U. S. NAVAL AIR ENGINEERING CENTER

PHILADELPHIA, PENNSYLVANIA

AERONAUTICAL MATERIALS LABORATORY

REPORT NO. NAEC-AML-1790 DATE 6 NOVEMBER 1963

SYNTHESIS OF ORGANIC POLYMERIC SYSTEMS CAPABLE OF WITHSTANDING TEMPERATURES GREATER THAN 900°F

PROGRESS REPORT

PROBLEM ASSIGNMENT NUMBER C 08 RMA 32-13 UNDER
BUREAU OF NAVAL WEAPONS WEPTASK RRMA 03 015/200 1/R007 03 01

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PREPARED BY: H. J. Lee
H. J. LEE
Project Engineer

APPROVED BY: E. K. Rishel
E. K. RISHEL, HEAD
Plastics Branch

C. A. Cassola
C. A. CASSOLA, SUPERINTENDENT
High Polymer Division

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ABSTRACT

The major objective of this work is the synthesis of organic polymeric systems that have exceptionally high thermal stability i.e., the ability to withstand temperatures greater than 900°F.

Several types of polymer systems investigated, which includes polyesters and polyamides, indicated exceptional promise. One aromatic polyamide, in particular, synthesized by interfacial polycondensation process withstood muffle furnace temperatures as high as 1100°F with no softening at or below this temperature. Color change increased when temperature was raised from 920°F to 1060°F in a 15 minute period. From 1060°F to 1100°F in a 25 minute period the polymer became a blacker brown.

I. INTRODUCTION

A. This report discusses the limited research, of an exploratory nature, on the synthesis of organic polymeric systems that have the exceptional ability to withstand temperatures greater than 900°F. The exploratory work was initiated 5 October 1962.

B. Concurrent with present day technological advances, particularly in space technology, is the need for new materials with unique properties. One important property is that of extremely high temperature resistance. Among present day materials, that are wholly organic, the ability to fulfill this function is rare and the development of such a material, or materials, no doubt will also aid the initiation of advances in other technological endeavors.

C. The nature of the work described herein concerns the synthesis of organic polymeric systems that have the capability of undergoing temperatures greater than 900°F. The scope of the work naturally involves studies on:

1. Types of polymeric systems such as polyesters, polyamides, epoxies phenolics, etc.

2. Techniques and methods of polymerization to effect:

   a. high yields

   b. reasonably high molecular weight polymers

   c. satisfactory degrees of polymerization

   d. Optimum reaction conditions

3. Areas of thermal stability involving:

   a. first order transition points

   b. second order transition points or softening points

   c. degradation and weight loss

4. Mechanical and structural strength characteristics under thermal stress.

D. Of the types of polymeric systems investigated, polyesters and polyamides indicated exceptional promise, notwithstanding the fact that the groups $\overset{O}{\overset{\|}{C}}\text{-O}$ and O-CH_2 in polyesters tend to increase chain flexibility with attendant lowering of softening point or melting point.

E. This study to attain the objective polymer, or polymers, was based on the relationship of molecular structure of monomers and polymers with such factors as polarity, orientation, symmetry, flexibility, etc., of final product synthesized.

F. An aromatic polyamide system synthesized from an aromatic diamine and terephthaloyl chloride by interfacial polycondensation in acid medium withstood temperatures as high as 1100°F in a muffle furnace. Preliminary observations showed no softening at or below this temperature. However, a color change from gingerbread brown to black-brown was noted when the temperature was raised from 920°F to 1060°F in a 15 minute period. Some small pieces, broken with a metal rod, exhibited yellow-brown interior. From 1060°F to 1100°F in a 25 minute period the color changed to a darker black-brown; more black than brown, still without any softening or melting.

II. GENERAL DISCUSSIONS

A. Initially, hydroxyl terminated polymeric starting materials were synthesized and considered for possible conversion to various types of polymers such as epoxies, cross-linked superpolyesters, polyurethanes, polyamides, polyureas, phenolics, etc. However, only the corresponding polyglycidyl derivatives of many of these hydroxyl rich materials were experimented with, which proved disappointing from the standpoint of high thermal stability.

B. These starting materials were synthesized by two distinct methods. Wherever possible melt polymerization was practiced and in the case where it was not applicable, interfacial polymerization was resorted to.

C. Exploratory work in the polyesters and polyamides have yielded several interesting and worthwhile systems, among which are approximately eight high polymeric ones that have no melting point or softening point at or below 900°F at least. Thus far, preliminary tests on these systems indicate promise, but additional and extensive studies on these are required. Two of these are outstanding in that they can withstand 900°F (one for 3/4 hour duration, and the other tested for 10 minutes at this temperature exhibited increased hardness; this latter system will be studied at 900°F for longer time exposures).

D. The polyamide, (polyterephthalamide of p-p'-methylene dianilin) described previously, exhibited the greatest potential in high thermal resistance and any future work will be centered about this system. (A disclosure on this has already been submitted to the Naval Air Engineering Center patent office).

E. Several unusual monomers for polymer synthesis such as 3,3'-Bis (p-hydroxy phenyl) phthalide and other structurally related monomers were studied. Results thus far have been encouraging in that many of the varied types of reactive sites these monomers possess have been reacted in stages to yield relatively heat stable polymers initially or in subsequent stages of reaction.

F. It may be noted that a literature search indicates that not much work has been carried out on these types of monomers in this Country although some limited studies have been undertaken in Russia.

G. Since all work performed was of an exploratory nature, characterization of the promising polymeric systems synthesized was relegated to secondary considerations. The requirement of polymer characterization will be met in future work which will be more exacting and detailed.

III. EXPERIMENTAL PROCEDURES FOR THE MOST PROMISING SYSTEMS

A. Preparation of Terephthalamide of p-p'-methylene dianilin by Interfacial Polymerization in Acid Medium.

PREPARATION:

Solution 1 - To 1.502 gram (.0075M) of terephthaloyl chloride was added approximately 140 cc of toluene and heated approximately to 105°F to completely dissolve.

Solution 2 - To 1.453 gram (.0075M) of p-p'-methylene dianilin in a separate beaker was added approximately 70 cc of 0.06 - 0.07 molar HCl and the solution heated to approximately 105°F to completely dissolve.

Solutions were both mixed in a Waring Blendor for 15 minutes at the end of which time the temperature of the mixture was approximately 105°F.

Mixture poured into beaker containing 1 liter of acetone and allowed to stand overnight.

Resulting white precipitate was filtered through a Buchner funnel with #41 paper, washed with 200 mls of acetone, then 4 times with 200 - 250 mls of distilled water each time. Finally washed with 200 mls of acetone. The polymer precipitate was dried in a circulating oven at 230°F for 3 hours.

Yield of product was 65.8%. Color was off-white with yellowish tinge.

Weight-loss determination was made in a muffle furnace with recording potentiometer. Inability to maintain the temperature at one value for any length of time accounts for the continued increase in temperature readings.

No weight-loss determination was made in the temperature interval of 920°F - 1060°F and 1060°F - 1100°F as the potentiometer for recording temperatures malfunctioned in this region.

TABLE 1

DETERMINATION OF WEIGHT LOSS
OF POLYTEREPHTHALAMIDE OF P-P'METHYLENE DIANILIN

Time	Duration of Exposure	Temp. °F	Color of Polymer	Weight Loss %
1:20		500		
1:30	10 Min.	720	Hard - Very Lt. Violet Tan	3.0
1:35		710		
1:41		750		
1:45		780		
1:50	15 Min.	800	Hard Sl. Darker Lt. Tan	0.3
1:53		800		
1:55		820		
2:01		820		
2:15		840		
2:17	24 Min.	850	No Change	8.8
2:20		850		
2:30		880		
2:37		890		
3:05		920		
3:08	48 Min.	920	Hard - Very Sl. Browner	20.6

Total Exposure Time = 1 Hour, 37 Minutes
Total Weight Loss = 32.7%

MATERIAL PUT BACK IN FURNACE

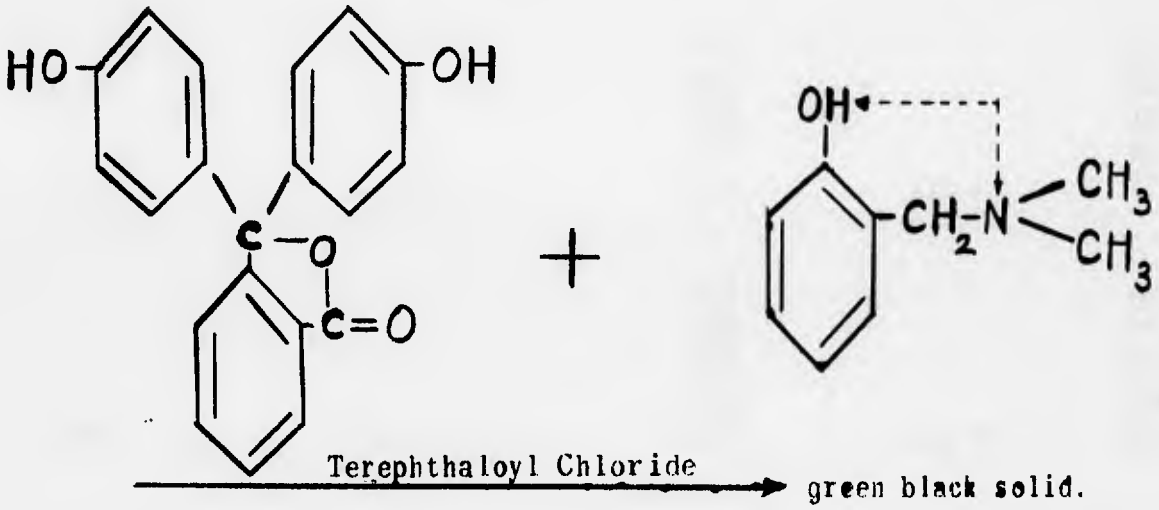
3:30		920		
3:45	15 Min.	1060	Hard Black-Brown	Weight Loss - Not Determined
10:45		1060	Blacker-Brown	Weight Loss - Not Determined
11:10	25 Min.	1100		

B. Terephthalate of 3,3'-Bis-(p-hydroxy phenyl) phthalide and Hydroquinone by Melt Polymerization in Molar Ratio of 0.25:0.75:1.0 = phthalide: hydroquinone:terephthaloyl chloride, 4.0 grams of 3,3'-Bis-(p-hydroxy phenyl) pethalide, 4.1 grams of hydroquinone, 10.0 grams of terephthaloyl chloride were mixed together in a beaker and heated. Partially liquefied and then set up into a heterogeneous hard grayish white solid at approximately 800°F.

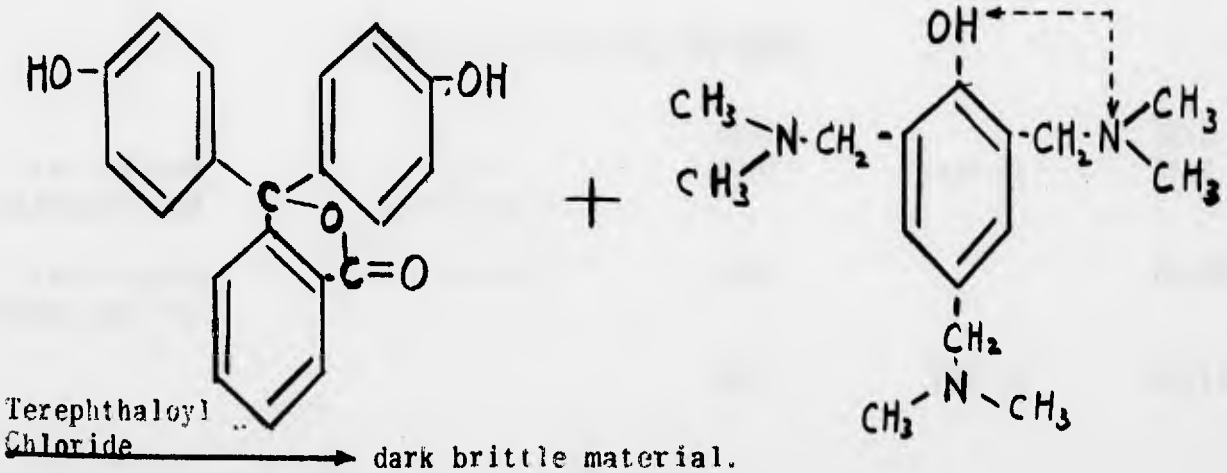
After 5 minutes at 800 - 840°F the material increased in hardness and turned a grayish tan. No softening or melting occurred at 900°F. Material was dull dark brown spotted with white and hard at this temperature.

C. Preliminary studies made on 3,3'-Bis(p-hydroxy phenyl) phthalide and structurally related compounds that showed no melting or softening at 900°F (at least).

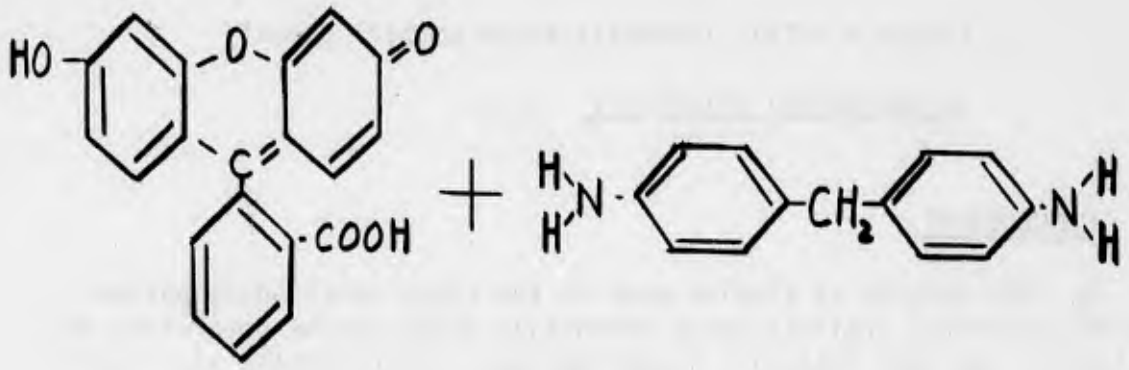
1. 3,3'-Bis-(p-hydroxy phenyl) phthalide + O-dimethyl-amino-methyl phenol.



2. 3,3'-Bis-(p-hydroxy phenyl) phthalide + Tris (dimethyl-amino-methyl) phenol.

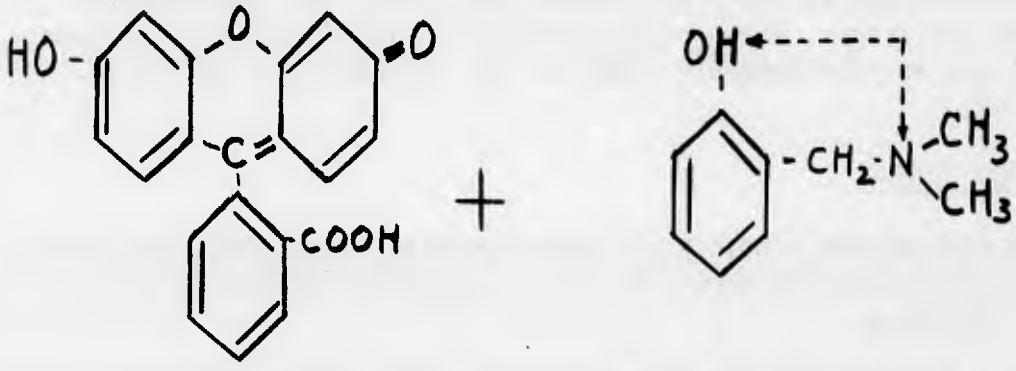


3. Fluorescein + p,p'-methylene dianilin.



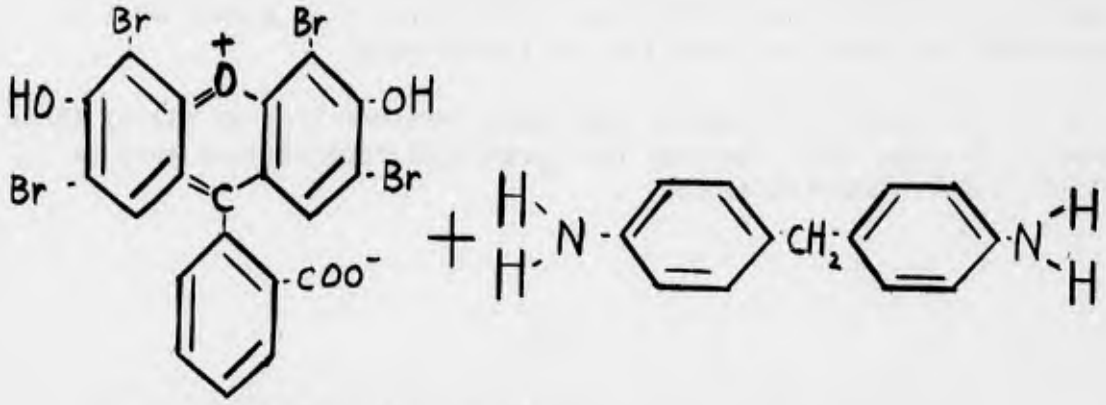
Terephthaloyl Chloride → dull black solid.

4. Fluorescein + dimethyl-amino-methyl phenol



→ brittle red foam.

5. Eosein A (Brominated Fluorescein) + p,p'-methylene dianilin.



Terephthaloyl Chloride → dull hard solid.

6. Eosin A + Tris (dimethyl-amino-methyl) phenol

Terephthaloyl Chloride → Hard

IV. CONCLUSIONS

A. The results of studies made on the eight outstanding polymer systems certainly indicate great potentials which can be determined only by further and more intensive investigation. These results also verify and justify the logic and method of approach to the problem.

B. Further work is necessary to advance the systems to those having properties that would make them useful as plastics, fibers, adhesives, etc., without any sacrifice in thermal resistivity.

C. Several other systems which did not possess the attribute of temperatures resistivity at 900°F or greater exhibited other advantageous property possibilities. These characteristics, such as fiber potentials and non-melting or non-flammable foams, may be desirable and worthy of consideration.

V. RECOMMENDATIONS

A. In view of the findings of these investigations, additional work of a more intensive and extensive nature is warranted particularly as regard the following:

Preparation 1 - polyterephthalamide of p,p'-methylene dianilin synthesized interfacially in acid medium.

Preparation 2 - polyterephthalate of 3,3'-Bis-(p-hydroxy phenyl) phthalide and hydroquinone by melt polymerization.

B. As stated previously, since all these studies were of an exploratory nature characterization of the promising polymers synthesized was relegated to secondary considerations. Therefore, this requirement of characterization should be fulfilled in future work.

C. It is hoped that further work would advance some or all of these systems to a stage where they can have practical applications such as plastics, fibers, adhesives, etc.

ACKNOWLEDGEMENTS

Assistance was received from J. Carney, Test Mechanic, on a part time basis during the investigation.

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(c) USSR Patent 132,401

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2. PAN C 08 RMA 32-13

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