

WADC TECHNICAL REPORT 56-534

PART III

ASTIA DOCUMENT No. AD 131029

NUCLEAR RADIATION EFFECTS ON STRUCTURAL
PLASTICS AND ADHESIVES

PART III EXPERIMENTAL RESEARCH

*R. Y. MIXER
D. B. PARKINSON*

STANFORD RESEARCH INSTITUTE

AUGUST 1957

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-3632
PROJECT 1252

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Continents
FOREWORD

This report was prepared by Stanford Research Institute under USAF Contract No. AF 33(616)-3632. This contract was initiated under Project No. 1252, "ANPP Support", Task No. 73023, "Radiation Effects". The work was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Arlook as project officer. Parts I and II of this report are entitled "Literature Survey" and "Extension of Literature Survey" respectively.

This report covers work conducted from 15 April 1956 to 15 March 1957.

The assistance of Shell Development Company in supplying the Epon X-131 laminates is gratefully acknowledged.

WADC TR 56-534 Pt III

Nuclear radiation damage mechanisms are presented for model compounds representing several typical aircraft structural adhesives and laminates. Laminates were prepared from eight resin-curing agent systems and irradiated to 10^9 and 10^{10} rep for determination of the threshold dose for damage. The threshold dose for one system was found to be less than 10^8 rep. In the case of typical amine-cured, epoxy -type adhesives, radiation appears to cleave the amine groups with volatilization of some fragments and to crosslink the polymer chain. Small amounts of chemical changes result in large changes in physical properties of the cured adhesive. Beta and gamma irradiation have produced equal effects on one vinyl-phenolic and one epoxy-type adhesive. One organic scintillator, 2,5-diphenyloxazole, appears to be partially effective in preventing irradiation damage in an epoxy-type adhesive.

PUBLICATION REVIEW

This report has been reviewed and is approved

FOR THE COMMANDER:



R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

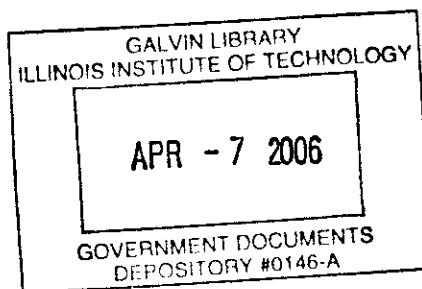


TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION	1
II METHODS OF APPROACH	4
A. Adhesives	4
B. Laminates	4
III SUMMARY AND CONCLUSIONS	5
A. Laminates	5
B. Cured Epon 828 and 1001 Systems	5
C. Equivalency of Beta and Gamma Radiation	5
D. Model Compounds - Epon Series	5
E. Model Compounds - Others	6
F. Antirads and Scintillators	6
IV DISCUSSION OF RESULTS	7
A. Laminates	7
B. Cured Epon 828 and 1001 Systems	7
C. Equivalency of Beta and Gamma Radiation	9
D. Model Compounds - Epon Series	10
E. Model Compounds - Others	16
F. Antirads and Scintillators	17
V EXPERIMENTAL PROCEDURES	19
A. Laminates	19
B. Cured Epon 828 and 1001 Systems	22

Contents
TABLE OF CONTENTS (Continued)

	<u>Page</u>
C. Equivalency of Beta and Gamma Irradiation	22
D. Model Compounds - Epon Series	24
E. Model Compounds - Others	31
F. Antirads and Scintillators	32
G. Treatment of Data	32

Continued
LIST OF TABLES

<u>Table</u>	<u>Page</u>
I MATERIALS SELECTED FOR STUDY BY THE STEERING COMMITTEE	2
II PHYSICAL PROPERTIES VERSUS IRRADIATION DOSE FOR EPON 1001 LAMINATES	8
III EFFECT OF IRRADIATION UPON EPON 828 and 1001 CURED WITH <u>META-PHENYLENEDIAMINE</u>	9
IV IRRADIATION OF MODEL COMPOUNDS - EPON SERIES Physical and Chemical Properties	14
V IRRADIATION OF MODEL COMPOUNDS - EPON SERIES Gas Analyses	15
VI PROTECTIVE AGENTS IN ADHESIVES.	18
VII PREPARATION AND PHYSICAL PROPERTIES OF LAMINATES	20
VIII PREPARATION OF EPON X-131 LAMINATES	21
IX DOSIMETRY FOR LAP SHEAR SPECIMENS	25
X EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF EPON VIII AND FM-47	26
XI PREPARATION OF MODEL COMPOUNDS - EPON SERIES	27
XII DISTILLATION OF PURIFIED EPON 828	28
XIII FRACTIONATION OF EPON X-131	29

Control
LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
1 EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF EPON VIII	11
2 EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF FM-47.	11
3 A PORTION OF A HYPOTHETICAL AMINE-CROSS-LINKED EPOXY RESIN	13
4 INFRARED SPECTRA	34
a. Resin from EC-1469	
b. Diglycidyl ether of Bisphenol A (DEBA)	
5 INFRARED SPECTRA	35
a. Model Compound: DEBA + \underline{n} -C ₃ H ₇ OH	
b. Irradiated 4.5×10^8 rep	
6 INFRARED SPECTRA	36
a. Model Compound: DEBA + C ₆ H ₅ OH	
b. Irradiated 4.5×10^8 rep	
7 INFRARED SPECTRA	37
a. Model Compound: DEBA + \underline{n} -C ₄ H ₉ NH ₂	
b. Irradiated 4.8×10^8 rep	
c. Liquid Deposit from Irradiation	
8 INFRARED SPECTRA	38
a. Model Compound: DEBA + (C ₂ H ₅) ₂ NH	
b. Irradiated 7.1×10^8 rep	
9 INFRARED SPECTRA	39
a. Model Compound: DEBA + C ₆ H ₅ NH ₂	
b. Irradiated 4.5×10^8 rep	
c. Liquid Deposit from Irradiation	

LIST OF ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
10	INFRARED SPECTRA	40
	a. Model Compound: Epon 1001 + n-C ₄ H ₉ NH ₂	
	b. Irradiated 5.1 x 10 ⁸ rep	
	c. Liquid Deposit from Irradiation	
11	INFRARED SPECTRA	41
	a. Model Compound: Epon 1001 + (C ₂ H ₅) ₂ NH	
	b. Irradiated 4.5 x 10 ⁸ rep	
12	INFRARED SPECTRA	42
	a. Model Compound: Epon 1001 + C ₆ H ₅ NH ₂	
	b. Irradiated 4.5 x 10 ⁸ rep	
	c. Liquid Deposit from Irradiation	
13	INFRARED SPECTRA	43
	a. Model Compound: Epon X-131 + C ₄ H ₉ NH ₂	
	b. Irradiated 7.1 x 10 ⁸ rep	
14	INFRARED SPECTRA	44
	a. Model Compound: Epon X-131 + C ₆ H ₅ NH ₂	
	b. Irradiated 7.1 x 10 ⁸ rep	
	c. Liquid Deposit from Irradiation	

Contrails

NUCLEAR RADIATION EFFECTS ON STRUCTURAL
PLASTICS AND ADHESIVES

Part III Experimental Research

I INTRODUCTION

It is well known that organic polymers undergo irradiation damage, which may be the result of crosslinking, additional crosslinking, or chain degradation. The polymers in adhesives and laminates used as structural material for air frames are subject to radiation damage, the extent of which appears to be dependent upon the presence of other materials, such as fillers and reinforcing fibers. A study of the chemical damage resulting from irradiation can therefore provide desirable information not only for air frame design, but also for formulation of more radiation-resistant adhesives and laminating resins. Because of the generally greater stability of laminates (probably due to their lower organic content), more emphasis was placed on the study of damage to structural adhesives.

A Steering Committee composed of members from Wright Air Development Center and Stanford Research Institute selected the area of work for this investigation. The glass laminates and commercial adhesives chosen for study are indicated in Table I. The objective of the study of laminates was to establish the threshold damage for gamma radiation. With the exception of Epon 1001 cured with dicyandiamide, all of the laminates listed in Table I had shown no damage up to 10^9 rep (1, 2).

A number of studies have been made on irradiation damage, but none has covered all of the materials used in structural adhesives and laminates. Two recent publications cover the general changes in physical properties of commercially available, compounded adhesives (3) and structural laminates (1) due to gamma irradiation.

Manuscript released by authors 15 March 1957 for publication as a WADC Technical Report.

- 1 R. C. Tomashot and D. G. Harvey, WADC Technical Report 56-296.
- 2 1 rep (roentgen equivalent physical) is that quantity of ionizing radiation which, upon absorption in the material, deposits 93 ergs of energy per gram of material.
- 3 R. S. Arlook and D. G. Harvey, WADC Technical Report 56-467.

MATERIALS SELECTED FOR STUDY BY
THE STEERING COMMITTEE

Material	Chemical Type
Laminates	
Epon 828 + Curing Agent A	Epoxy
Epon 1001 + Dicyandiamide	Epoxy
Epon X-131 + BF ₃ 400	Epoxy
Epon X-131 + Dicyandiamide	Epoxy
Laminac 4232 + Benzoyl Peroxide	Polyester
Selection 5003 + Benzoyl Peroxide	Polyester
CTL 91-LD	Phenolic
DC-2106 + XY-15	Silicone
Adhesives	
FM-47	Vinyl-phenolic
AF-6	Nitrile rubber-phenolic
EC-1469	Epoxy
Metlbond 4021	Nitrile rubber-phenolic
Metlbond MN3C	Buna N-Nylon-phenolic
422	Epoxy-phenolic
1236 Formulation of Epon X-131	Epoxy-polyvinyl formal

Contrails

As background for this study, a literature survey was made on irradiation of organic materials, and this appeared as Part I of this report at the beginning of the program. Part II of this report, entitled "Extension of Literature Survey," was necessary because of the number of articles that were received later on the irradiation of organic materials.

II METHODS OF APPROACH

A. Adhesives

Model compounds were studied as the main method of approach to achieve the principal objective. Model compounds are easier to handle than the formulated and cured adhesives. Due to the solubility of the model compounds, tests can be run on them more easily and accurately. Their low molecular weight makes any rupture of crosslinking easier to detect. It was assumed for this study that the fillers merely dilute the effect of irradiation.

Adhesives containing epoxy resins were selected for initial studies because more is known about the composition of these adhesives and the chemical nature of the epoxy resins. Very little information was obtainable on the composition of the other adhesives, including structural and chemical details on the organic resins involved. Thus, preparation and study of model compounds from epoxy resins constituted the main effort in this program.

Because of a desire to use beta rays as the source of irradiation, it was desirable to establish the equivalency of beta and gamma radiation for lap shear specimens bonded with several adhesives.

It was felt that antirads (which had been useful as protecting agents in other systems) and possibly scintillators would act as protective agents for adhesives. Some attempts were made to evaluate this method of approach.

B. Laminates

It was desirable to establish the threshold damage for a number of resin-glass laminates (see Table I). In a recent study (1) these laminates, with the exception of those made from Epon 1001, showed no change in physical properties upon gamma irradiation up to 10^9 rep. In order to elucidate the causes for the differences in laminates made from Epon 828 and 1001 resins, it was desirable to study the radiation resistance of these Epon resins cured with a common curing agent.

Since many of the resins, particularly epoxy resins; that are employed in the adhesive formulations are also used as resins in the laminates, all of the information gained from the model compound studies on adhesives would apply to the corresponding laminates.

III SUMMARY AND CONCLUSIONS

A. Laminates

Glass laminates were prepared from the eight resin-curing agent systems listed in Table I. Flexural, compressive, and tensile specimens from these laminates were irradiated at the Materials Testing Reactor (MTR), Idaho Falls, Idaho, receiving a dose of 10^9 rep (gamma). Other samples are now being irradiated for an ultimate dose of 10^{10} rep. Testing of all these specimens is being carried out by WADC.

The specimens from Epon 1001-dicyandiamide laminates received only 7.9×10^7 and 3.0×10^8 rep. The results of testing these specimens were in agreement with results from similar tests performed by WADC (1).

B. Cured Epon 828 and 1001 Systems

Irradiation studies on Epon 828 and 1001 cured with meta-phenylenediamine showed that the two systems had similar radiation resistance. The poor showing of laminates made from Epon 1001 + dicyandiamide (see above and reference (1) must be due to the curing agent per se, or to improper utilization of the curing agent.

C. Equivalency of Beta and Gamma Radiation

Beta and gamma rays were shown to produce almost identical results in tests on irradiated lap shear specimens of adhesives Epon VIII and FM-47.

D. Model Compounds - Epon Series

Model compounds of diglycidyl ether of Bisphenol A (DEBA), Epon 1001, and Epon X-131 were prepared by reacting these materials with n-propyl alcohol, phenol, n-butylamine, diethylamine, and aniline. The compounds thus represent segments of the cured polymer chain between crosslinks and in some cases (with amines) they represent the segment including the crosslinking amine groups.

Irradiations of these model compounds were carried out using the same range of dosage (1 to 7.1×10^8 rep, beta) as the compounded adhesives received in a recent study (3).

The chemical damage resulting from irradiation appears to be a cleavage of the amine groups, which volatilize, and a crosslinking of the polymer moieties. The order of stability of resins appears to be

Contrails

Epon X-131 > Epon 1001 > Epon 828 and the stability of the crosslinking agents ϕNH_2 > Et_2NH ~ BuNH_2 . A comparison of damage to model compounds and to adhesives at the same dosage range shows that a small amount of chemical damage can result in large changes in physical properties in the cured adhesive. In view of the similar constitution (resin-wise) of glass laminates, it is apparent that the high glass filler content (65-70%) in the laminates exerts a tremendous protective effect.

Thus, it seems desirable to test anhydride curing agents (particularly aromatic types) with adhesives and, perhaps, laminates in the hope that they will impart more radiation resistance. A model compound study representing anhydride curing could well precede these tests.

E. Model Compounds - Others

Model compounds of nonepoxy-type adhesives were not prepared due to lack of information and time. Components of some of the other adhesives were acquired. From analyses, adhesive EC-1469 appears to be silica-filled diglycidyl ether of Bisphenol A.

F. Antirads and Scintillators

Preliminary attempts to improve the radiation resistance of two commercial compounded adhesives with two protective agents (scintillators) were partially successful. Lap shear specimens from Epon VIII, containing 9.1% of 2,5-diphenyloxazole, an organic scintillator, lost only 11% of its strength after receiving a dose of 8×10^8 rep (beta), compared with 40% loss for the control specimens. This phase of the work should be expanded; certainly, this approach with antirads was successful in elastomers (4).

4 J. W. Barn. WADC Technical Report 55-58 Part II. September 1956.

IV DISCUSSION OF RESULTS

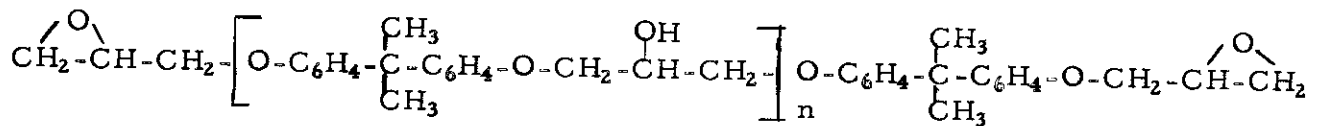
A. Laminates

In order to provide data on the threshold dose for irradiation damage to resin-glass laminates, a number of laminates were prepared for irradiation testing (see Table I). Flexural, compressive, and tensile specimens from these laminates were irradiated at the gamma facility of the MTR, receiving dosages of 10^9 and 10^{10} rep. These specimens were shipped to WADC for testing. Due to the long irradiation times involved, these results were not available for inclusion in this report.

The specimens from Epon 1001 laminates received 7.9×10^7 and 3.0×10^8 rep to match the dosages received in a previous study by Tomashot and Harvey (1). These irradiated specimens were tested at room temperature both dry and after 2-hr immersion in boiling water. The results given in Table II agree with those from the above study. This resin system is severely damaged at dosages of 3.0×10^8 rep as indicated by delamination after only five minutes exposure in boiling water. This sensitivity to radiation appears to be unique with this system, as the laminate system Epon 1001-Plyophen 5023 cured with dicyandiamide and adhesive 422 (containing the same ingredients) are quite stable to 10^9 rep. The phenolic component (Plyophen 5023) appears to stabilize the Epon 1001-dicyandiamide system in some manner.

B. Cured Epon 828 and 1001 Systems

Laminates prepared from Epon 828 plus Curing Agent A (diethylaminopropylamine) show no damage when irradiated up to 10^9 rep (gamma), whereas laminates from Epon 1001 plus dicyandiamide are badly damaged at 2.9×10^8 rep (1). In order to understand these differences better, Epon 828 and 1001 were cured with a common curing agent, meta-phenylenediamine, and no filler, to see if the difference in the curing agent was responsible. Epon 828 and 1001 belong to the same family of resins, differing only in molecular weight as shown in the formula.



where for Epon 828, $n=0$ and for Epon 1001, $n=2-3$. Intuitively, one would not expect the longer chain between crosslinks in Epon 1001 to be responsible for its poor showing. meta-Phenylenediamine was the only curing agent that would give acceptable cures with both resin systems.

Table II
PHYSICAL PROPERTIES VERSUS IRRADIATION DOSE
FOR EPON 1001 LAMINATES

Condition	Dosage, ^a rep x 10 ⁻⁷	Flexural Strength, psi x 10 ⁻³		Flexural Modulus, psi x 10 ⁻⁶	Tensile Strength, psi x 10 ⁻³		Compressive Strength, psi x 10 ⁻³	
		Average	σ		Average	$\bar{\sigma}$	Average	$\bar{\sigma}$
Dry	0	77.4	1.4	3.44	50.9	1.3	50.7 ^b	3.4 ^b
	7.9	71.1 ^b	0.6 ^b	3.36	47.9	2.4	42.8 ^b	3.0 ^b
	30	27.4 ^b	1.1 ^b	3.54	38.8 ^b	1.0 ^b	27.8	4.0
After 2 hrs. in boiling water	0	70.9	1.7	3.24	47.0 ^b	1.1 ^b	44.8	0.4
	7.9	67.6	1.7	3.26	44.5	2.3	44.2	1.8
	30	delaminated	delaminated	--	delaminated	delaminated	delaminated	delaminated

a As supplied by MTR dosimetry

b Adjusted

These cured systems were irradiated (beta) and the change in acetone soluble material, change in nitrogen content, and G-value for total gas liberated were determined. These results given in Table III indicate that resin systems have essentially the same radiation stability. The decrease in nitrogen content of the liquid deposits from irradiation as compared to the increase in nitrogen content of those from model compounds is expected in view of the two or more points of attachment in the cured systems. The G-value for gas evolution is in the same range as corresponding values from model compound studies. Essentially the same relative increase in acetone soluble material was noted for each system.

Table III

EFFECT OF IRRADIATION ON EPON 828 AND 1001
CURED WITH META-PHENYLENEDIAMINE

<u>Resin</u>	<u>Amount of $\Phi(\text{NH}_2)_2$ phr</u>	<u>Dose, rep</u>	<u>Acetone Soluble, %</u>	<u>Nitrogen %</u>	<u>G gas</u>
Epon 828	14	0	0.6	3.50	--
		5×10^8	1.5	1.14 ^a	0.30
Epon 1001	5.4	0	2.0	1.40	--
		5×10^8	6.2	0.90 ^a	0.31

a Analysis on liquid deposit

From the data available, there is every indication that the instability of the Epon 1001-dicyandiamide system is due to the dicyandiamide.

C. Equivalency of Beta and Gamma Radiation

It became necessary to establish the equivalency of beta and gamma radiation because of the desire to use beta irradiation for lap shear specimen and model compound studies. The use of beta rays as the radiation in this contract resulted in shorter irradiation times and eliminated many equipment problems. Due to the absorption characteristics of beta rays, it was necessary to use 20-mil aluminum for one member of the lap shear joint, and the adhesive was irradiated through

Contrails

the 20-mil aluminum. To reduce the bending moment of the joint the 20-mil strip was backed with a 63-mil aluminum strip using adhesive Epon VI cured at room temperature.

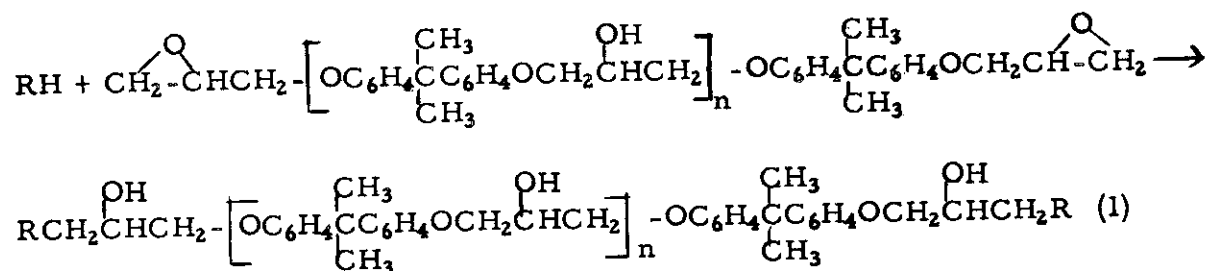
Reductions of lap shear strength were measured for adhesive Epon VIII and FM-47 as a function of beta and gamma ray dosage. The measurements for Epon VIII and FM-47 are plotted in Figures 1 and 2, respectively. With Epon VIII the equivalency was well established, not only between sources at the Institute but also between the gamma sources at the Institute and WADC. The results from using FM-47, although showing the equivalency of beta and gamma radiation, agree with WADC gamma results only to 31×10^7 rep and disagree at 81×10^7 rep. The reasons for this discrepancy are unknown.

Concerning the equivalency of radiation sources, methyl methacrylate exposed to 46×10^6 r from a Co^{60} source showed the same decrease in molecular weight as a sample receiving 45×10^6 rep from 1-Mev electrons (5). Furthermore, the amount of unsaturation produced in polyethylene during irradiation is identical for both beta and gamma rays (5).

D. Model Compounds - Epon Series

The model compounds were prepared as a means of studying the chemical damage that occurs upon irradiation of epoxy-type adhesives. Three resins, Epon 828, 1001, and X-131, were used for the preparations. Epon 828 was purified and distilled, yielding the diglycidyl ether of Bisphenol A (DEBA), and this material was used exclusively. Attempts were made to purify Epon X-131 but they were unsuccessful (see Section V, Experimental Procedures).

The reactions of DEBA and Epon 1001 with n-propyl alcohol, phenol, n-butylamine, diethylamine, and aniline are indicated in the following equation:



where R represents $\text{C}_3\text{H}_7\text{O}-$, $\text{C}_6\text{H}_5\text{O}-$, $\text{C}_4\text{H}_9\text{NH}-$, $(\text{C}_2\text{H}_5)_2\text{N}-$, and $\text{C}_6\text{H}_5\text{NH}-$, $n=0$ for DEBA, and $n=2-3$ for Epon 1001.

⁵ P. Morgan. "Plastic Progress, 1955." Iliffe and Sons, Ltd., London, 1956, p. 16.

Contrails

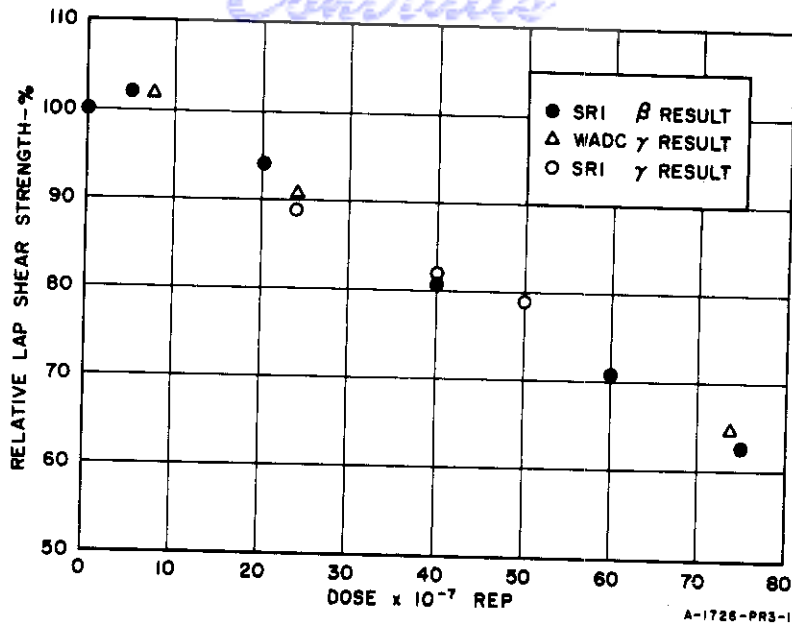


FIG. 1

EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF EPON VIII

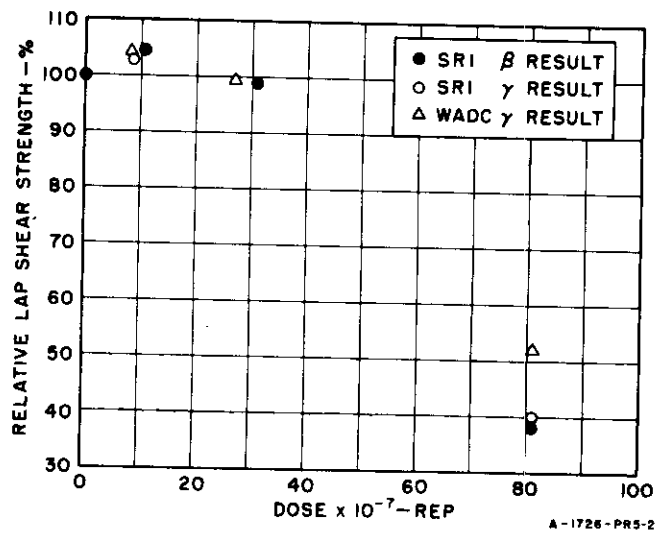
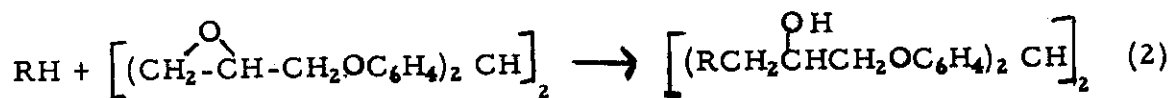


FIG. 2

EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF FM-47

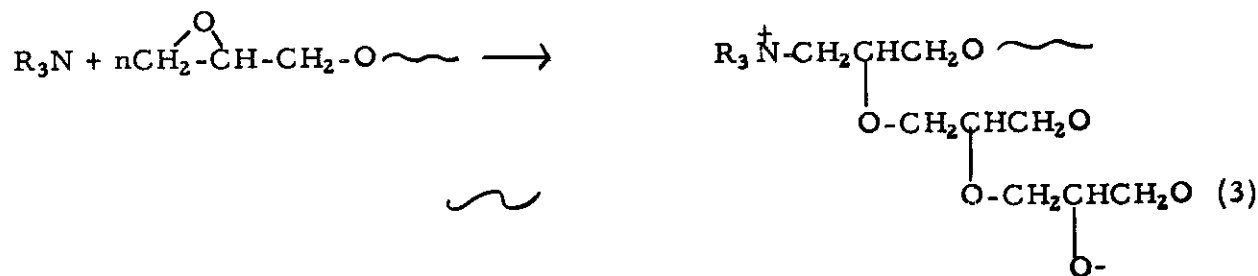
The corresponding reactions of Epon X-131 are indicated by equation (2).



Catalysts and conditions for these reactions have been recently and adequately discussed (6).

The purpose of these particular model compounds is to represent the polymer segments between crosslinks, in some cases including the crosslinking group. For example, the product from phenol and resin represents the polymer chain between, but not including, the crosslinking sites and is shown in Figure 3 as portion A of a hypothetical amine-crosslinked epoxy resin. The products from n-butylamine, diethylamine, and aniline represent the polymer chain between and including the crosslinking sites for aliphatic primary amine curing from agents such as ethylene diamine, aliphatic secondary amine curing from agents such as diethylene triamine, and aromatic primary amine curing from agents such as meta-phenylenediamine, respectively. These are shown as portion B in Figure 3.

The model compound from n-propyl alcohol and epoxy resin is intended to represent the polymer chain between crosslinking sites when a tertiary amine cure is involved. This is shown in equation (3).



The results of tests on these model compounds before and after irradiation are shown in Tables IV and V. Not all of the compounds prepared were irradiated because the irradiations were producing similar changes in similar compounds and because of time restrictions. The doses received by the model compounds cover the same range of doses (up to 8×10^8 rep) received by several adhesives in the study by Arlook and Harvey (3). In this range most of the adhesives suffered considerable loss in strength properties.

6 L. Shechter, et al., Ind. Eng. Chem., 48, 86, 94 (1956).

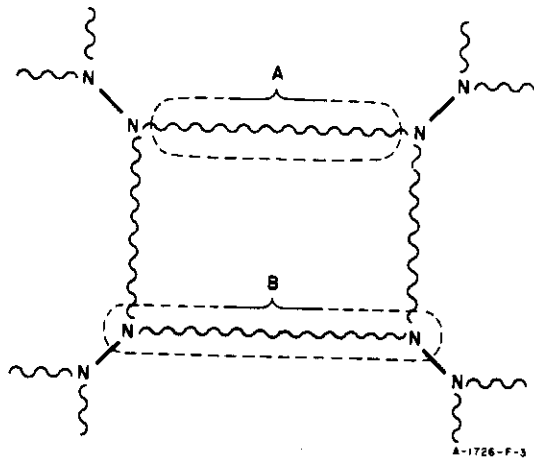


FIG. 3

A PORTION OF A HYPOTHETICAL AMINE-CROSSLINKED EPOXY RESIN.
 N-N is the amine-crosslinking agent and
 ~ is the epoxy polymer chain between
 crosslinks.

The model compounds were darkened by irradiation, as expected for organic materials. In addition, small amounts of a viscous liquid material condensed on the bottom (inside) side of the diaphragm when nitrogen-containing compounds were irradiated. Both this liquid and the irradiated parent compound had strong nitrogenous odors. More liquid material was formed when model compounds prepared from primary amines were used. In some cases the odor was quite distinctly amine-like even though the unirradiated compound had no such odor.

It was the original intent to follow the cleavage or crosslinking changes by measuring molecular weights ebulliscopically; however, they were followed satisfactorily by measuring the reduced specific viscosity, η_{sp}/c , in ethylene dichloride before and after irradiations. The increase in reduced specific viscosity (Table IV) as the result of irradiation shows that crosslinking occurred. In some instances the irradiated model compound was not soluble.

There was a decrease in nitrogen content after irradiation in essentially all model compounds prepared from amines. This indicated that a cleavage reaction was taking place. This is also verified by the high nitrogen content and nitrogenous odor of the liquid material found on the diaphragm (see Experimental Procedure section). It was not possible to determine whether a C-N, a C-C, or a C-O bond was broken. Infrared spectrum (Figure 7c) of one liquid sample (produced by irradiating the model compound from butylamine and DEBA) showed definitely stronger OH or NH absorption bands and no absorption bands which could be assigned to the phenyl group. There appears to be no trend in stability of the model compounds from the change in nitrogen content.

Infrared spectra on irradiated and nonirradiated model compounds are essentially identical (see Figures 5 through 14 at the end of the report).

The results of the gas analyses (Table V) give little or no clue as to the type of damage that occurred. From the total volume of gas produced and hydrogen content, it can be seen that the aromatic model compounds

IRRADIATION OF MODEL COMPOUNDS - EPON SERIES

Physical and Chemical Properties

Parent Resin	Reactant	Dosage, rep x 10 ⁻⁴	Infrared Spectrum, Fig. No.	η sp/c ^b	Epoxy Content, eq/100 g	%N		%OH		
						Calcd.	Found	Calcd.	Found	
DEBA	n-PrOH	0	5A	0.0423	0.012	-	-	7.35	6.43	
		4.5	5B	0.0425	-	-	-	-	6.62	
	ΦOH	0	6A	0.0422	0.016	-	-	6.44	7.23	
		4.5	6B	0.0492	-	-	-	-	6.98	
	n-BuNH ₂	0	7A	0.0418	0	5.73	5.37	6.96	(11.81) ^g	
		4.8	7B	0.0472	-	-	4.97	-	-	
		liquid ^a	4.8	7C	-	-	-	-	-	
	Et ₂ NH	0	8A	0.0318	0	5.73	5.91	6.96	(11.58) ^g	
		1	-	0.0447	-	-	5.60	-	-	
		7.1	8B	0.0473	-	-	5.29	-	-	
	liquid ^a	7.1	-	-	-	-	8.78	-	-	
	ΦNH ₃	0	9A	0.0531	0	5.30	5.16	6.43	(11.85) ^g	
		4.5	9B	0.0498	-	-	5.00	-	-	
		4.5	9C	-	-	-	-	-	-	
		7.1	-	0.0571	-	-	5.20	-	-	
Epon 1001	n-PrOH	0	-	-	0.012	-	-	-	-	
		0	-	-	0.010	-	-	-	-	
	n-BuNH ₂	0	10A	0.0686 ^c	0	-	2.45	-	-	
		5.1	10B	0.0714	-	-	2.03	-	-	
		5.1	10C	-	-	-	-	-	-	
	Et ₂ NH	0	11A	0.0609	0	-	2.49	-	-	
		4.5	11B	0.0747	-	-	2.34	-	-	
	ΦNH ₂	0	12A	0.0649	0.001	-	4.55	-	-	
		4.5	12B	0.0807	-	-	(3.16)	-	-	
		4.5	12C	-	-	-	-	-	-	
	Epon X-131	n-BuNH ₂	0	13A	not run ^c	e	4.52 ^f	4.71	-	-
			7.1	13B	not run ^d	-	-	4.71	-	-
7.1		-	-	-	-	10.8	-	-		
Et ₂ NH		0	-	0.120	0.002	4.52 ^f	4.97	-	-	
ΦNH ₂		0	14A	0.0704 ^c	0.005	4.24 ^f	5.29	-	-	
		7.1	14B	not run ^d	-	-	4.70	-	-	

- a. Liquid product from irradiation
b. Run in ethylene dichloride at 25°C
c. Solutions very cloudy
d. Not soluble
e. Free Cl present
f. Calculated from values supplied by Shell Development Co.
(equivalent weight 202 and molecular weight 693)
g. High value due to interference from amine group

Table V
IRRADIATION OF MODEL COMPOUNDS - EPON SERIES

Gas Analyses

Parent Resin	Reactant	Dosage, rep x 10 ⁻⁸	Gas evolved, moles/g sample x 10 ⁵	G _{gas}								
				Total	H ₂	N ₂	CO ₂	CH ₄	C ₂ H ₄	C ₃ H ₆ †	Others	
DEBA φOH	n-PROH	4.5	18.7	0.43	0.36	--	<0.015	<0.015	0.030	<0.015		
	φOH	4.5	6.5	0.15	0.107	--	<0.021	--	--	<0.021		
Epon 1001	n-BuNH ₂	4.8	24.9	0.52	0.47	0.032	0.018	--	--	--		
	Et ₂ NH	1 7.1	11.9 15.2	1.23 0.22	1.10 0.18	--	0.026 <0.004	0.051 <0.009	0.051 <0.009	--	--	{ acetone 0.016 C ₂ H ₄ <0.008
	φNH ₂	4.5 7.1	4.5 6.3	0.10 0.092	0.10 0.09	--	--	--	<0.018	--	<0.018	
	n-BuNH ₂	5.1	22.8	0.46	0.37	0.090	--	--	--	--	<0.018	
Epon X-131	Et ₂ NH	4.5	19.5	0.45	0.33	--	0.073	0.033	0.033	0.012		
	φNH ₂	4.5	1.8	0.041	0.041	--	--	--	--	--	--	
Epon X-131	n-BuNH ₂	7.1	22.4	0.33	0.28	--	<0.002	<0.017	<0.009	<0.027	butene-1 <0.009 C ₂ H ₄ <0.009	
	φNH ₂	7.1	5.8	0.085	0.076	--	<0.003	<0.003	--	--	cyclopropane <0.009	

Contrails

(i.e., from phenol and aniline) are definitely more stable than those from aliphatic reactants and that the compounds from Epon 1001 are slightly more stable on a weight basis than those from DEBA.

The over-all effect of irradiation seems to be a cleavage of nitrogen-containing material coupled with a crosslinking reaction. It is not known whether or not the crosslinking is entirely independent of cleavage. Certainly crosslinking occurs in nonnitrogenous model compounds.

From these results it is apparent that for best radiation resistance the epoxy-type adhesives, and for that matter laminating resins, ought to be cured with nitrogen-free aromatic curing agents. Thus, the radiation resistance of aromatic anhydride cured epoxy resins should be investigated.

E. Model Compounds - Others

1. Adhesive EC-1469

Adhesive EC-1469 was listed as an epoxy-based material but the type of epoxy resin was unknown. Due to some of its unique properties (resistance to salt water tests), it was desirable to analyze this adhesive. The resin was separated from the filler by dissolving the adhesive, filtering the solution, and carefully removing the solvent. The recovered resin, except for a slight greenish color, is identical to DEBA in infrared spectrum (see Figure 4), refractive index, and viscosity. Interestingly enough, this adhesive can be cured by heat alone even though the filler (ca. 4%) is a silica of some type (no other metals present) and the resin per se is not heat curable.

Certainly the radiation resistance of this resin would be the same as that of Epon 828 or 1001. The resistance of the compounded adhesive might be considerably different than that of Epon VIII due to the nature of the filler and, more particularly, to the lack of amine curing agents.

2. Other Adhesives

It was the intent of this study to apply the model compound approach to other systems for which information was available on composition and resin-type and to the phenolic components of epoxy-phenolic based adhesives. Time permitted only the collection of the components of a few of the nonepoxy resins listed in Table I.

F. Antirads and Scintillators

Antirads have been successful in increasing the radiation resistance of elastomers (4). It was the purpose in this phase of the work to screen some of the more promising antirads in adhesive formulations and also to include some well-known, organic scintillators of very high efficiency (7). Epon VIII was chosen as the adhesive because its handling characteristics and radiation resistance were well known, and because of its low viscosity which resulted in easy compounding with the additive. Time limited the testing and only two scintillators, N-vinylcarbazole and 2,5-diphenyloxazole, were evaluated. The former compound was also tested in FM-47 primer.

The results (Table VI) show that one of the scintillators, 2,5-diphenyloxazole, at 1% in Epon VIII, did not change the bond strengths after various doses. When used at 9.1%, the adhesive retained 89% of its strength after 80×10^7 rep (beta), whereas the corresponding blank retained only 60%. Also, it is important to note that the addition of this scintillator raised the strength of the adhesive approximately 10% instead of causing an expected decrease. N-Vinylcarbazole failed to show any improvement after high radiation doses.

7. R. C. Sangster and J. W. Irvine, Jr., J. Chem. Phys., 24, 670 (1956).

Table VI
PROTECTIVE AGENTS IN ADHESIVES

Adhesive	Additive ^c	Weight %	Beta Radiation rep x 10 ⁻⁷	Average Shear Strength psi(S)	$\bar{\sigma}$ psi	$\bar{\sigma}/(\bar{T})$	Adjusted Shear Strength psi(T)	$\bar{\sigma}$ psi	$\bar{\sigma}/(\bar{T})$	Estimated Failure, % Adhesive	Percent of Original With Additive	Percent of Original Without Additive ^f	
Epon VIII ^a	N-vinyl carbazole	0.99	0	2900	92	0.032	2350	42	0.018	100	100	100	
			20					950	28	0.030	100	81	94
	9.1	0						2100	130	0.063	100	33	60
		20						1800	120	0.066	100	100	100
		80						800	53	0.066	100	86	94
											53	53	60
FM-47 ^{a, b}	N-vinyl carbazole	0.99	0	2250	97	0.043	2200	290	0.13	30	100	100	
			20								35	98	94
	9.1	0						1350	50	0.037	20	60	60
		20						2450	120	0.049	30	100	100
		80						2300	83	0.036	25	94	94
								2200	220	0.10	20	89	60
		17	0	2700	250	0.092	2600	550	0.21	100	100	100	
			10.3					2200	0	0.00	90	96	102
			31								60	89	99
		81		300	92	0.31			50	11	38		

- a. Lap shear specimens from 20 mil bonded to 63 mil; irradiated through 20-mil strip; 20-mil strips reinforced with 63-mil prior to breaking
- b. 1/4-in. lap instead of normal 1/2-in. lap
- c. Added directly to adhesive
- d. Added to primer liquid
- e. From 1-Mev resonance transformer
- f. From Figures 1 and 2

V EXPERIMENTAL PROCEDURES

A. Laminates

1. Preparation

The laminates from Epon 828, Epon 1001, Laminac 4232, Selectron 5003, CTL 91-LD and DC-2106 were prepared by Coast Manufacturing and Supply Company, Livermore, California in a manner following as closely as possible that of recommended commercial procedures. These laminates were pretested to be sure of acceptability. Data on the preparation and physical properties of these resins are shown in Table VII. Laminates (0.125 and 0.55 in. thick) from Epon X-131 resin were prepared by Shell Development Company, Emeryville, California. Details on the batches of resin and the preparation of the laminates are given in Table VIII. Flexural, compressive, and tensile test specimens from these laminates were cut and finished to the following tolerances (all meet the requirements of Federal Specification LP406B):

<u>Specimen Type</u>	<u>Width, in.</u>	<u>Length, in.</u>
Flexural	$1 \pm 1/16$	$4 \pm 1/16$
Compressive	$1/2 \pm 1/32$	$3 \pm 1/16$
Tensile	LP406B Type I	$9 \pm 1/16$

The thick section laminates from Epon X-131 resin were forwarded to WADC for testing of irradiation effects upon electrical properties.

2. Irradiation

Flexural, compressive, and tensile test specimens cut from these laminates were sent to MTR for irradiation. The specimens, except for those from Epon 1001 laminates, received 10^9 and 10^{10} rep. The specimens from Epon 1001 laminates received 7.9×10^7 and 3.0×10^8 rep to match similar exposures obtained by WADC on laminates prepared from this resin (1).

3. Testing

After irradiation, MTR specimens from Epon 1001 laminates were tested at the Institute as received (dry) and after immersion for two hours in boiling water. The results of these tests are shown in Table II. All other specimens were sent to WADC for testing.

Contrails

Table VII
PREPARATION AND PHYSICAL PROPERTIES OF LAMINATES^a

Resin	Curing Agent	Amount		Curing		Postcure		Resin Content, %	Contract Requirement		Published Data		Measured Values	
		phr	phr	Time, min	Temp., °F	Time, min	Temp., °F		Flex. Str., psi	Mod., psi x 10 ⁻⁶	Flex. Str., psi	Mod., psi x 10 ⁻⁶	Flex. Str., psi	Mod., psi x 10 ⁻⁶
Epon 828	"A"	6		60	325		none	33.3	60,000	3.0	63,900 ^f	3.0	66,700	3.6
Epon 1001	Dicyandiamide	4		60	350		none	35.9	65,000	3.0	70,000 ^f	3.0	74,900	3.1
Selectron 5003	Benzoyl Peroxide (ATC)	1		30	230		none	33.5	50,000	2.7	58,000 ^g	2.8	66,700	3.2
Laminac 4232	Benzoyl Peroxide (ATC)	0.5		60	230		c	38.3	45,000	2.7	h	-	60,400	2.7
CTL 91-LD	b	-		30	325		d	34.6	50,000	3.0	i	-	58,300	3.3
DC-2106	XY-15	0.2		60	350		e	35.2	40,000	2.6	40,000 ^j	2.6	31,300 ^k	2.4

a. 0.125 ± 0.010 in. positive pressure laminates prepared by Coast Mfg. and Supply Co. from IP81 cloth with Volan A prefinish, except that F12 heat-cleaned cloth was used with DC-2106

b. Supplied as preimpregnated cloth

c. 2 hr each at 250°, 300°, 350°, 400°, 450° and 500°F

d. 24 hr at 300°, 12 hr at 350°, 12 hr at 400°F

e. 16 hr at 200°, 2 hr each at 250°, 300°, 350°, 400°, 440° and 12 hr at 480°F

f. Shell Chemical Corp. Technical Bulletin SC: 54-71

g. Pittsburgh Plate Glass Co.

h. Not available

i. Not available

j. Dow Corning Corp. Silicone Notes 10-231

k. Coast Mfg. and Supply Co. comments: "To this laboratory's knowledge no one in the industry is producing a positive press laminating material with this resin system and obtaining 40,000 psi flexural strength at room temperature."

Contrails

Table VIII
PREPARATION OF EPON X-131 LAMINATES^a

<u>Laminate No.</u>	1349 1350	1354 1355	1401	1402
<u>Thickness, in.</u>	0.125	0.125	0.55	0.55
<u>Resin</u>				
Lot No.	3523-147-1	3523-87	3523-43	3523-87
Epoxy Content, eq/100 g	0.464	0.494	0.469	0.494
Hydroxyl Content, eq/100 g	0.13	0.09	0.099	0.09
Chloride Content, %	1.29	0.6	1.16	0.6
Molecular Weight	696	693	717	693
<u>Curing Agent</u>				
	BF ₃ -400	Dicyandiamide	BF ₃ -400	Dicyandiamide
Amount used, phr	1.0	4.0	1.0	4.0
<u>Curing Conditions</u>				
Temp., °F	310	345	155	174
Time at contact, min	6	3	6	3
at 100 psi, min	54	57	54	57
<u>Cementing Conditions^b</u>				
Temp., °F (platen)	-	-	155	155
Time at contact, min	-	-	18	14
at 100 psi, min	-	-	42	46
<u>Postcuring Conditions</u>				
Temp., °F	400	400	-	-
Time, min	180	60	-	-

^a Prepared by Shell Development Co. from 12 plies of 181 Volan A glass cloth
^b Of 0.125-in. laminates.

B. Cured Epon 828 and 1001 Systems

1. Preparation

Epon 828 (30 g) and approximately 50 g of meta-phenylenediamine were heated in separate containers at 150° F until the latter had melted. The molten meta-phenylenediamine (28 g) was then mixed thoroughly into the hot Epon 828 by means of a spatula. The remainder of the Epon 828 (170 g) was then added to the mixture. The total formulation was transferred to a large glass test tube and stirred by means of a motor-driven, spiral glass stirrer, while being heated at 150° F. This mixture was then cast on a preheated Teflon sheet and the formulation was allowed to stand for 19 hr at room temperature. The mixture was cured for 30 min at 90° C followed by a postcure for 1 hr at 175° C. The casting was broken into small particles by means of a diamond mortar and the material between 10 and 20 mesh was retained for further testing.

The curing of the Epon 1001 + meta-phenylenediamine was carried out in a similar manner, using 100 g of the resin and 5.4 g of the curing agent. The curing and postcuring conditions were the same as indicated above.

2. Irradiation

Samples of the cured Epon 828 and 1001 systems were irradiated, using the same equipment and dosimetry as outlined in the section on irradiation of model compounds below. No gas collection apparatus was used during the irradiations. The total pressure was measured and G-values for the total gas evolved were calculated. (See Table III.)

3. Testing

Samples of the cured resins before and after irradiation were extracted with acetone for 88 hr to determine the amount of soluble material. The results of these tests and nitrogen determination before and after irradiation are listed in Table III.

C. Equivalency of Beta and Gamma Irradiation

1. Preparation

Lap shear specimens were prepared from adhesives Epon VIII and FM-47. The specimens for gamma irradiation were prepared from 63-mil Alclad 2024-T-3 alloy sheet in accordance with specification

Continued

MIL-A-5090B, Amendment I, and the latest, specific manufacturer's recommendations. Lap shear specimens for beta irradiation were similarly prepared with the following exceptions: (a) 20-mil sheet was bonded to 63-mil to form the joint instead of using two 63-mil sheets, (b) the lap was restricted to 0.25 in. when the FM-47 adhesive was used, because this adhesive was stronger than the 20-mil strip when larger areas were used, (c) prior to testing, the 20-mil portion of the specimens were etched and reinforced with 63-mil strips using adhesive Epon VI cured at room temperature.

2. Irradiation

Gamma irradiations were performed by means of a cobalt-60 source, and beta irradiation by means of a 1-Mev General Electric resonance transformer. The lap shear specimens for beta irradiation were mounted in groups of 5, in such a way that three of the specimens were parallel and adjacent to each other, and the remaining two specimens were placed perpendicular to, and just outside the bond areas of the other three. Thus, the dosage of all five specimens was within 10%, at the distances (from the beam window) normally used.

3. Dosimetry

The measurement of dose delivered to adhesive specimens is best made by a dosimeter which can occupy the same space as the adhesive in a lap shear specimen. This imposes requirements such as (1) solid material, (2) thin film, (3) good sensitivity, and (4) availability. Cellophane containing a radiation sensitive dye (dimethoxy-diphenyl-diazobis-8-amino-1-naphthol-5,7-disulfonic acid) and polyethylene seem likely possibilities but the former was selected on the basis of its greater sensitivity and simpler analysis. (The absorption of light at 6500 Å is used for the cellophane dosimeter; measurement of absorption of light at wavelengths between 50-130 Å is required for the polyethylene.)

For the calibration of the dyed cellophane dosimeter, the following technique was used.

Absorption of bombarding electrons in a stack of alternating strips of cellophane and polyethylene was measured by differential calorimetry, i. e., the energy absorbed by the calorimeter less the energy absorbed by the calorimeter after passing through the stack. The measured energy absorption was allocated between the cellophane and the polyethylene on the basis of their relative thicknesses and densities. (Stopping powers were considered to be proportional to density only.) The change in optical density for a given energy absorption (irradiation) varied with position in the stack. This could be predicted as the ratio of secondary

Continued

to primary electrons changes in the first few collision lengths of penetration into the materials. The cellophane foil at 1-cm depth in the stack (equivalent in stopping power to 0.012-in. aluminum) was selected as having a ratio of primary to secondary electrons representative of that to be found in aluminum from 0.010 to 0.040 in. thick. Measurement of the change in optical transmission for foils at this point gave a calibration of 2.50 change in percent transmission of the dyed cellophane for each million rep of absorbed dose.

The sensitivity of the cellophane foil under 0.020-in. aluminum appears to be 10^5 rep. The accuracy has not been determined but has been estimated to be within 10%.

Using the above value of 2.50 change in percent transmission of the dyed cellophane for each 10^6 rep of absorbed dose, the dosages reported in Table IX were obtained for lap shear specimens in which the cellophane replaced the adhesive. The positions referred to in the first column are those of five lap shear specimens laid side by side with the geometrical center of the transformer window corresponding to the geometrical center of position C.

4. Testing

The lap shear specimens were tested in accordance with the specification MIL-A-5090-B Amendment 1, using a Baldwin-Tate-Emery testing machine, Model No. PTE-61. The data are presented in Table X and summarized in Figures 1 and 2.

D. Model Compounds - Epon Series

1. Preparation

All of the model compounds were prepared from epoxy resins in essentially an identical manner. These preparations are summarized in Table XI. A typical preparation is as follows: 104 g (0.15 moles (8)) of Epon X-131 (Sample No. 3523-87 from Shell Development Company, 0.6%Cl) was dissolved in about 150 ml of chloroform; the resulting solution was filtered; the filtrate was added to a refluxing mixture of 88 g (1.2 moles) n-butylamine and 36 g (0.16 moles) n-propyl alcohol, with stirring, under an atmosphere of nitrogen. The addition was made over a 1-hr period. The reaction mixture was refluxed for 10 hr while still under an atmosphere of nitrogen. The excess reactants and solvent were

⁸ Based on theoretical equivalent weight of 176 for tetraglycidyl ether of tetraphenol ethane. Actually the equivalent weight of this sample was 202.

DOSIMETRY FOR LAP SHEAR SPECIMENS

<u>Position</u>	<u>Change in % Transmission</u>	<u>Dosage</u>	
		<u>rep x 10⁻⁶</u>	<u>rep/μa-sec x 10⁻²</u>
15.2 cm below window			
A	14.1 ^a	5.6	4.7
B	19.4 ^a	7.8	6.5
C	19.7 ^a	7.9	6.6
D	17.2 ^a	6.9	5.7
E	11.9 ^a	4.8	4.0
19.2 cm below window			
A	4.7 ^b	1.9	3.17
B	5.5 ^b	2.2	3.67
C	5.8 ^b	2.3	3.84
D	5.8 ^b	2.3	3.84
E	5.1 ^b	2.0	3.34

a. For 12000 μ a-sec

b. For 6000 μ a-sec

Contrails

Table X
EFFECT OF RADIATION ON LAP SHEAR STRENGTH OF
EPON VIII AND FM-47

Adhesive	Radiation Source	Dose, rep x 10 ⁻⁷	Average Shear Strength, psi(s)	$\bar{\sigma}$, psi	$\bar{\sigma}/(s)$	Adjusted Shear Strength, psi(T)	$\bar{\sigma}$, psi	$\bar{\sigma}/(T)$	Percent of Original	Failure, Estimated % Adhesive	
Epon VIII	Beta ^a	0				2267	110	0.049	100	10	
		5				2350	105	0.046	103.7	10	
		20				2124	99	0.049	93.7	20	
		40				1841	199	0.11	81.2	20	
		60				1632	457	0.28	72.0	70	
		75				1437	527	0.37	63.4	50	
		Gamma	0	3385	25.0	0.00729				100	10
		24				3023	30	0.0098	89.3	30	
		40				2780	5.8	0.0021	82.1	20	
		50				2671	37	0.014	78.9	10	
	FM-47	Beta ^{a, b}	0	4250	31.6	0.0074				100	100
			10	4450	50.0	0.011				104.7	100
			31	4200	38.7	0.0092				98.8	100
			81	1600	59.2	0.037				38	100
Gamma		0	3600	150	0.042				100	100	
		8.5	3700	220	0.059				103	100	
		81	1500	134	0.089				40	100	

a. Lap shear specimens from 20 mil bonded to 63 mil; irradiated through 20-mil strip; 20-mil strips reinforced with 63-mil prior to breaking
b. 1/4-in. lap instead of normal 1/2-in. lap

Table XI

PREPARATION OF MODEL COMPOUNDS - EPON SERIES

Parent Resin	Amount, moles	Reactant	Amount, moles	Solvent	Amount, ml	Catalyst	Amount	Addition Time, hr	Reflux Time, hr	Atmosphere
DEBA ^a	0.5	n-PrOH	2.0	CHCl ₃	150	SnCl ₄ ^e	0.2 ml	1/2	16	N ₂
	0.5	φ OH	2.0	φ CH ₃	300	KOH	0.4 g	none	48	air
	0.5	n-BuNH ₂	2.0	none	-	i-PrOH	60 g	none	8	N ₂
	0.42	Et ₂ NH	1.7	none	-	i-PrOH	51 g	none	8	N ₂
	0.5	φ NH ₂	2.0	none	-	none	-	none	12	N ₂
Epon 1001 ^b	0.15	n-PrOH	1.0	CHCl ₃	350	SnCl ₄ ^e	0.2 ml	1/2	16	N ₂
	0.15	φ OH	1.0	φ CH ₃	500	KOH	0.3 g	none	23	air
	0.15	n-BuNH ₂	1.0	CHCl ₃	150	i-PrOH	18 g	none	9	N ₂
	0.15	Et ₂ NH	1.0	CHCl ₃	150	i-PrOH	18 g	none	8	N ₂
	0.15	φ NH ₂	1.0	Dioxane	500	i-PrOH	18 g	none	17	N ₂
Epon X-131 ^c	0.15	n-PrOH	1.2	CHCl ₃	d	SnCl ₄ ^e	0.4 ml	2	46	N ₂
	0.15	n-BuNH ₂	1.2	CHCl ₃	150	n-PrOH	36 g	1	10	N ₂
	0.25	Et ₂ NH	2.0	CHCl ₃	150	n-PrOH	60 g	none	8	N ₂
	0.15	φ NH ₂	1.2	Dioxane	ca 600	none	-	2	19	N ₂

a. Distilled material; assumed molecular wt 340

b. Assumed molecular wt 900

c. Lot 3523-87. Measured molecular wt 693 (see Table VIII)

d. Not measured

e. Anhydrous; catalyst removed by treatment with Na₂CO₃ and washing with water.

Contracts

removed by means of a Rinco rotating evaporator at 1 mm pressure and 100°C. The molten model compound was cast on a Teflon sheet and, after cooling, the material was powdered for subsequent irradiation studies.

The DEBA used in the preparation of model compounds was obtained from Epon 828. Epon 828 (400 g) and 1000 g of cyclohexane were mixed while heating to 70°C. While at this temperature the phases were allowed separate. The upper layer was decanted and allowed to cool, separating into two phases. The lower phase was freed of residual solvent and distilled in a short-path distillation apparatus as indicated for a typical distillation in the table below.

Table XII
DISTILLATION OF PURIFIED EPON 828^a

<u>No.</u>	<u>Fraction Weight, g</u>	<u>Vapor Temp., °C</u>	<u>Pressure, mm Hg</u>	<u>20.5 n_D</u>
1	15	30-177	0.07	1.5609
2	135	177-178	0.075	1.5709
3	136	178-185	0.08	1.5709

a Charged 365 g

Fractions 2 and 3 constitute the product, DEBA. The infrared spectrum of this compound is shown in Figure 4B. The epoxide equivalent weight was found to be 172, compared with the theoretical value of 170.

Attempts were made to purify and fractionate a sample of Epon X-131 (1.2% Cl, epoxide equiv. wt 217) by a precipitation method, using acetone as the solvent and cyclohexane as the nonsolvent. The analytical results (Table XIII) show that essentially no purification was achieved, but that some fractionation resulted.

FRACTIONATION OF EPON X-131

<u>Cut</u>	<u>Recovered, wt %</u>	<u>Epoxide equiv. wt.</u>	<u>Cl, %</u>
1	31.5	251	1.30
2	42.5	209	1.54
3	12.5	203	1.35

2. Irradiation

a. Equipment Used

The model compounds were irradiated with beta rays from a 1-Mev electron accelerator (resonance transformer type) with a maximum dose rate of 70×10^6 rep per min. These irradiations were carried out in an aluminum cell (10.2 cm ID x 4.2 cm) under a helium atmosphere. The sample was held in a glass liner (a 100 mm crystallizing dish). The electron beam passed through a 2-mil stainless steel diaphragm in order to reach the sample. Cooling was maintained by means of a circulating ice water system, and the irradiation was interrupted periodically to prevent internal heat build-up. The gases evolved during irradiation were collected in bombs through a simple manifold system and were analyzed by means of a mass spectrophotometer. Results were obtained as volume % and were converted to G-values as indicated in Table V.

In those cases where an amino group was present in the model compound, there was a strong nitrogenous odor to the irradiated compound. In all cases of irradiation, a small (unmeasured), viscous liquid deposit formed on the inside (bottom) of the diaphragm. When the deposit was large enough, attempts were made to obtain micron nitrogen analyses and infrared spectra. In some instances solutions of these deposits in chloroform precipitated material upon standing, indicating that some active material had been present and had condensed to form gel structures.

Control

Small amounts of dichloromethane and chloroform found in the gases from several runs are presumably due to traces of the reaction solvent left in the model compound.

b. Dosimetry

The dosimetry for the system in which the model compound was irradiated was carried out under another contract, AF 33(616)-3738. The details of this dosimetry are quoted from the second quarterly progress report of that contract dated 6 November 1956:

"A calibration of the electron accelerator (GE resonant transformer) which provides a correlation between beam current and dose delivered to the irradiation cell has been completed. The ceric sulfate dosimeter was used successfully; in experiments reported in the previous quarterly report, use of the ferrous dosimeter was unsuccessful.

"The G-value for electrons of the ceric dosimeter was established by irradiation of the ceric solution in a calorimeter. Energy input was measured in standard fashion and ceric depletion estimated by measurement of the change in optical density at 315 microns. The G-value measured, 2.53 ± 0.17 , was constant for the rate of energy input as high as 5.1×10^3 rep/sec. This measured G-value is in agreement with an accepted value of 2.59 ± 0.03 (9).

"The calibration of the electron accelerator was performed by exposing ceric sulfate solution to the electron beam. The solution was contained in the identical irradiation cell and in the exact geometry proposed for the organic liquid during irradiation. The data from five runs yield a dose rate of 97.9 ± 1.2 rep/ μ a-sec of exposure of a 150-g sample to the electron beam when the diaphragm of the cell was 8.8 cm below the window of the beam. The estimated accuracy ($< 2.5\%$ bias) and precision ($< + 1.5\%$) of this method of measuring radiation dose is judged adequate for the current study."

In all irradiations, less than 150 g was exposed to the beam: thus, the dose rate was multiplied by the factor $150/x$ where x is the actual weight of the sample. To insure complete absorption of the incident energy, at least 1/4 in. of material covered the bottom of the glass liner. In some cases where insufficient material was available

⁹ J. Weiss, Nucleonics 10 (7), 28-31 (1952);

R. H. Schuler and A. O. Allen, J. Chem. Phys. 24, 56 (1956)

Continued

to cover the bottom of a 100-mm liner, smaller liners were used and held on center by a spacer. The dose rate for these cases was multiplied by the ratio of the relative intensities for the smaller areas to that for the large area. The relative intensities were taken from the charts supplied by the manufacturer of the transformer.

3. Physical and Analytical Measurements

Infrared spectra were obtained from the model compounds before and after irradiation, using a Perkin-Elmer Model 21 double beam spectrophotometer. These spectra are presented at the end of the report as Figures 5 through 14, grouped as indicated in Table IV. Reduced specific viscosity determinations were made at 25°C, using ethylene dichloride as the solvent for model compounds before and after irradiation.

Analytical determinations on the model compounds consisted of epoxy content to determine the completeness of reaction and % nitrogen and OH to indicate the point of chemical damage. In the compounds containing amine groups, the hydroxy determinations were found to be unsatisfactory due to the presence of these amine groups.

All of the analytical and physical measurements are reported in Table IV and gas analyses in Table V.

E. Model Compounds - Others

1. Adhesive of EC-1469

Compositional analyses were started on the epoxy-type adhesive EC-1469 because of some of its unique physical properties. The adhesive was dissolved in anhydrous ether, leaving a clear liquid layer which was separated from the filler by decantation and filtration. The ether was removed from the resin at room temperature with the aid of a Rinco rotating evaporator. The residue was a clear, viscous, almost water-white material. The viscosity was almost the same as that of Epon 828. The following refractive indices are of interest:

	²⁰ n	D
Resin from EC-1469	1.5722	
Epon 828	1.5715	
DEBA	1.5712	

The infrared spectra of the resin from EC-1469 and DEBA are identical; see Figure 4. The resin from the adhesive is not curable by heat alone; whereas in combination with the filler it can be heat-cured without additional curing agents. The emission spectrum of the filler showed only silicon, presumably from a silica of some type. The filler content was found to be 3.9% by ashing.

2. Other Adhesives

Compounds from other adhesives whose composition was known have been collected. They are Plyophen 5023, polyvinyl butyral (Bakelite's XYSG), and phenolic resin (Bakelite's BLS-2700).

F. Antirads and Scintillators

1. Preparation

The lap shear specimens for these tests were prepared in the same manner as indicated in Section V, Part C, above. In all cases, except when using FM-47, the additive was weighed into the Epon VIII adhesive, mixed thoroughly, and then Curing Agent A was mixed into the formulation. For the FM-47 adhesive, the additive was dissolved in the primer liquid, giving a 17% solution.

2. Irradiation and Testing

The irradiation and testing was carried out in the same manner as was described in Section V, Part C.

G. Treatment of Data

All of the destructive testing on laminate specimens (tensile, compressive, and flexural) and adhesive specimens (lap shear) were conducted with five specimens in order to gain some indication as to the precision of the resulting data. Standard deviations (corrected to account for the small number of specimens in each group) were computed in the usual manner for each test group as follows:

Contrails

$$\bar{\sigma} = \sqrt{\frac{(x - \bar{x})^2}{N - 1}}$$

where $\bar{\sigma}$ = corrected standard deviation
of the group

x = strength test value of particular
specimen

\bar{x} = arithmetical average of the five
specimens undergoing a
particular test

N = number of specimens in the
group

Where one of the five test values deviated by greater than 3 (being calculated for the remaining four values) this value was discarded and the new average was listed as the "adjusted" figure for the group of four.

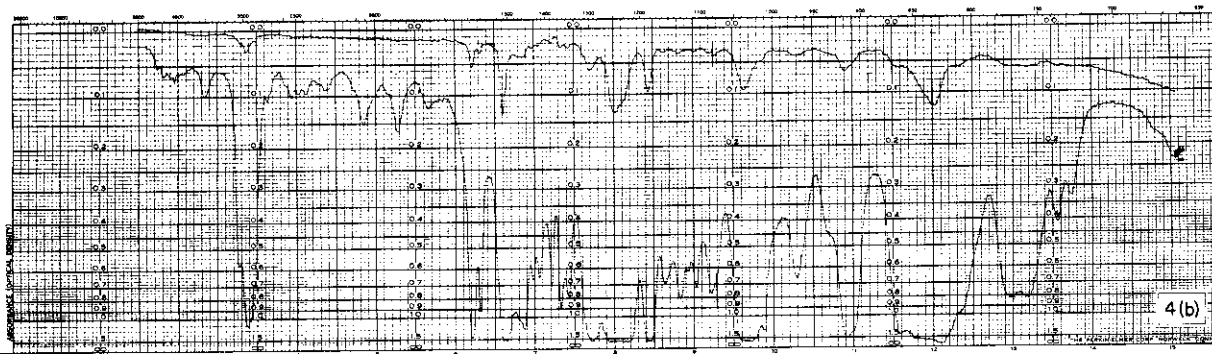
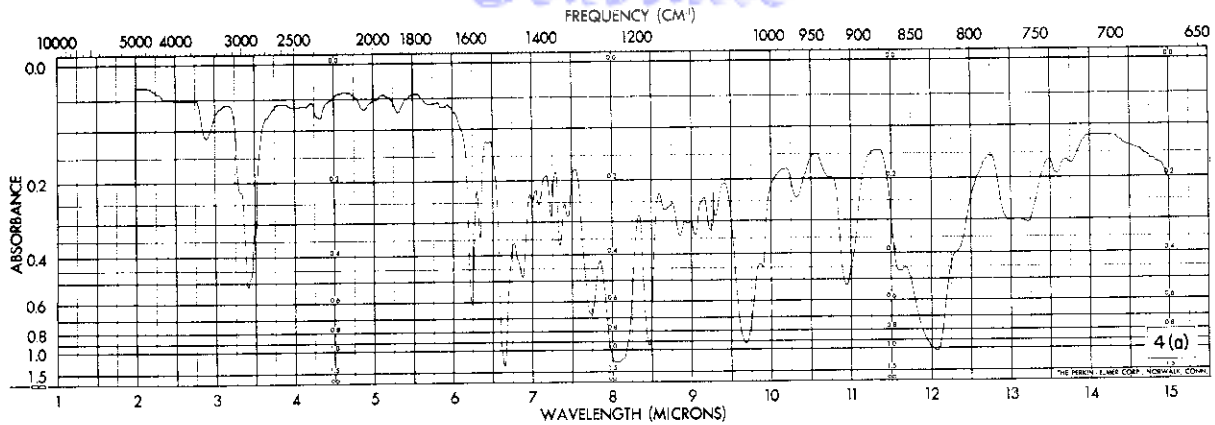


FIG. 4
INFRARED SPECTRA
a. Resin from EC1469
b. Diglycidyl ether of Bisphenol A (DEBA)
D-1726-F-4

Contrails

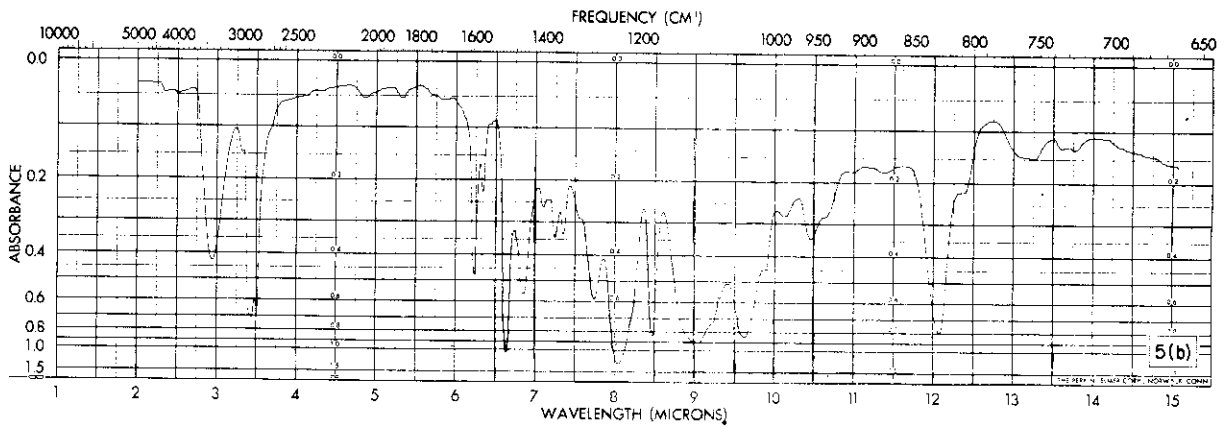
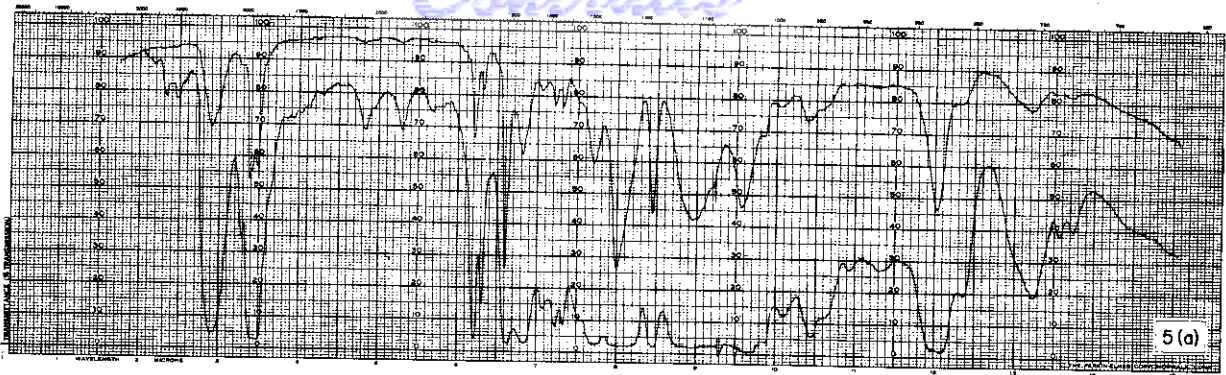


FIG. 5
INFRARED SPECTRA
a. Model Compound: DEBA + n - C₃H₇OH
b. Irradiated 4.5 x 10⁸ rep

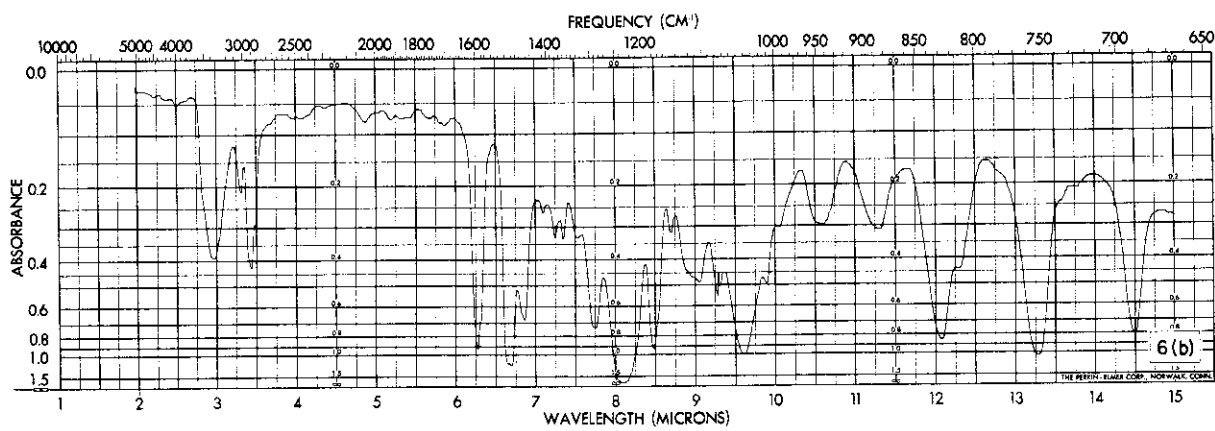
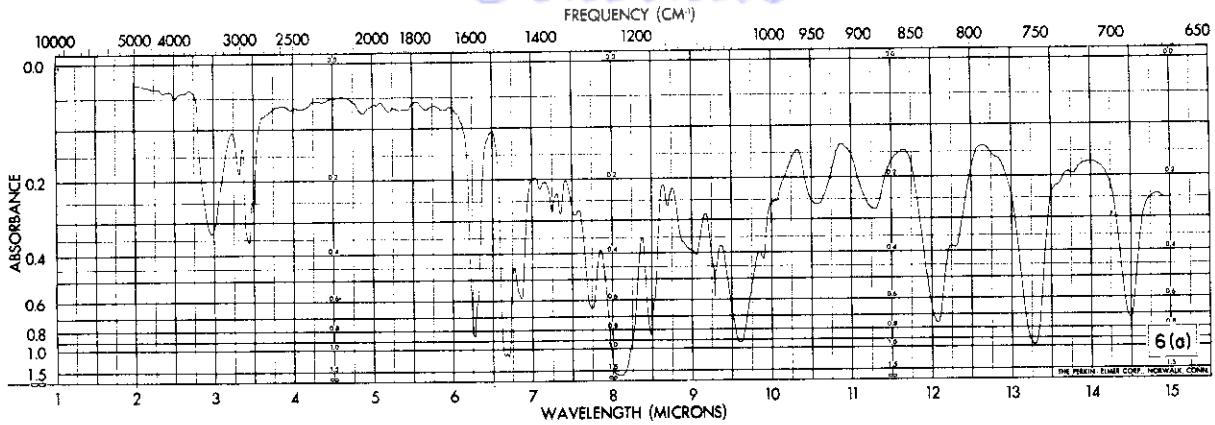


FIG. 6
INFRARED SPECTRA
a. Model Compound: DEBA + C₆H₅OH
b. Irradiated 4.5 x 10⁶ rep

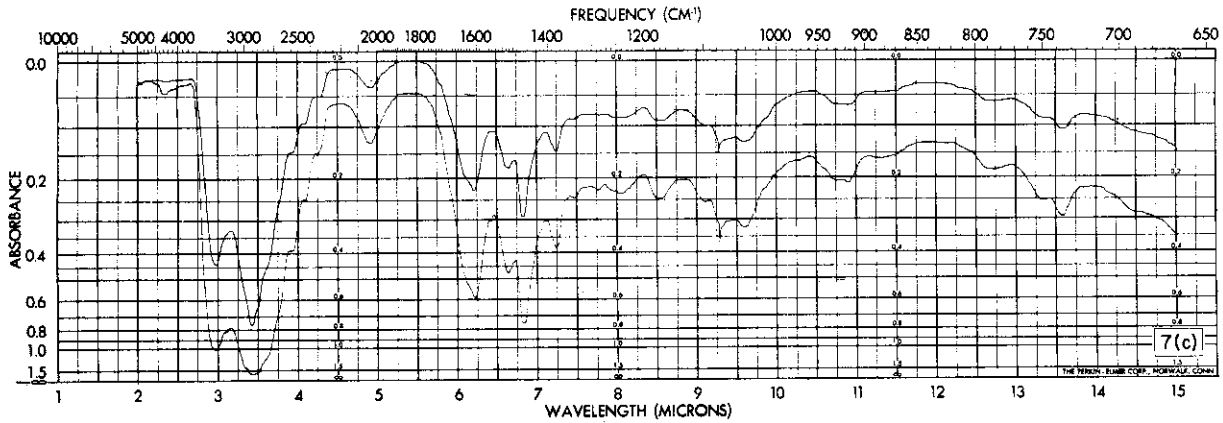
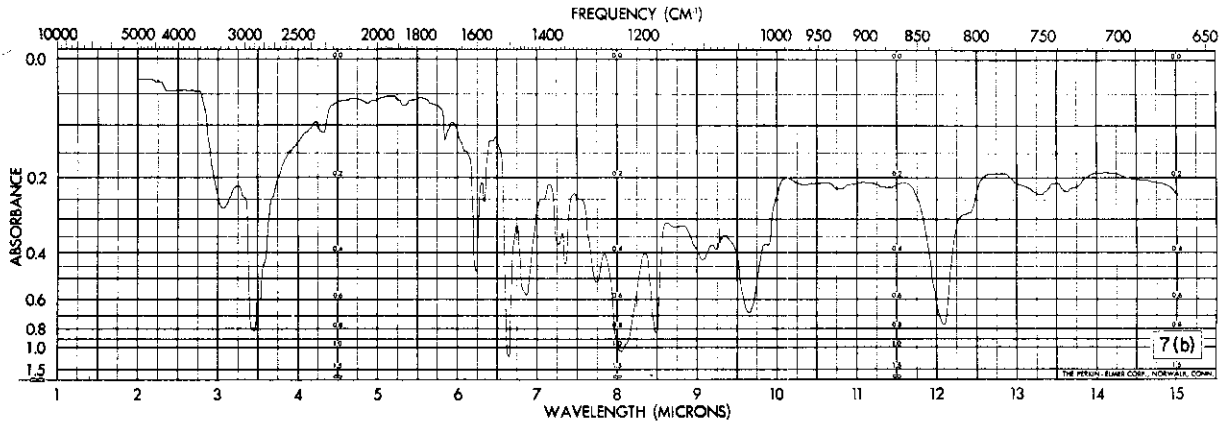
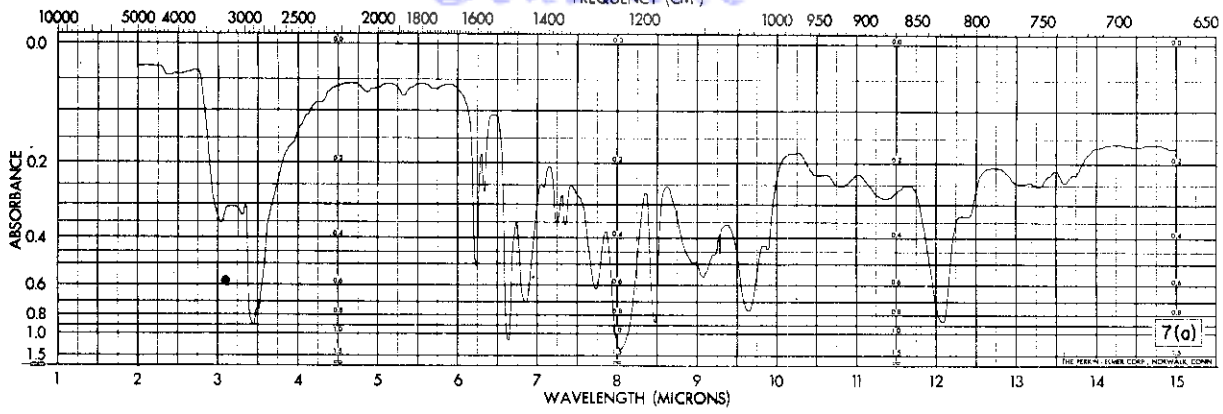


FIG. 7
INFRARED SPECTRA
a. Model Compound: DEBA + n-C₄H₉NH₂
b. Irradiated 4.8 x 10⁶ rep
c. Liquid Deposit from Irradiation
D-1726-F-7

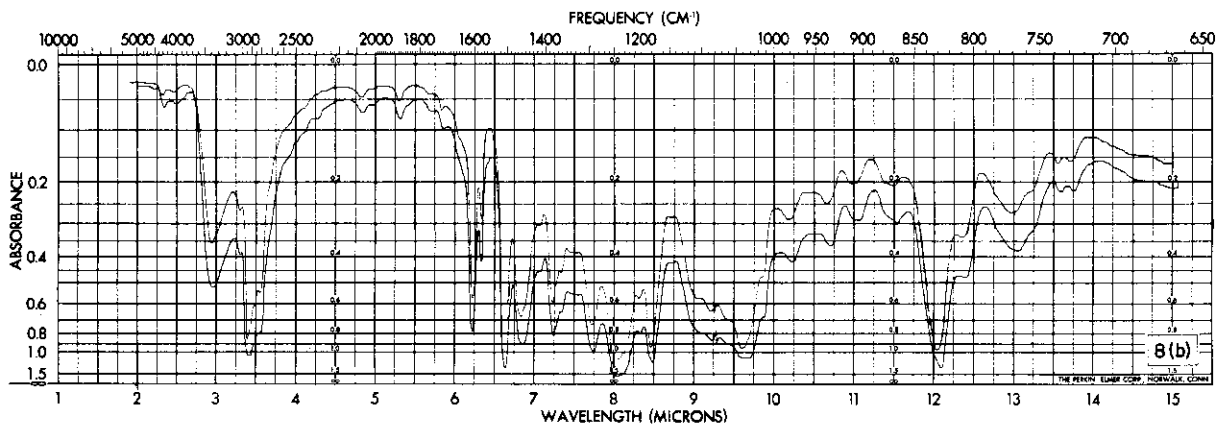
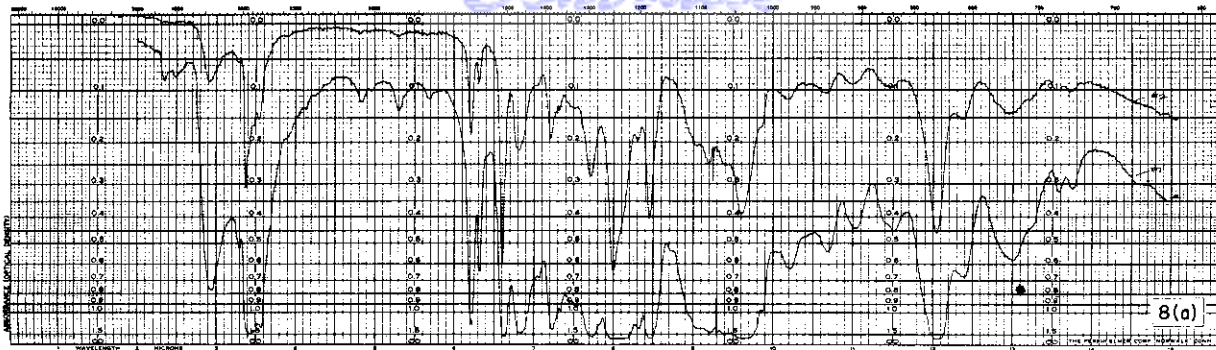


FIG. 8
INFRARED SPECTRA
a. Model Compound: DEBA + (C₂H₅)₂NH
b. Irradiated 7.1 x 10⁸ rep

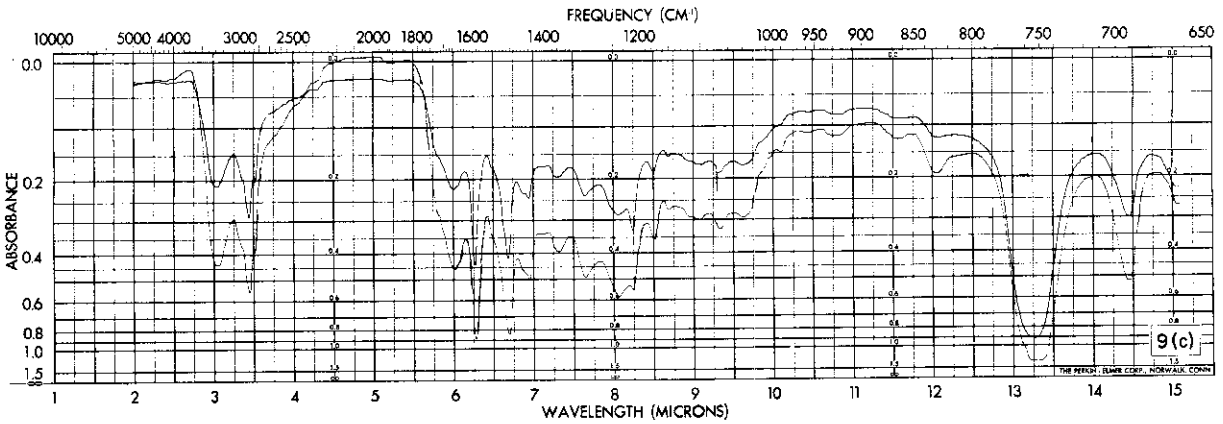
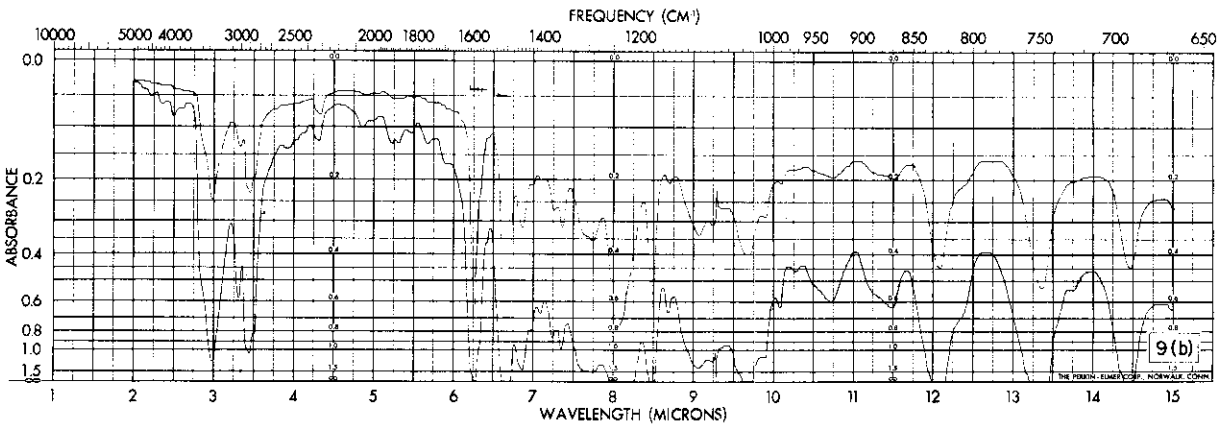
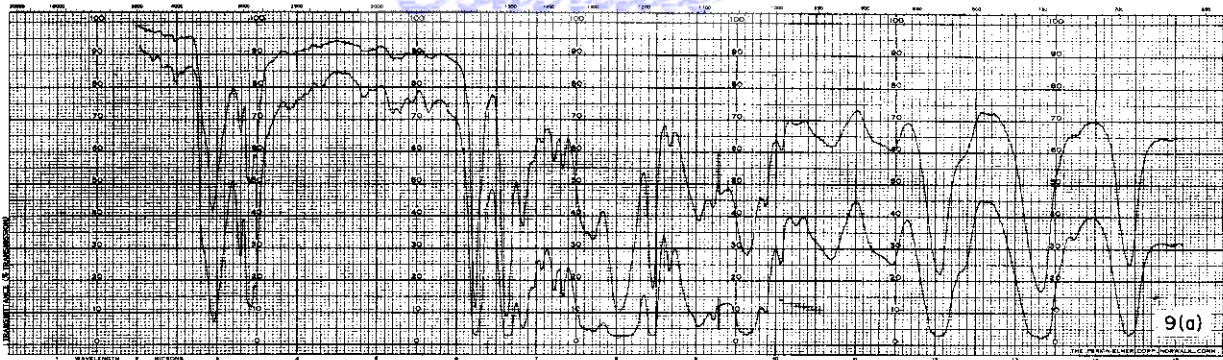


FIG. 9
INFRARED SPECTRA
a. Model Compound: DEBA + C₆H₅NH₂
b. Irradiated 4.5 x 10⁶ rep
c. Liquid Deposit from Irradiation

Contrails

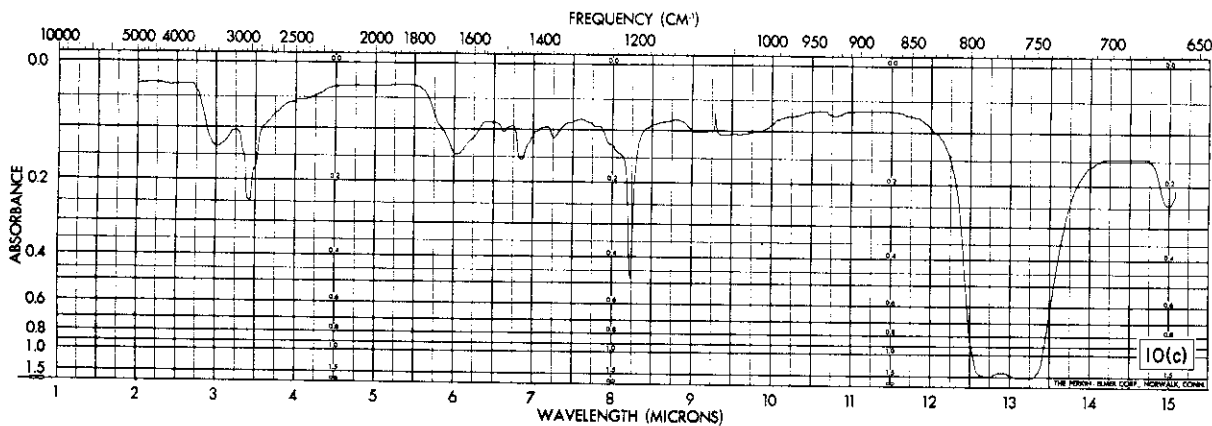
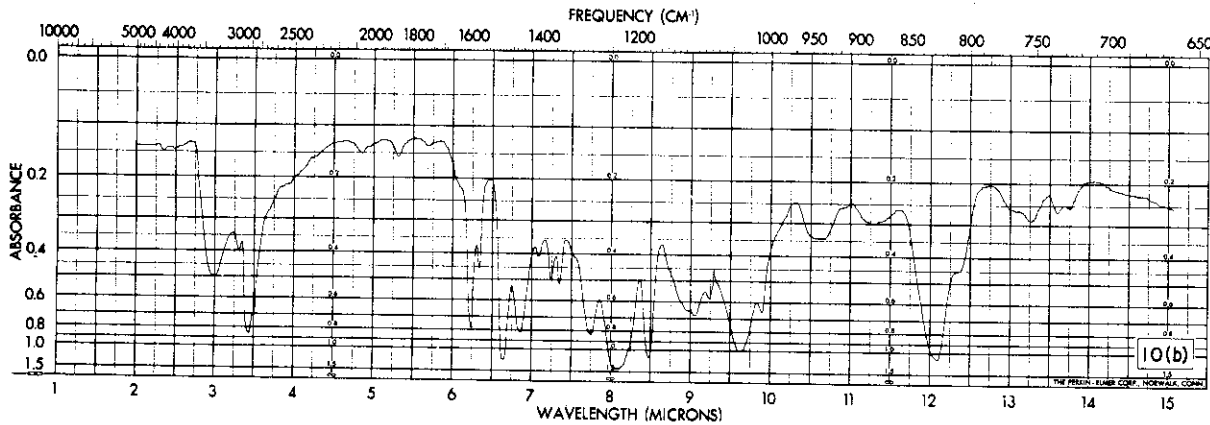
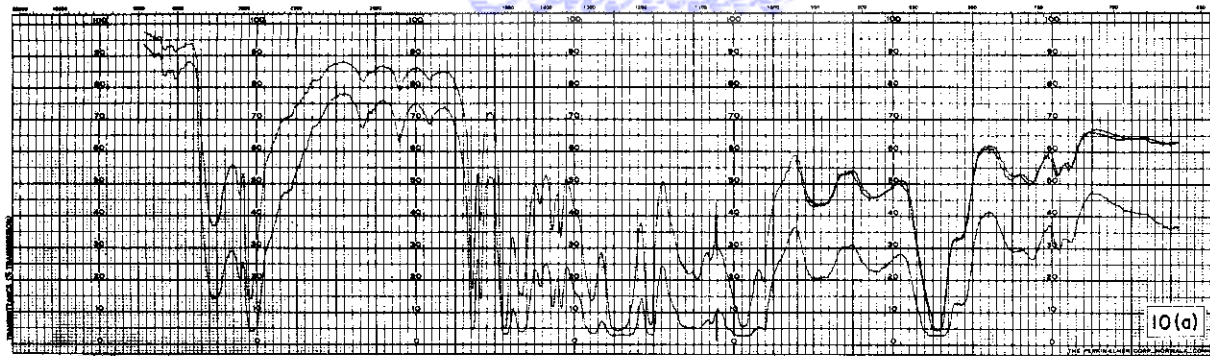


FIG. 10

INFRARED SPECTRA

- a. Model Compound: Epon 1001 + n-C₄H₉NH₂
- b. Irradiated 5.1 x 10⁸ rep
- c. Liquid Deposit from Irradiation

-1726-F-10

Controls

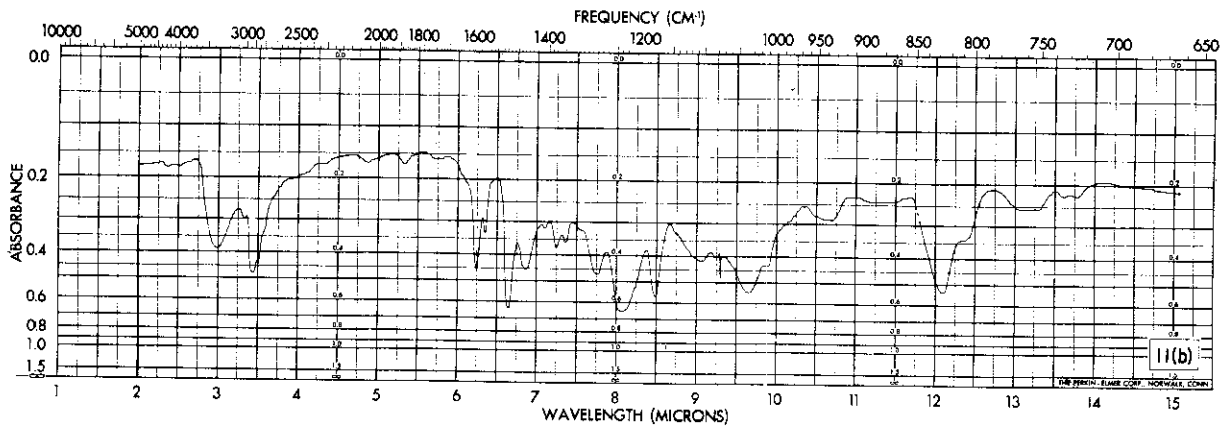


FIG. 11
INFRARED SPECTRA
a. Model Compound: Epon 1001 + (C₂H₅)₂NH
b. Irradiated 4.5 x 10⁸ rep

D-1728-F-11

Contrails

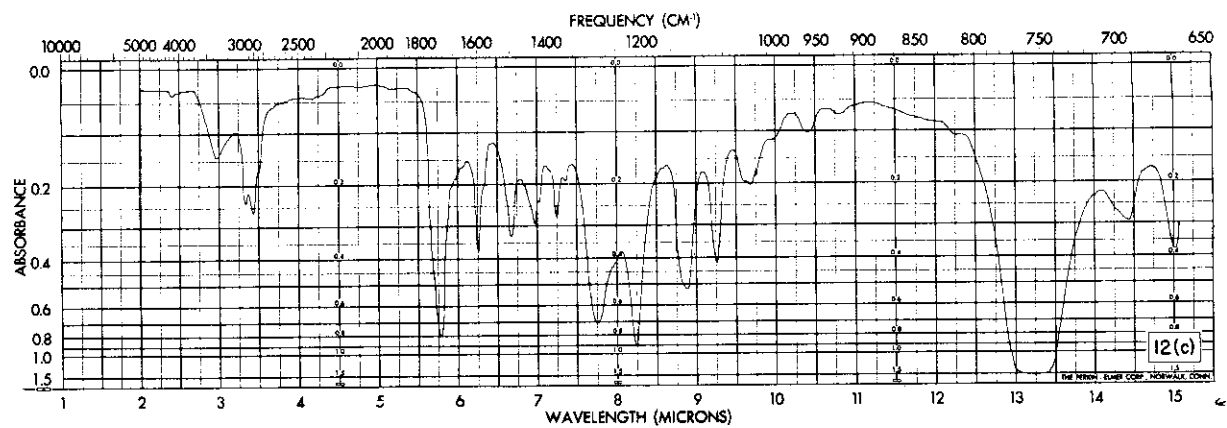
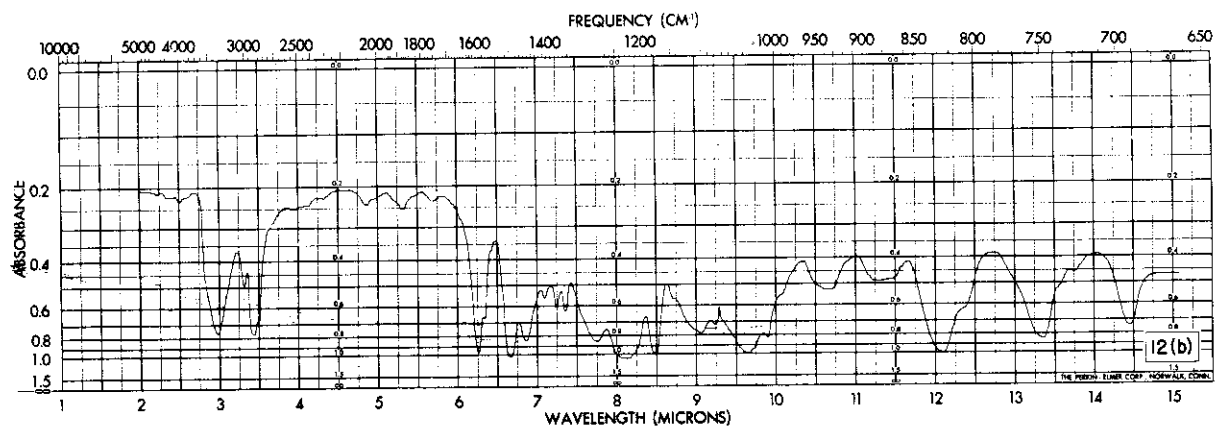
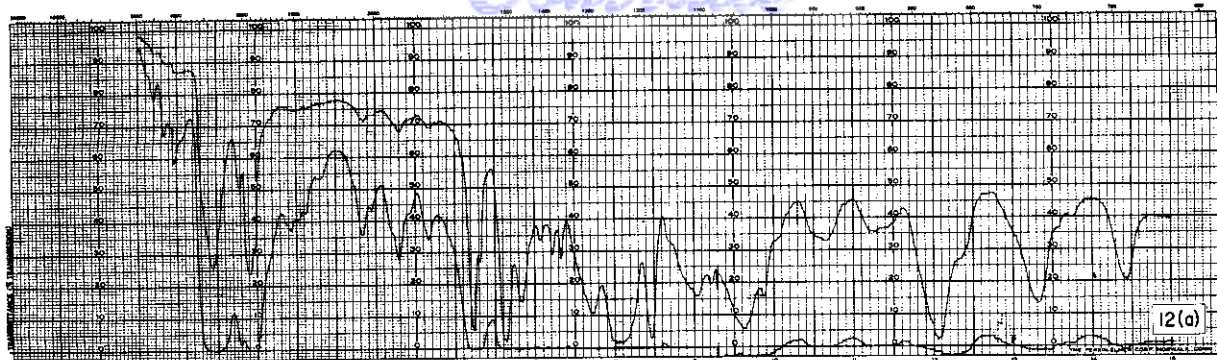


FIG. 12

INFRARED SPECTRA

- a. Model Compound: Epon 1001 + C₆H₅NH₂
- b. Irradiated 4.5 x 10⁸ rep
- c. Liquid Deposit from Irradiation

Controls

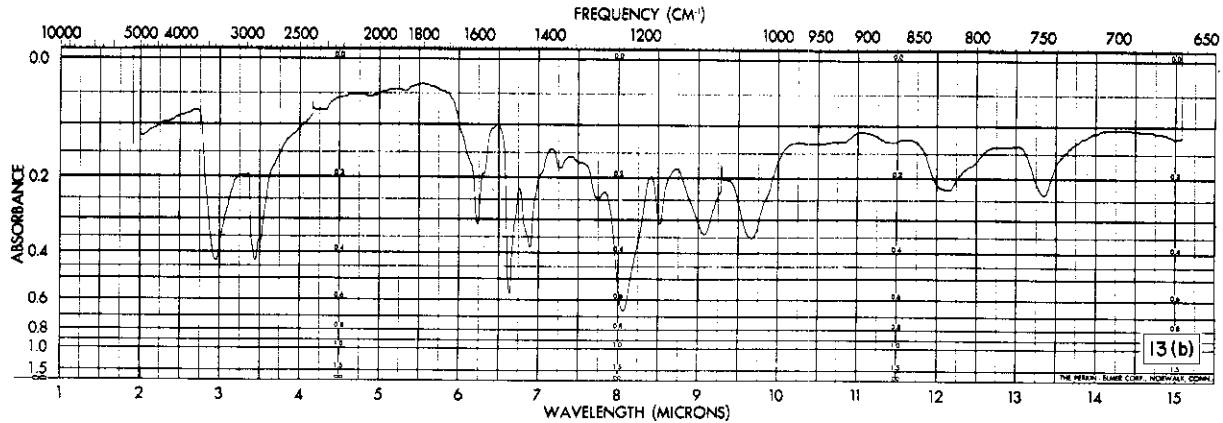
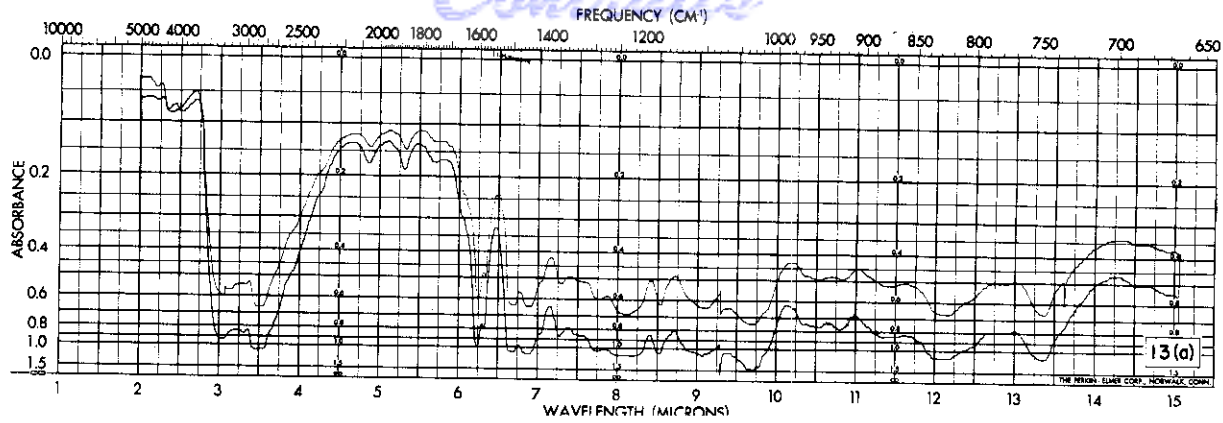


FIG. 13
INFRARED SPECTRA
a. Model Compound: Epon X-131 + C₄H₉NH₂
b. Irradiated 7.1 x 10⁸ rep

0-1726-F-13

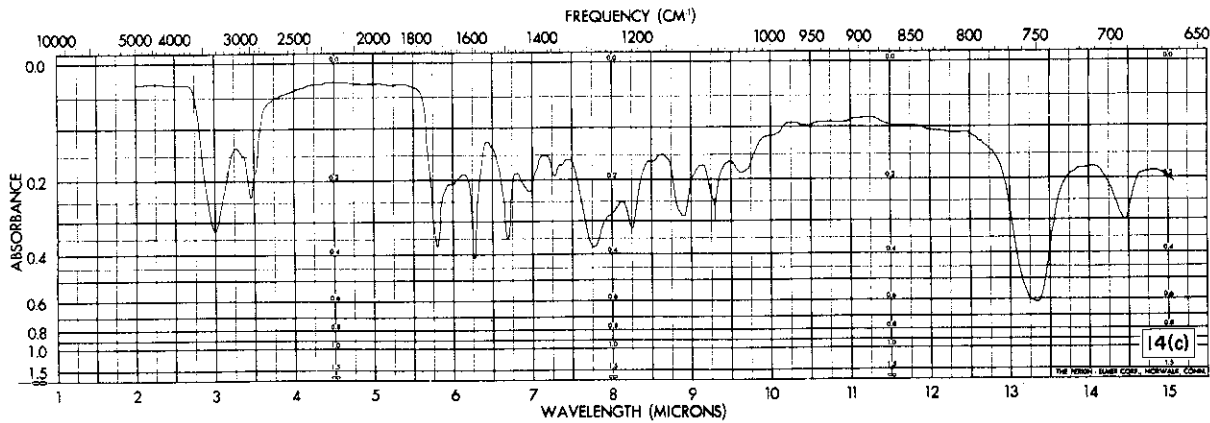
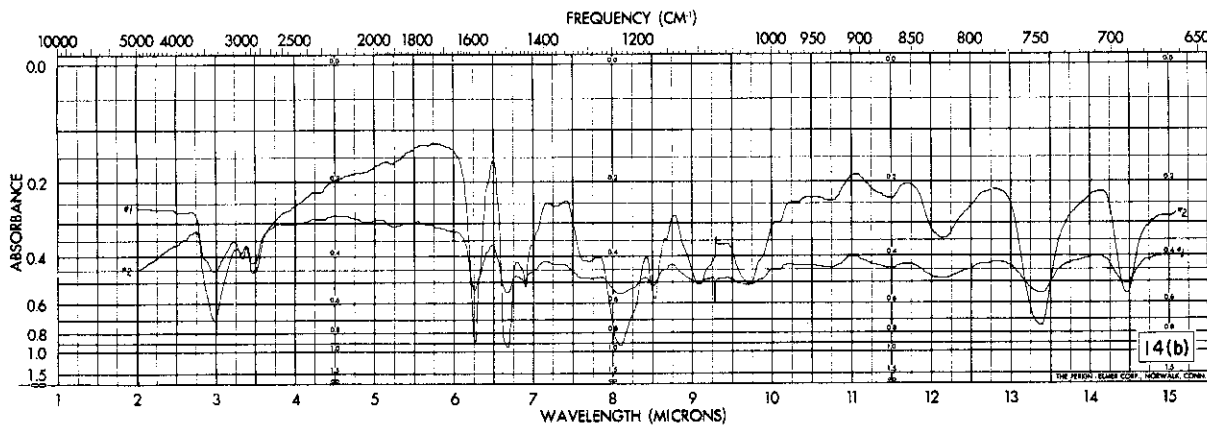
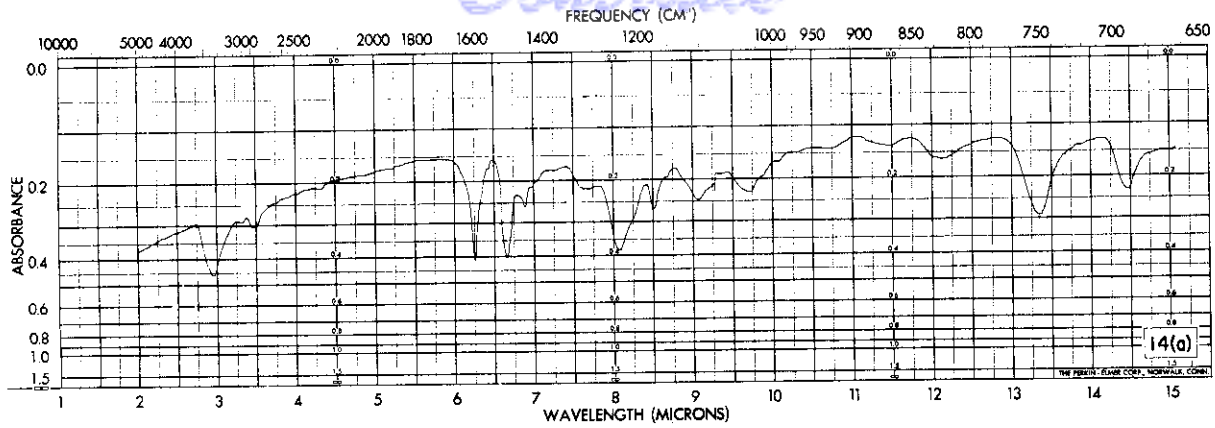


FIG. 14

INFRARED SPECTRA

- a. Model Compound: Epon X-131 + C₆H₅NH₂
- b. Irradiated 7.1 x 10⁸ rep
- c. Liquid Deposit from Irradiation