The free radical initiated cure reaction was selected to allow the investigation of alternate materials in cure reaction with the polyester prepolymers. Cure reactions involving copolymerization of unsaturated polysuccinate prepolymer and vinyl acetate or allyl diglycolcarbonate were tried. The vinyl acetate/polysuccinate prepolymer copolymerization resulted in the most successful cure. Unsaturated polysuccinate prepolymer can be represented by the structure



Where:



The addition polymerization reaction between unsaturated polysuccinate prepolymer and vinyl acetate can be represented as follows:



Where methyl ethyl ketone (MEK) peroxide is the free-radical initiator. The procedure used for cure reactions is the same as outlined in Section III, 5.b, except that the MEK peroxide is added with the vinyl acetate curing agent.

SECTION IV

CONCLUSIONS

The goal of the pyrotechnic binder development program was to produce a material that would allow pour casting of pyrotechnic compositions with no degradation in flare or marker performance. The approach chosen was to develop a liquid organic polymer of low viscosity when uncured (to allow mixing and fluidizing of pyrotechnic ingredients) and of sufficient strength and stability when cured to maintain the structure of a pyrotechnic grain within the item container under the range of environmental conditions. Achieving a pourable pyrotechnic composition by increasing the amount of binder generally has degraded flare performance. Minimizing these two contrasting effects was to be achieved by using the lowest viscosity binder obtainable to produce fluid pyrotechnic compositions at the lowest possible binder content and using high oxygen content binder to limit degradation of flare performance.

1. POLYTARTRATE PREPOLYMER

The polytartrate prepolymers examined during this project were of too great a viscosity to warrant further consideration as pyrotechnic binder ingredients.

2. POLYCARBONATE PREPOLYMER

Work was discontinued on the ester interchange synthesis of polycarbonate prepolymer when the same material was synthesized by a contractor using a different procedure (Reference 6). This synthetic procedure was easier to control and cheaper to scale up to production quantities. The polycarbonate synthesized by the ester interchange reaction was used to compare characteristics with the contract-produced material. The synthesis and characteristics of the polycarbonate prepolymer are discussed in References 6 and 7.

3. POLYDIGLYCOLATE PREPOLYMER

The polydiglycolate prepolymer was identical to the contractor-developed polymer system discussed in the previous paragraph. Work on this synthesis was directed toward examining additional polyglycols that were not used by the contractor. As a result of this work, the contractor substituted triethylene glycol for diethylene glycol in the synthesis because a lower viscosity prepolymer could be achieved (Reference 6).

4. POLYSUCCINATE PREPOLYMER

The polysuccinate prepolymer was basically a similar material to the prepolymer used in the current Air Force LUU-2B illumination flare. The stoichiometry of the reaction was changed to yield a prepolymer with terminal

hydroxyl groups instead of carboxyl groups. The hydroxyl groups required the use of a different cure reaction for cure of the binder as a polyurethane instead of the epoxy cure mechanism used for the carboxyl groups of the LUU-2B binder.

Synthesis of polysuccinate with a variety of polyglycols resulted in the selection of the polymer from a 4 to 3 ratio of triethylene glycol (TEG) and succinic anhydride (SA) as the best combination of viscosity (~1000 centipoises) and oxygen content (41%) obtainable with this chemical structure. The 4/3 TEG/SA prepolymer was cured as a polyurethane with HDI using the reaction outlined in Section III, 5.a. The cured material in the absence of pyrotechnic materials proved to be quite flexible and tough. A single half-pint batch of experimental illuminant composition was mixed at 51° C with this binder material and was pour castable.

5. UNSATURATED POLYSUCCINATE PREPOLYMER

The 4/3 TEG/SA prepolymer just described was used as a starting material for the modification of a polyester prepolymer for use of free radical initiated cure reactions. Incorporation of double bond terminal groups on the saturated polysuccinate prepolymer by post-reaction with maleic anhydride and methanol raised the prepolymer viscosity from 1000 to 15000 centipoises at 27° C. Copolymerization of this material with vinyl acetate in the absence of pyrotechnic materials resulted in a good cure, producing a tough flexible solid. Further work was halted by the termination of the binder project.

6. POLYOXALATE PREPOLYMER

Synthesis of polyoxalate prepolymers with diethylene glycol and triethylene glycol in the range of stoichiometries 3/2 and 5/4 (glycol/acid) yielded products with viscosities in the range of 1500 to 5500 centipoises at room temperature. Cure of these prepolymers with TDI and HDI in the absence of pyrotechnic ingredients yielded solids with adequate properties of strength and toughness. However, the cured products returned to the liquid state upon exposure to room temperature air and ambient humidity within a period of 3 to 6 months. Work to increase the stability of the cured product had just begun when the project was terminated.

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Note: Reports cited in this bibliography refer to development of flares using both pour cast and tamp cast production techniques.

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