

WADC TECHNICAL REPORT 56-534

PART II

ASTIA DOCUMENT No. AD 130838

**NUCLEAR RADIATION EFFECTS ON STRUCTURAL  
PLASTICS AND ADHESIVES**

**PART II EXTENSION OF LITERATURE SURVEY**

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*JUNE 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**

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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." It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. R. S. Arlook as project engineer.

This report covers a supplementary literature survey from 30 September 1956 to 1 February 1957.

WADC TR 56-534 Pt II

## ABSTRACT

A survey was made of literature on radiation chemistry available during the period 30 September 1956 to 1 February 1957. Information pertinent to the effect of radiation on the synthesis and the properties of polymers, elastomers, and adhesives was tabulated. A brief summary of the more general observations on the effects of radiation on these materials was prepared.

The literature available prior to 30 September 1956 was covered in Part I.

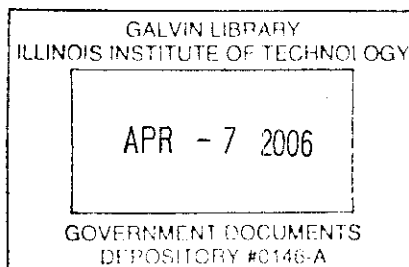
## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. T. SCHWARTZ  
Chief, Organic Materials Branch  
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NUCLEAR RADIATION EFFECTS ON STRUCTURAL  
PLASTICS AND ADHESIVES

Part II Extension of Literature Survey

I INTRODUCTION

Structural plastics and adhesives are damaged by nuclear radiation. A study of the chemical damage resulting from such radiation would be of great value in the design of more radiation-resistant materials. For this purpose a literature survey can be very helpful in guiding not only the scope of the research program, but also the thinking of the personnel connected with it. While a recent publication (13) describes the change in physical properties of commercial adhesives due to irradiation, no studies have been made on the chemical damage of compounded, structural adhesives, nor on the organic components of these adhesives. Thus, the literature survey must be an indirect guide.

This report is a supplementary literature survey covering the pertinent articles received between 30 September 1956 and 1 February 1957. The articles received prior to 30 September 1956 are covered in WADC Technical Report 56-534 Part I, Literature Survey.

II METHOD OF APPROACH

In the attempt to make this survey complete, searches were made not only through the technical, but also through semi- and nontechnical publications. These latter releases can yield up-to-date information in what is a very rapidly changing field. The patent literature contains more and more issues on the radiation chemistry of organic materials and this source, too, was surveyed.

The bibliography contains all the articles which were considered to be related to the current contract, and, in general, continues the coverage set forth in the Literature Survey, Part I. The papers were abstracted and they are included within the bibliography. The following delineates the categories into which the articles are placed:

1. Polymerization by Irradiation
  - A. General
  - B. Thermoplastic Materials

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

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2. Effects of Irradiation of Polymers
  - A. General
  - B. Crosslinking
  - C. Degradation
  - D. Grafting
3. Effects of Irradiation of Organic Materials
  - A. General
  - B. In Presence of Oxygen

## III DISCUSSION

A brief review of the literature surveyed during this period is presented in this section. The general picture is one of a reinvestigation of details in order to establish principles of the gross effects observed earlier plus, perhaps, an extension into new phases.

### 1. Polymerization by Irradiation

As the work in this general field progresses, the number of review articles and bibliographies (1, 3, 5, 14, 24, 71) is increasing. The interest in polymerization in the solid state is exemplified by a study (10) of a number of acrylates including potassium, calcium, and barium salts of acrylic acid.

### 2. Effects of Irradiation of Polymers

As was indicated in Part I of this report, polyethylene continues to receive the major attention as far as effects of irradiation are concerned; however, a number of studies on elastomers (15, 18, 27, 28, 32, 35, 37, 47, 48) shows intensive effort in this field. One group (15, 32), working on elastomers, found numerous inhibitors of radiation damage (Anti-Rads) and is testing them extensively. The majority of these Anti-Rads are recognizable as oxidation or pseudo-oxidation inhibitors. Studies on fillers of rubbers (48) showed that enhanced radiation resistance can be attributed to the fillers, probably as a result of scattering or other interactions with the photons.

Two recent articles dealing with the effects of nuclear radiation on structural adhesives (13) and resin-glass laminates (39) are quite pertinent to the subject of this contract, but work on the nature and extent of chemical damage was not an objective of these investigations.

Improvements in physical properties while crosslinking polymers have been effected by irradiation of a cold drawn polymer to set the

orientation (42), and, in an opposite sense, by irradiation at temperatures where the crystallinity is partly destroyed (43).

When copolymers are crosslinked (47) the irradiation behavior can be expressed in terms of the corresponding properties of the constituents, e. g., styrene even in minor amounts helps in the radiation resistance of a styrene-acrylonitrile copolymer.

More information is being obtained on the degradation of polymers, particularly when air or oxygen is present during irradiation (51, 54, 58). Degradation of polymethylmethacrylate (54, 56) appears to be main chain breaking and side chain decomposition. This latter decomposition is of interest in the general study of irradiation of esters and, more particularly, of diesters used as lubricants.

Radiation-induced graft copolymerization is receiving more attention (59-63). It is unfortunate that the position of grafting on the polymer is unknown, for this information could indicate potential sites for chemical damage.

### 3. Effects of Irradiation of Organic Materials

Studies on the irradiation of organic compounds, particularly low molecular weight materials, is of great importance, for they are essentially model compounds of higher molecular weight, polymeric, or complex materials. For example, the results of studies of hydrocarbons (76, 80, 86, 82) in both inert and oxygen atmospheres would be useful in interpreting data on irradiation of polyethylene; similarly, results on alkylbenzenes (67, 76) would apply to potential radiation-resistant lubricants and hydraulic or cooling fluids.

Radiation-induced oxidation of organic compounds appears to follow typical auto-oxidation processes (81, 82, 84, 86).

IV BIBLIOGRAPHY, WITH ABSTRACTS

1 Polymerization by Irradiation

A. General

1. Morgan, P.

Plastics Progress 1955. Iliffe and Sons, Limited, London, 1956.

This book contains a chapter by A. Charlesby which reviews sources of radiation, energy required for crosslinking, crosslinking and polymerization, degradation, radiation protection, and radiation of solutions of polymers.

2. Mund, W. and W. Koch.

On the Polymerization of Acetylene by the Action of Alpha Particles. Bull. Soc. Chem. Belg., 34, 241-55(1925).

The velocity of the polymerization of acetylene containing an approximate proportion of radon of  $5 \times 10^{-5}$  percent was measured. The mixture, in a round bottom flask of 5 cm radius, was kept at  $0^{\circ}\text{C}$  under a pressure of 70 cm mercury. If one takes into account the effect of RaA and RaC in equilibrium with the radon, as well as the absorption by the walls of the flask, the results thus obtained permit a calculation that one alpha particle having a path of 3.94 cm in air (at  $0^{\circ}\text{C}$  and 760 cm) will cause the disappearance of about  $4.38 \times 10^6$  gaseous molecules in acetylene under the described conditions.

3. Roche, A.F.

Polymerization. Ind. Eng. Chem., 48, 1643-52(1956).

A general review of radiation polymerizations during 1956.



B. Thermoplastic Materials

4. Chapiro, A.

The Polymerization of Vinyl Chloride Initiated by Gamma-Rays. J. chim. phys., 53, 512-14(1956).

Studies by Mund (C. A., 47, 9051f) of the gas-phase, beta-ray-initiated reaction indicated several anomalies attributed to the localization of free radicals along the path of the ionizing particles. The present study was conducted in the liquid-phase with gamma-rays to reduce these effects. Results indicate that the radiation-induced polymerization has the same kinetic features as normal chain-initiated polymerization. Aspects of the polymerization related to the radiation of the polymer differ from normal polymerization and are still obscure. The radiated polymer appears to be the cause for new chains which produce more branching than is found in classical polymerization reactions.

5. Chapiro, A., M. Magat, A. Prevot-Bernas, and R. Sebban.

The Production of Vinyl Polymers by Means of Ionizing Radiation. Ind. plast. mod., 7, 44-6, No. 10(1955).

The type of source of radiation, the activity of the source, distribution of the molecular weight, and effect of temperature are discussed in relation to the commercial production of vinyl polymers by radiation.

6. Fields, M.

Chemical Systems Sensitive to Radiation. Contract No. DA 18-108CML2562, Monthly Report No. 6, Dec. 1, 1951 - Dec. 31, 1951.

A procedure has been developed for the preparation of halogenated plastic masses containing pH indicators by polymerization of oxygen-free solutions of halogenated compound and a monomer. Combinations of halogenated compound and monomer have been found that yield clear, hard plastic masses on polymerization. Several plastics, prepared from a mixture of monomer and a commercial vinyl chloride-vinylidene chloride resin, on exposure to Co 60 gamma radiation have evidenced a visible change after exposure to several thousand roentgens and a period of standing of two to three weeks. The spectral characteristics of three irradiated plastics have been determined spectrophotometrically, and limited data clearly point to significant changes in the irradiated samples on standing.

7. Mund, W., J. A. Hermán and P. Huyskens.

The Radiochemical Polymerization of Vinyl Chloride and Isobutene. Bull. Classe Sci. Acad. Roy. Belge, 37, 696-705(1951).

New experiments on the radiochemical polymerization of vinyl chloride lead to a simpler expression of the velocities of the reactions so far observed, if one discards the hypothesis of an initial disturbance brought about by a cause foreign to the kinetics of the reaction itself.

8. Mund, W. and P. Huyskens.

The Polymerization of Isobutene by the Action of Alpha-Rays. Bull. Classe Sci. Acad. Roy. Belge, 36, 610-15(1950).

Isobutene polymerization by alpha-rays according to a method analogous to that given for vinyl chloride is discussed. The ionic yield decreases with an increase in temperature.

9. Prevot-Bennas, Mme, A. and J. Sebban-Danon.

Certain Characteristics of the Radiochemical Polymerization of Acrylonitrile. I. Variation of Total Velocity and Molecular Masses as a Function of Intensity. J. chim. phys., 53, 418-21(1956).

A theoretical treatment of the velocity of the radiochemical polymerization of acrylonitrile.

10. Restaino, A.J.

Gamma-Ray-Initiated Polymerization of Crystalline Vinyl Monomers. University Microfilms (Ann Arbor, Mich.), Pub. No. 16049, 46pp; Dissertation Abstract, 16, 1074-5(1956).

In order to determine whether the ordered arrangement of molecules in the lattice of crystalline vinyl monomers influences the rate of polymerization and the structure of the resultant polymer, a number of vinyl compounds have been polymerized in the solid state by Co 60 gamma-rays. Those monomers polymerized include acrylamide, methacrylamide, methylene-bisacrylamide, N-vinyl-carbazole, vinyl stearate, acrylic acid, methacrylic acid, and potassium, calcium, and barium acrylates.

11. Ronzio, A.R.

The Synthesis of Deutero-Polythene. LA-1478,  
Oct., 1952.

A small-scale preparation of deutero-polythene, starting from deuterium oxide and calcium carbide, was investigated. The procedure adopted gives about 60 percent yields of deutero-polythene having a melting point of 120 to 130°C and a density of 1.02 to 1.05. The ethylene-d<sub>4</sub> gave appreciably greater yields and polymerized at lower temperatures than ethylene-H<sub>4</sub>.

## 2 Effects of Irradiation of Polymers

### A. General

#### 12. Allen, A.O.

Effects of Radiation on Materials. MDDC-962,  
May 20, 1947.

High-energy radiations have long been known to produce changes in chemical constitution and physical properties in the materials which they traverse. Study of such changes is important to nuclear engineering in two respects: (1) use of materials in and around pile structures is limited by radiation damage which they undergo; (2) biological effects of radiation are of great practical importance, and study of the chemical effects of radiation provides the necessary physico-chemical background for interpretation of the biological findings. The mechanisms by which these changes are brought about are complex, and the responses of different types of material to radiations are extremely variegated. The time available allows only a qualitative survey of this complicated subject.

#### 13. Arlook, R.S. and D.G. Harvey.

Effects of Nuclear Radiation on Structural Adhesive Bonds. WADC TR 56-467, Aug. 1956.

A group of nine commercially available metal-to-metal adhesives comprising six chemical types was investigated to determine the effect of gamma radiation upon their strength properties. They were FM-47, AF-6, Epon VIII, 422, and Cyclewelds A-Z, 55-9, C-3, C-6, and C-14. The approximate dosages were  $9 \times 10^7$ ,  $3 \times 10^8$ , and  $9 \times 10^8$  roentgens. Tensile shear and bend tests were conducted at room temperature, at  $180^\circ\text{F}$ , and at  $260^\circ\text{F}$ . Two adhesives were also tested at  $500^\circ\text{F}$ . Fatigue tests were performed at room temperature. Only one adhesive, 422, was essentially unaffected by gamma radiation at all testing temperatures. The remaining adhesives were affected to varying degrees.

#### 14. Ballantine, D.S.

Irradiation of Plastics. Soc. of Plastics Eng. J.,  
12, No. 7, 27-31(1956).

During the past several years an increasing interest in the effect of radiation on the properties of organic plastic materials has been developing. A number of papers and review articles have been written describing in detail the physical and mechanical property changes which occur when polymeric materials are subjected to intense radiation dosages. These are of great value if one is interested in tensile strength, Rockwell hardness, elongation changes, and other

physical properties of a particular plastic. In a number of cases, however, conflicts in the data derived from experiments conducted at different laboratories have appeared, so that areas of confusion exist. There has been little attempt to delineate the underlying reactions which occur, and their relationship to the changes observed. It is the object of this review paper to depict the chemical reaction mechanisms involved as a result of irradiations, to show how these reactions can be modified, and to summarize the significant results obtained to date.

15. Born, J. W.

A Study of the Effects of Nuclear Radiations on Elastomeric Compounds and Compounding Materials. WADC Technical Report 55-58 (Part II) Sept. 1956.

Continuous stress relaxation measurements in air detail the effects of temperatures ranging from 25 through 80°C on radiation damage to rubber compounds. The order of decreasing resistance to damage is natural rubber, GR-S, Neoprene GN, and Hycar 1002 for gum rubber compounds and GR-S, Hycar 1002, natural rubber, and Neoprene GN among the black compounds. Graphs illustrate these results.

Stress relaxation measurements, volume swell measurements, infrared absorption analyses, and mass spectral analyses provided fundamental information about radiation damage. They further showed that heat and radiation damage differ significantly.

The Anti-Rad screening program and the study of the effect of radiation upon dynamic properties of rubber have reached the physical testing stage. Compounds containing 91 specially selected, potential Anti-Rads have received optimum cures, and samples have undergone gamma irradiation. The purpose of the screening is to provide criteria for the synthesis of specific new Anti-Rads.

16. Bresee, J. C., J. R. Flanary, J. H. Goode, C. D. Watson, and J. S. Watson.

Damaging Effects of Radiation on Chemical Materials. Nucleonics, 14, No. 9, 75-81(1956).

Quantitative measurements were made to determine how radiation affects the chemical resistance and chemical decontaminability of protective coatings. Materials such as polyethylene, polystyrene, Teflon, Kel-F, and Hycar rubber PA-21 and OR-25 were tested. Coatings such as Amercoat Strip, Brevon, GE Cocoon, and Tygofilm were used.

17. Calkins, V.P.

Radiation Damage to Nonmetallic Material. APEX 167.

The type and amount of radiation damage a given material will suffer under any set of radiation conditions can be predicted with a fair degree of certainty if the radiation damage of various classes of compounds as a function of absorbed energy can be established on a sound, experimental basis. In lieu of such experimental data, the existing available data on radiation damage have been examined, and on the basis of calculated energy absorption values broad generalizations have been made regarding the estimated radiation damage thresholds of various components of a typical nuclear power plant.

18. Charlesby, A.

Improvements In or Relating to Polymeric Substances. British Patent 742,933, Jan. 4, 1956.

This patent relates to the mixing of polymeric, carbon compounds (e. g., polyethylene) with carbon black (5 to 50% w/w) and subjecting the mixture to radiations from high energy sources to produce a product of increased tensile strength as compared with the unirradiated product. In addition, the degree of oxidation during irradiation was reduced.

19. Charlesby, A.

Effect of High-Energy Radiation on Long-Chain Polymers. Nature, 171, 167(1953).

The mechanical properties, tensile strength, effect of mineral acids, and electrical properties of irradiated and non-irradiated polyethylene are briefly described.

20. Collins, C.G. and V.P. Calkins

Radiation Damage to Elastomers, Organic Liquids and Plastics. APEX 261 Sept. 1956.

This report is comprised principally of tables and graphs of the experimental data assembled into individual sections -- Elastomers, Plastics, and Organic Liquids. The data are preceded by a section devoted to a general discussion of preliminary considerations, including important factors in radiation damage to organic materials, and to the basis and limitations of the dosage conversion procedure.

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21. Day, M. J. and G. Stein

Effects of X-rays upon Plastics. Nature, 168,  
644-45(1951).

The effect of X-rays on colored plastics such as "Prespex," as well as on uncolored material, was observed. A reaction mechanism is proposed.

22. Dienes, G. J.

Effects of Nuclear Radiations on the Mechanical Properties of Solids. Jour. of Applied Physics,  
24 (6), 666-674(1953).

The general nature of radiation effects in solids is reviewed briefly. Current theoretical understanding of the mechanical properties of solids is critically evaluated. The effect of nuclear radiation on the mechanical properties is discussed in detail. It is shown that the changes in the mechanical properties of crystalline substances (mostly metals) can be quite satisfactorily interpreted on the basis of the production of interstitial atoms and vacant lattice sites by fast particle irradiation. Isolated vacancies and interstitials may not be able to account for all the observations, and attention is called to the possible need of postulating the existence of aggregates of these lattice defects. In molecular solids (mostly high polymers) nuclear radiations bring about changes in the substance which are best described as chemical. Ions and free radicals are formed leading to subsequent chemical reactions, thereby altering the properties of the substance. Drastic changes in the mechanical properties of high polymers are observed. Correlation with structural changes has hardly been started. Experiments are suggested which, in the author's opinion, should give further insight into the fundamental processes involved.

23. Dole, M.

Effect of Radiation on Colloidal and High Polymeric Substances. Report of Symposium IV Chemistry and Physics of Radiation Dosimetry. ATI 115479, Sept. 18, 19, 20, 1950, Army Chemical Center, Maryland.

Polyethylene in the form of sheet film was subjected to the radiation of the Argonne heavy water pile for 45, 90, and 180 hours at the 300 kw operating level. Irradiations in air and in vacuum were carried out. Chemical analyses of film and gas liberated, infrared absorption studies, and tensile strength and stress-strain studies were made. Possible mechanisms for the changes are proposed and a review and discussion of previous work are given.

24. Fowler, J. F.

X-Ray Induced Conductivity in Insulating Materials.  
Proc. Roy. Soc., 236A, 464-480(1956).

A co-ordinated explanation of the conductivity induced by ionizing radiation in solid insulating materials (conductivity  $\sim 10^{-20}$   $\Omega^{-1} \text{cm}^{-1}$ ) including amber, mica, and a number of plastics, is put forward for the first time. A model based on conduction by free electrons and including the presence of electron traps is proposed, and the theoretical predictions based thereon are shown to be in good agreement with the experimental results. The dependence of induced conductivity and of the subsequent decay upon temperature and dose rate have been investigated. Physical parameters are given for each material: recombination cross section, number of traps and their distribution in energy, mean distance diffused by free electrons, and probability factors of release from traps. The results suggest that when crystalline regions are present in a material (e. g. polyethylene), the boundaries of these regions provide trapping sites in addition to traps of unspecified nature which are present in completely amorphous materials.

25. Gehman, S. D. and L. M. Hobbs.

Changes in Elastomers Due to Radiation from  
Cobalt 60. Rubber Chem. Tech., 28, 12-18(1955).

The present work is a survey of the effects of a large dose of gamma radiation on a variety of elastomers and compounds. It adds to work already published, by the greater variety of elastomers and elastomer compounds studied, by giving the formulas of many of the compounds used, by the more exact specification of the type of radiation and the temperature during the exposure, and by the exclusion of possible effects due to the presence of oxygen.

26. Graham, P. C. C.

Effects of High-Energy Radiations on Rubber and  
Other High Polymers. Research Association of  
British Rubber Manufacturers. Intelligence Division.  
Confidential Information Bureau Circular No. 434,  
March 1956.

A bibliography of current literature.

27. Little, K.

The Effects of Ionizing Radiation on Organic High  
Polymers. Symposium on Utilization of Radiation  
from Fission Products. AERE C/R 1231, Feb. 1953.



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The purpose of the present investigations was to find the effects produced when organic high polymers, both natural and synthetic, were subjected to ionizing radiations. The survey was qualitative rather than quantitative, and the chief method of examination of the products was by X-ray diffraction. Experiments with electrons from a Van de Graaf generator and with pile radiation indicate that the effects of different types of ionizing radiation are similar in kind and differ only in degree. The Harwell pile, BEPO, was therefore used for the greater part of this work as a convenient source of high intensity. Care was taken to avoid, during the irradiation, temperatures which would affect the degree of crystallinity of the polymers.

28. Loughborough, D.L. and J.W. Born.

A Study of the Effects of Nuclear Radiations on Elastomeric Compounds and Compounding Materials. AD 72314. B.F. Goodrich Co. for WADC, July 5, 1955.

See Reference No. 15 for full report.

29. Loughborough, D.L., A. Hawthorne, E.H. Rose, and J.W. Born.

A Study of the Effects of Nuclear Radiations on Elastomeric Compounds and Compounding Materials. AD 72313. B.F. Goodrich Co. for WADC, May 5, 1955.

See Reference No. 15 for full report.

30. Loughborough, D.L., A.E. Juve, J.R. Beatty, and J.W. Born.

A Study of the Effects of Nuclear Radiations on Elastomeric Compounds and Compounding Materials. WADC Technical Report 55-58.

A comprehensive study of the effects of nuclear radiation upon elastomeric compounds and compounding ingredients is reported. Two hundred nineteen compounds were selected for study. One hundred ninety were irradiated and tested. Stress-strain and stress-relaxation measurements were made, along with special analyses of irradiation products. The investigations exhibit three principal results: a catalog of stress-strain data for many elastomeric formulations has been compiled; a group of inhibitors of radiation deterioration in rubber has been discovered; and evidence has been gathered that the effect of Co 60 gamma-irradiation on rubber is different in air from that in high vacuum. The rubber compounds which are most resistant to deterioration are cited by recipe.

31. Luy, M. and K. Schumacher.

The Influence of Electron and X-Ray Irradiation of Medium Energy on Polyethylene. Z. angew. phys., 8, 222-7(1956).

The effects of 0.06 and 0.05 Mev X-ray radiation on polyethylene films of 30-40 microns thickness were studied. Temperature-dilatation curves and infrared spectrograms for various irradiation doses are given. The electrical properties of the films were measured before and after irradiation. All effects observed did not depend upon the nature of the radiation but only upon the energy absorbed. (1) Films irradiated under N<sub>2</sub> show a considerable increase of crosslinking. After a spontaneous dilatation in the melting range of the crystalline components, owing to previous deformation during manufacturing, these samples do not change their length considerably with increasing temperature. Nonirradiated samples, on the other hand, rupture at 105°C. No change in electrical properties is noted. The infrared spectrogram shows a new absorption band at 10.35 microns. (C=C bond) proportional to the radiation dose. (2) Films irradiated in air show strong oxidation effects and altered electrical properties. Crosslinking is weaker and in the infrared spectrogram bands of oxidation products appear. After irradiation with  $1.8 \times 10^9$  roentgens the dielectric constant of a 80-micron film changes from 2.2 to 3.1, the power factor at 800 cycles per second from  $4 \times 10^{-4}$  to  $350 \times 10^{-4}$  and the specific dc resistance from  $10^{18}$  to  $10^{13}$  ohm-cm.

32. Mayburg, S.

The Conductivity Change in Good Insulators During Gamma-Irradiation. The Conductivity of Teflon. WAPD-RM-122, May 1, 1952.

33. Miller, A.J. and G. Steel.

Behavior of Certain Plastics and Elastomers Under Irradiation. AECD-3634, 1948.

Data here presented show the effects of X-rays and electrons on the properties of various plastics and elastomers. The properties investigated were electrical resistance, tensile strength, elasticity, hardness and optical properties, dependent on the proposed use of the material. In general, radiation causes a decrease in electrical resistance, tensile strength, elasticity, and light transmission and an increase in hardness.

34. Rose, D.G.

The Effect of Ionizing Radiation upon Polyethylene. A Preliminary Study. Thesis. Northwestern University, June 1949. (Microfilm)

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Films and granules of polyethylene were irradiated in the heavy water chain reacting pile and changes in physical and chemical properties were measured. The tensile strength remained the same or decreased, the elongation at break decreased, and the shape of the stress-strain curve changed markedly. Ultraviolet and infrared spectra are given.

35. Sears, W.C. and W.W. Parkenson, Jr.

Postirradiation Oxidation in Rubber and Plastics.  
J. Polymer Sci., 21, 325-6(1956).

In this study, polystyrene, polyethylene, polybutadiene, GR-S, natural rubber, deproteinized natural rubber, polymethyl methacrylate, polyvinyl chloride, and Teflon have been irradiated in order to observe effects in their infrared spectra. These irradiations have been carried out in vacuum and in oxygen atmospheres. Dosages of the order of  $10^8$  to  $10^{10}$  rads are required in most polymers to produce significant changes in their infrared spectra.

36. Sears, W.C., O. Sisman, W.W. Parkenson, Jr., and R.L. Towns.

Infrared Spectra of Plastics and Elastomers After Irradiation. ORNL 2051, 16-24, Solid State Division, Oak Ridge National Laboratory. Feb. 29, 1956.

See above abstract.

37. Sisman, O. and C.D. Bopp.

A Summary of the Effect of Irradiation on Some Plastics and Elastomers. Preprint No. 182 ASTM, Los Angeles, Sept. 17-21 (1956).

Two general classes of reactions have been recognized which can explain most of the changes that are observed in the physical properties of plastics and elastomers. The reactions are termed cleavage or scission and crosslinking.

38. Terrell, W.B.

Effects of Gamma Radiation on Linear Polyethylene. Thesis AD81519, March 1955.

Changes in physical properties of two plastic materials as a result of gamma irradiation are shown in graphical and tabular form. The plastics have linear polyethylene structures and identical formulas, but differ extensively in some of their normal physical properties.

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Tests were made of the following physical properties as a function of total radiation dosages up to  $10^9$  roentgens: tensile strength, percent elongation, hardness, impact strength, specific gravity, water absorption, heat distortion temperature, dielectric constant, arc-resistance, and color changes. In addition, infrared studies were made on specimens before and after irradiation.

39. Tomashot, R.C. and D.G. Harvey.

Nuclear Radiation on Reinforced Plastic Radome Material. WADC TR 56-296, ASTIA Document No. AD 97254.

Nine different reinforced plastic laminate materials (from Selectron 5003, DC-2104, CTL-91-LD, Epon 828, Epon 1001, Epon 1001/Plyophen 5023, Vibrin 135, Laminac 4232, and Paraplex P-43) and a foam sandwich were subjected to integrated gamma radiation doses up to  $10^9$  roentgens. After completion of the radiation exposures, the materials were tested to determine flexural, tensile, and compression strengths under both standard and wet conditions. The mechanical properties of the heat resistant plastic laminates were also determined at elevated temperature. Dielectric constant and loss tangent measurements were conducted on irradiated samples to determine the effect of radiation on the electrical properties of these materials. Data obtained from these tests show that the mechanical properties were not significantly affected except for one epoxy-type resin laminate (from Epon 1001). None of the materials showed any significant change in electrical properties due to radiation.

B. Crosslinking

40. Black, R.M.

Effect of Temperature on the Crosslinking of Polyethylene by High-Energy Radiation. Nature, 178, 305-6(1956).

"Alkathene" grade-7 polyethylene (I) samples were irradiated in a 400-c. Co-60 source at -196 to 75°C. From the elastic moduli of the samples and the energy absorbed, the amount of crosslinkage per 100 ev was calculated. Plots of the amount of crosslinkage of I and the amount of chain breakage of polymethyl methacrylate and polyisobutylene per 100 ev versus temperature are similar. Black proposes that the mechanism for crosslinking or degradation involves at least three stages: energy absorption, dissociation with ion or radical formation, and interaction of the ions or radicals.

41. Charlesby, A.

Effects of Radiation on Substances with Long Chains. Industrie chim. belge, 21, 27-33(1956).

The nature of transition from a chain molecule to a crosslinked network is discussed.

42. Charlesby, A.

Improvements in or Relating to Treatment of Polymeric Substances. British Patent 739,709, Nov. 2, 1955.

This patent relates to the cold drawing of carbon back-bone polymers to bring about orientations of at least a substantial proportion of the molecules and to the subjecting of the oriented substance to radiation to set the orientation wholly or in part. Examples are polyethylene, polystyrene, and polyvinyl chloride.

43. Charlesby, A.

Improvements in or Relating to Polymeric Substances. British Patent 740,899, Nov. 23, 1955.

This patent relates to the treatment of polymeric substances. By irradiating at temperatures above the melting point or at temperatures where crystallinity is partly or wholly destroyed, the random crosslinking gives rise to structures of greatly increased pliability and elasticity as compared with those irradiated at lower temperatures. Examples are polyethylene, polystyrene, and polyvinyl chloride.

44. Charlesby, A.

Improvements in or Relating to Polymeric Substances.  
British Patent 741,826, Dec. 14, 1955.

This patent relates to the treatment of polymeric, carbon compounds (e. g., polyethylene) to produce low solubility (crosslinking). Treatment involves the action of ionizing radiations which consist of thermal neutrons in the presence of atomic species (e. g., cadmium) which have a high capture cross section for thermal neutrons and emit gamma radiation following such capture.

45. Charlesby, A.

The Crosslinking of Rubber by Pile Radiation.  
Rev. Gen. Caoutchouc, 32, 39-46(1955).

Rubber becomes crosslinked when subjected to high energy radiation such as is present in atomic piles. This offers a means of studying the change in properties of rubber as the degree of crosslinking is varied, without the use of chemical vulcanizing agents. In this article the efficiency of crosslinking, the variation of the gel fraction, and the molecular weight of gel and sol fractions are studied.

46. Charlesby, A.

The Crosslinking of Rubber by Pile Radiation.  
Rubber Chem. Tech., 28, 1-11(1955).

See above abstract.

47. Charlesby, A. and D. Groves.

Crosslinking and Radiation Effects in Some Natural and Synthetic Rubbers. Proc. 3rd Rubber Technol. Conf., London 1954, 317-33(Pub. 1956), cf. C.A. 48, 4999b.

Of various methods available for the detection of crosslinking in irradiated polymers, two methods, based on solubility and swelling, respectively, were utilized to study the effect of high-energy radiation on some elastomers (including natural rubber, polychloroprene, polyisobutylene, and thioplasts) and copolymers (butadiene-styrene, butadiene-acrylonitrile, isobutylene-isoprene, and isobutylene-styrene). The behavior of the polymers can be expressed in terms of the properties of their constituents; e. g., isoprene, chloroprene, and butadiene units crosslink, whereas isobutylene units degrade rapidly. This fundamental distinction is not related to unsaturation, for polyethylene crosslinks readily and polymethyl methacrylate degrades, whereas polymethyl acrylate does not. For many polymers, the energy absorbed per crosslink or main

chain fracture is approximately 20 ev. Monomers other than the main constituent of copolymers confer some degree of resistance to radiation of copolymers of which they form a constituent part, e.g., styrene with acrylonitrile. The results with Thiokol-N indicate that where crosslinking initially present is not extensive, irradiation promotes further linking between main chains containing sulfur. In general, the degree of crosslinking is proportional to the radiation dose. The irradiation method of vulcanization makes possible the quantitative study of the effect of different degrees of crosslinking on the physical properties of elastomers, the study of the role of carbon black in modifying the properties of elastomers, the study of the formation of copolymers from monomers which cannot be linked together by more conventional chemical techniques, and the production of vulcanizates containing a certain degree of orientation as a permanent characteristic by irradiating the raw elastomer while stretched.

48. Gehman, S.D. and I. Auerbach

Gamma-Ray Vulcanization of Rubber. Intern. J. Appl. Radiation and Isotopes, 1, 102-114(1956).

An experimental study was made of the vulcanization of rubber by the crosslinking action of intense gamma radiation from a Co 60 source. Vulcanization by heat and chemicals is an important, highly developed industrial process, the essential feature of which is the chemical crosslinking of the rubber molecules by sulfur atoms. With gamma-ray vulcanization, the crosslinking occurs by the elimination of hydrogen and the formation of carbon-carbon bonds, which are more stable than sulfur bonds. The usual vulcanizing agents and sulfur were found to have only slight influence on gamma-ray vulcanization, but fillers enhanced the effects of the radiation, probably through scattering or other interaction with the photons. The tensile strengths developed with a series of fillers were found to increase with the specific volumes of the fillers. Tensile strengths obtained with gamma-ray vulcanization were not as high as can be secured by conventional vulcanization. The radiation dose required for vulcanization was relatively large, 1 to  $5 \times 10^7$  reps. If there were no heat losses, such a dose would raise the temperature of the rubber to ordinary vulcanizing temperatures. Typical potential advantages of gamma-ray vulcanization include uniform vulcanization of thick articles, more stable, better ageing vulcanizates, cold vulcanization of extruded shapes or preforms, and faster preliminary processing of the rubber stock. The development of industrial applications of gamma-ray vulcanization may be contingent on the economical utilization of fission-waste products or spent reactor-fuel elements and developments in the technology of working with intense radiations.

49. Newton, E.B.

Method of Vulcanizing Rubber. U.S. Patent 1,906,402 to B.F. Goodrich Co., Feb. 19, 1929.

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This invention, in brief, consists of vulcanizing rubber or converting rubber to an isomeric substance by exposure to a bombardment of electrons moving with a high velocity. The electrons impinging on the rubber hydrocarbon cause a rapid vulcanization or similar modification of the rubber.

50. Pearson, R. W.

The Radiation Chemistry of Polyethylene. Chem. and Ind., 903(1956).

A survey of published experimental data shows a relationship between vinylene group formation and hydrogen evolution. The hydrogen evolution is linear with dose while vinylene unsaturation approaches a maximum. The results of application of stationary state kinetics to the discussed sequence of reactions agree with experimental data. The rate of formation of crosslinkages, which is not initially linear, follows the calculated curve.



C. Degradation

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51. Alexander, P. and D. Toms.

The Effect of Oxygen on the Changes Produced by Ionizing Radiations in Polymers. J. Polymer Sci., 22, 343-8(1956).

The presence of oxygen when irradiating (1-Mev electrons) polyethylene leads to main-chain breaks; at least one per crosslink but the number of crosslinks is not altered. It is thought that main-chain breaks are produced by  $O_2^-$  ( $O_2 + e^- \rightarrow O_2^-$ ). How  $O_2^-$  breaks chains was not clear.

52. Chapiro, A.

The Action of Gamma-Rays on Polymers in the Solid State. II. Degradation of Polymethyl Methacrylate and Cellulose Acetate. J. chim. phys., 53, 295-305(1956).

Both polymethyl methacrylate and cellulose acetate show a progressive decrease in melting point on irradiation with gamma-rays from a 25-c. Co 60 source. With methyl methacrylate the melting point continues to decrease after the irradiation has been stopped. A study of the coloration and the absorption spectra during the irradiation showed the existence of two independent processes: a displacement of an absorption band from the ultraviolet towards the visible, and the appearance of a band at 5050 A. The author proposes the formation of a  $COOCH_3$  radical which leads to the formation of  $CO$ ,  $CO_2$ , and  $CH_4$ . At the end of the irradiation certain free radicals are trapped in the solid structure and react only slowly, giving rise to the observed aftereffects.

53. Chapiro, A.

The Mechanism of the Radiochemical Degradation of Polymers. J. chim. phys., 53, 306-7(1956).

This is a discussion of the radiochemical degradation of polyisobutylene (Alexander, et al., C.A. 50, 682d) which proposes a multiple cleavage at the tertiary carbon atom as one of the primary reactions. Other reactions, such as cleavage of the secondary C--H and of the C-- $CH_3$  bonds, are also postulated. The reactions of the various radicals account for the observed products.

54. Chapiro, A., J. Durup, M. Fox, and M. Magat.

Degradation of Polymers in Solution Under the Influence of Gamma-Rays. Sym. Intern. chim. Macromolecolare. La Ricerca Scientifica (1955).

*Continued*

The degradation of diluted solutions of polymers was carried out by means of gamma-rays in the presence of air. The system chosen was polystyrene in chloroform. The irradiation was made by means of a Co 60 source and degradation was measured by the decrease of viscosity of the solutions, using a Ubbelohde-type viscosimeter. In the absence of air the effect is very weak.

55. Charlesby, A. and M. Ross.

Improvements in or Relating to Polymeric Substances.  
British Patent 730,476, May 25, 1955.

A method of treating a polymeric ester of methacrylic acid (softening point above 40°C) to form an expanded cellular mass having a smooth skin comprising subjecting the polymer to a dose of  $5 \times 10^6$  roentgens at a temperature below the softening point until its average molecular weight is reduced to  $3 \times 10^5$  to  $10^4$  and subsequently heating at a temperature 0-10°C above its softening point to effect cellular expansion.

56. Charlesby, A., M. Ross, and P. Alexander.

The Degradation of Solid Polymethyl Methacrylate  
by Ionizing Radiation. Oct. 9, 1953. AERE M/R  
1269, Oct. 9, 1953.

When polymethyl methacrylate in the solid form is exposed to the atomic pile or to gamma radiation, two reactions predominate; breakdown of the main chain, and decomposition of the side chain with evolution of gases. The former is followed by changes in viscosity, the molecular weight of the irradiated polymer being inversely proportional to the radiation dose. The degradation is thought to proceed by random rupture of main chain C-C bonds by rearrangement of the excited polymer; 61 ev are absorbed per fractured bond. For each main chain rupture approximately one ester side chain is also decomposed.

The cage effect is thought to prevent direct dissociation and reaction occurs by rearrangement of the molecule to give relatively stable entities. Added substances reduce the amount of degradation, possibly by transfer of energy from the excited polymer molecule. This is possible only if the excited molecules have an appreciable life before decomposition. The degradation of polymethyl methacrylate may provide a means of measuring ionizing radiation dosage in the range 0.5 to 5 million roentgens.

57. Langton, N.H.

The Surface Degradation of Perspex by Ultrasonic  
Radiation. Plastics, (London), 118-20(1956).

*Conclusions*

The degradation of certain high polymers when exposed to ultrasonic irradiation seems to be a fairly well established experimental fact. Degradation has been shown to occur when solutions of polystyrene or polymethyl methacrylate are irradiated by ultrasonics of frequencies in the range 25 kilocycles up to about 1 megacycle. Most of the work seems to have been done using frequencies below 1 megacycle and at fairly low power inputs. The degradation which is observed appears to be a breaking down of the long molecules into particles of lower molecular weight. This change of molecular weight is investigated by measuring the viscosities of the solutions before and after irradiation using a capillary tube type of viscometer.

58. Wall, L. A. and D. W. Brown.

Chemical Activity of Gamma-Irradiated Polymethyl Methacrylate. J. Research Nat. Bur. Stds., 57, 131-36(1956).

In studies of polymerization and depolymerization with gamma-irradiated polymethyl methacrylate, observed effects were indicative of long-lived free radicals in the solid polymer. With a dose of  $10^7$  roentgens, the free-radical concentration as measured by both types of experiments, is estimated to be at least  $10^{-5}$  mole per liter. When irradiated in air the polymer contains peroxide structures of at least  $10^{-3}$  mole per liter concentration. The decomposition of these peroxidic groups is accelerated by tert-butylcatechol and is associated with the production of scissions in the polymer chain.

D. Grafting

59. Ballantine, D.S., P. Colombo, A. Glines, B. Manowitz, and D. J. Metz.

Progress Report on Fission Products Utilization.  
IX. Studies on Radiation-Induced Graft Copolymerization and Solid State Polymerization. BNL 414 (T-81)  
Oct. 1956.

A wide variety of graft copolymers has been prepared by the irradiation of a polymer in the presence of a monomer with Cobalt 60 gamma-rays. Some of the kinetic aspects of various systems are presented, and a partial physical evaluation of several of the graft copolymers formed is given.

References to work on gamma-ray-initiated polymerizations in the solid state are also cited.

60. Bevington, J.C. and D.E. Eaves.

Use of Irradiated Polymers as Initiators of Polymerizations. Nature, 178, 1112-13(1956).

Polymers, such as polystyrene, polyacrylonitrile, and nylon are irradiated in vacuum with gamma-rays and then exposed to the vapor of acrylonitrile. In some cases, as much as 10 percent by weight of acrylonitrile is introduced into the polymer. Nonirradiated polymers take up only a negligible amount of vapor.

61. Chapiro, A., M. Magat, and J. Sebban.

Improvements to Processes for Obtaining Grafted Copolymers. French Patent 690,659, April 29, 1955.

The invention relates to improvements in a process for obtaining grafted copolymers. These improvements consist principally of preparing grafted copolymers from polyethylene upon which at least one lateral branch of another polymer is grafted by first submitting polyethylene to the action of ionizing radiation in the presence of oxygen (air) and by then contacting irradiated polyethylene with a mono- or polyethylenic compound, the polymerization of which it initiates, under such conditions that several chains of the polymerized ethylenic compound are fixed by at least one of their extremities to the initial polyethylene, the length and the number of grafted branches being variable according to the operating conditions chosen for the treatment by the ionizing radiation as well as for the grafting reaction itself.

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62. Chapiro, A., M. Magat, and J. Sebban.

Improvements for Obtaining Grafted Copolymers, Allowing Especially Grafting on Finished or Semifinished Articles. French Patent 692,735, May 31, 1955.

Continuation in part of French Patent 690,659 (above).

63. Chapiro, A., M. Magat, and J. Sebban.

Improvements to Processes for Obtaining Grafted Copolymers. French Patent 692,736, May 31, 1955.

Continuation in part of French Patents 690,659 and 692,735 (above).

3 Effects of Irradiation of Organic Materials

A. General

64. Allen, A.O.

Survey of Recent American Research in the Radiation Chemistry of Aqueous Solutions. Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, 7, 513-19(1956).

A general review is given which includes a brief resumé of the work on irradiation of amino acids.

65. Baxendale, J.B. and D.H. Smithies.

The Irradiation of Aqueous Solutions of Organic Compounds. Z. physik. Chem., 7, 242-64(1956).

The oxidation of formic acid by X-rays in aqueous solutions of 0.1N H<sub>2</sub>SO<sub>4</sub> containing Cu<sup>++</sup> and/or Fe<sup>+++</sup> ions has been investigated experimentally and the kinetics of the observed processes have been analyzed to give G values for HO, H, H<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> for 190-kv X-rays. The use of D-containing formic acid confirms the abstraction of D from DCOOH by H atoms produced in the primary act, and also the primary production of H<sub>2</sub> from H<sub>2</sub>O. Other compounds give the same G values for H + OH with Cu<sup>++</sup> and Fe<sup>+++</sup>. Benzo- and duroquinones can replace the Cu<sup>++</sup> and Fe<sup>+++</sup> in their reaction with organic radicals and H atoms. The quinone system gives the same G values for H + HO and H<sub>2</sub>O<sub>2</sub>. A list of relative rates of reaction with hydrogen atoms is given based on the yields of hydrogen given by various compounds.

66. Burton, M.

Effects of High-Energy Radiation on Organic Compounds. J. Phys. Colloid Chem., 51, 786(1947).

All the processes which occur in photochemical reactions of organic compounds occur also in radiation-chemical processes. In addition, there are reactions resultant from the peculiar sequence characteristic of radiation chemistry, i. e., ionization, discharge, and decomposition. In general, any electron in the molecule is equally susceptible to ionization in the initial act; this fact must be constantly recalled in any interpretation of radiation-chemical mechanisms.

Since, in general, the excitation energy lies in any part of the molecule, the yield of a particular product is closely related to the number of parent groups in the molecule. Gas production, particularly in unsaturated compounds, is an inadequate criterion of

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the resistance of a compound to high-energy radiation. In the liquid state, the excessive excitation energy tends to minimize the Franck-Rabinowitch effect (i. e., decrease in yield due to collisional deactivation and cage effect). Factors which increase resistance of organic compounds to radiation (and ratio of ultimate molecules to free-radical processes) are molecular complexity, resonance in the molecule, and all properties of the molecule which tend to increase the correspondence between ionic and molecular configuration. Among the latter are molecular symmetry (cf. benzene) and molecular size (cf. palmitic acid). Apparently, increase of molecular size tends to channel the decomposition along a particular path rather than to diversify the products.

67. Burton, M., S. Gordon, and R. R. Hentz.

Effect of the Ring on Radiation Chemistry of Alkyl-Substituted Benzenes. J. chim. phys., 48, 190(1951).

Photolysis of liquid alkyl benzenes at 2537A produces gaseous volatiles at  $-120^{\circ}\text{C}$  with quantum yield of the order of  $10^{-4}$ . Energy absorbed in the  $\pi$ -electron system of the benzene ring causes rupture preferentially of bonds  $\beta$  to the ring, with the weaker bonds being most affected. Radiolysis of the same compounds with 1.5 Mev electrons gives 100 ev yields (G values) of the order of 0.2. Calculated primary G values according to the rule of averages (allowing for radical absorption by benzene rings) following methods elsewhere described are much higher than those estimated directly from the data here given. The discrepancy is attributed to a real protective effect, of the so-called "sponge" type, by the benzene nucleus. In this type of protection, energy originally liberated in the alkyl group by the radiation, either as excitation or ionization, is transferred to the ring and dissipated. Transfer of energy from the ring to the side group, with an ensuing chemical effect, also occurs, but such destructive effects play a minor role in comparison with protection.

68. Clarke, R. W.

Selected Abstracts of Atomic Energy Project Unclassified Report Literature in the Field of Radiation Chemistry and Bibliography of the Published Literature. AERE C/R 1575, May 1956. Part II. Organic compounds (including polymerization reactions).

Contains selected abstracts of atomic energy project unclassified report literature in the field of radiation chemistry and bibliography of the published literature.

69. Colichman, E. L. and R. Fish.

Pyrolytic and Radiolytic Decomposition Rate Studies on Ortho-, Meta-, and Para-Terphenyls. May 15, 1955. Decl. Dec. 5, 1955. 22 p. Contract AT-11-1-Gen-8. NAA-SR-211.

The pyrolytic (at 400°C and 450°C) and radiolytic (employing 1-Mev electrons) decomposition rates of the terphenyls have been determined. p-Terphenyl is apparently the most stable isomer. The rates of decomposition determined here are the lowest values reported in the literature for any compound under comparable conditions of temperature and radiation. The high pyrolytic and radiolytic stability obtained suggests possible high temperature application. Results presented here permit the appraisal of the terphenyls for anticipated use in nuclear reactors as coolants and/or moderators.

70. Colichman, E. L. and R. Gercke.

Radiation Stability of the Terphenyls and Other Polyphenyl Materials as Measured by Gas Evolution. NAA-SR-1288, North American Aviation, Inc., June 15, 1955.

The terphenyls and several other polyphenyls and mixtures were irradiated with 1-Mev electrons and the gas evolution rate determined as a means of evaluating the radiation stability. The low decomposition rates of the polyphenyls obtained are explained on the basis of a proposed fluorescence-protective mechanism.

71. Collinson, E. and A. J. Swallow.

The Radiation Chemistry of Organic Substances. Chem. Rev., 56, 471-568(1956).

Presents a review of the radiation chemistry of organic substances such as aliphatic compounds, aromatic compounds, polymers, oxidation-reduction systems and dyes, and substances of biochemical interest.

72. Dorfman, L. M.

Radiolysis of Ethane: Molecular Detachment of Hydrogen. J. Phys. Chem., 60, 826-28(1956).

The chief products in the radiolysis of ethane are hydrogen and a polymeric liquid, the yield for hydrogen formation being approximately 3.9 molecules per 100 ev. This note reports the results of experiments which show that a large fraction of the hydrogen is formed intramolecularly by direct detachment of molecular hydrogen without the apparent intermediate formation of single atoms of hydrogen.



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73. Henri, V.P., C.R. Maxwell, W.C. White, and D.C. Peterson.

The Chemical Effects of Alpha Particles upon Some C<sub>6</sub>-Hydrocarbons in the Vapor State. J. Phys. Chem., 56, 153-55(1952).

Some of the chemical effects of alpha particles upon n-hexane, cyclohexane, cyclohexene and benzene have been determined. The hydrocarbons were mixed in the vapor state with radon and allowed to stand for several weeks. The resulting gaseous mixtures were analyzed by the use of a mass spectrometer. Some of the physical properties of the liquids formed in each case were also determined.

74. Jones, S.T.

Irradiated Organic Materials. Can. Plastics 1955, 68, 70(1955).

This paper discusses in some detail how the physical and chemical properties of organic materials may be changed by the absorption of radiation. These changes are discussed in terms of (1) the stabilizing effect of aromatic rings, (2) specific forms of behavior of certain functional groups, and (3) environmental effects such as temperature, presence of oxygen, water, etc.

75. Luck, C.F. and W. Gordy.

Effects of X-Ray Irradiation Upon Some Organic Substances in the Solid State: Simple Alcohols, Amines, Amides and Mercaptans. J. Am. Chem. Soc., 78, 3240(1956).

Microwave magnetic resonance has been employed to study the effects of ionizing X-rays on some simple alcohols, amines, amides, and mercaptans in the solid state. The proton hyperfine structure of the electron spin resonance allows fairly definite identification of the radicals produced in certain of these.

76. Magat, M. and R. Viillard.

The Molecular Fission of Hydrocarbons Under the Impact of Electrons. J. chim. phys., 48, 385-98 (1951).

Many members of the following classes were studied: n-alkanes, 1-alkenes, 1-alkynes, dienes, methyl- and dimethylalkanes, cycloalkanes, cycloalkenes, and alkylbenzenes.

77. McClinton, L. T., W. M. Garrison, and M. Burton.

Organic Compound Bond Rupturing Process.  
(to U.S. Atomic Energy Commission). U.S. Patent  
No. 2,743,223, April 24, 1956.

Cyclohexane, when subjected to neutron radiation,  
decomposes into  $H_2$  and a polymeric material.

78. McLennan, J. C. and W. L. Patrick.

The Action of High-Speed Cathode Rays on the  
Simpler Alcohols, Aldehydes and Ketones, and on  
Ethylene. Can. J. Research, 5, 470-81(1931).

Sets forth the results of an experimental examination  
of the action of high-speed electrons on the vapors of acetaldehyde,  
acetone, methyl alcohol, and ethyl alcohol and on gaseous formaldehyde  
on ethylene. It has been shown that cathode rays form polymerization  
compounds with formaldehyde, acetaldehyde and acetone and that these  
decompose into simpler gases. The ultimate decomposition of  
acetaldehyde has been studied in some detail and has been shown to  
proceed through the polymer.

79. Microwave Laboratory, Duke University.

Quarterly Progress Report No. 11, Aug. 1 - Nov. 1,  
1955. (Contract AF 18(600)497. Continued  
AF 19(604)258, AD-79 522.

Abstracts are given of the following microwave-research  
projects: superconductivity at millimeter wavelengths; microwave  
analysis of radiation damage to biological substances; natural para-  
magnetic resonance in biological substances; radiation effects on  
organic solids, plastics and synthetic fibers; pure quadrupole spectrum  
of  $BiCl_3$  in the solid state; and solid-state theory. (See also AD-70 063).

B. In Presence of Oxygen

80. Bach, N.

Radiolytic Oxidation of Organic Compounds. Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, 7, 538-45(1956).

The effect of irradiation on such organic compounds as n-heptane, isooctane, cyclohexane, toluene, benzene, acetic acid, and ethyl and benzyl alcohols in the presence of molecular oxygen is discussed; products and G values are given. The action of irradiation in the presence of molecular oxygen on high polymers, aqueous solutions, and mixtures of organic compounds is also briefly discussed.

81. Bakh, N. A.

Oxidation of Organic Compounds by Molecular Oxygen Under the Action of Ionizing Radiations. I. Formation of peroxide compounds in liquid hydrocarbons. Sbornik Rabot Radiatsionov Khim., Akad. Nauk S. S. S. R., 145-55(1955).

X-ray irradiation of liquid hydrocarbons saturated with oxygen was examined. The process results in formation of  $(RO)_2$ ,  $RO_2H$ , and  $H_2O_2$  from heptane, isooctane, and MePh; cyclohexane yields  $(RO)_2$  and  $RO_2H$ , while  $C_6H_6$  yields only  $(RO)_2$  and  $H_2O_2$ . The yields of the peroxide derivatives do not exceed 1-2 molecules per 100 ev, and the process is apparently a typical radical reaction.

82. Bakh, N. A. and N. I. Popov.

Oxidation of Organic Compounds by Molecular Oxygen Under the Action of Ionizing Radiations. II. Formation of Stable Products of Oxidation in Hydrocarbons of Various Structures. Sbornik Rabot Radiatsionov Khim., Akad. Nauk S. S. S. R., 156-62 (1955).

X-ray irradiation and electron beams cause the mixtures of hydrocarbons with  $O_2$  to form carbonyl compounds in the following yields (moles per 100 ev): heptane 2, isooctane 1.2, cyclohexane 0.6, as well as acids in yields of 0.4, 0.6, and 0.2 respectively. Benzene yields phenol (0.6) and an aldehyde (0.45) but no acids. Radiation yield is independent of temperature and dosage.

83. Berry, P. J., S. Lipsky, and M. Burton.

Radiation-Induced Luminescence. Part II. The Effect of Oxygen and Bromobenzene. Trans. Faraday Soc., 52, 311-19(1956).

The quenching effect of oxygen and bromobenzene on the Co 60 gamma-induced luminescence of p-terphenyl in benzene has been studied as a function of the p-terphenyl concentration. In addition, the effects of oxygen and bromobenzene on the scintillator systems of m-terphenyl in benzene and in cyclohexane, of p-terphenyl in cyclohexane and in toluene, and of 1,4-diphenylbutadiene in cyclohexane and in benzene have been studied. The results are interpreted on the basis of electronic energy transfer (via emission of virtual photons) from excited solvent molecules to scintillator molecules. The quenching of the luminescence is shown to be almost completely attributable to an interaction between the quencher and excited solvent molecules. The efficiency of quenching remains constant with increasing bromobenzene concentration up to the highest concentrations studied ( $\approx 0.1$  M). For oxygen, the quenching efficiency shows, in general, a small increase with increasing oxygen pressure. This deviation can be attributed both to a slight quenching of the excited state of the scintillator and to a "static" quenching effect. In most systems studied, the rate constant for quenching of the solvent is approximately the same as the rate constant for transfer of energy from the solvent to the scintillator. An alternative mechanism to explain the high-energy-induced luminescence involving ionic species is briefly considered.

84. Dugan, L.R., Jr., and P.W. Landis.

Influence of High-Energy Radiation on Oxidation of Oleic Acid and Methyl Oleate. J. Am. Oil Chem. Soc., 33, 152-54(1956).

Gamma radiation from Cobalt 60 influences the oxidation of oleic acid and methyl oleate even at low temperatures. Determination of peroxide values, carbonyl values, and the  $E_{1\text{cm}}^{1\%}$  values at 224 millimicrons ( $m\mu$ ) revealed that high peroxide values could be obtained but that secondary products are formed in appreciable quantities. The products causing absorption at 224  $m\mu$  may be  $\alpha$ ,  $\beta$ -unsaturated ketones. The level of these substances can be increased by irradiation-oxidation in the presence of metal soaps such as cobalt stearate. Irradiation-oxidation of methyl oleate through a series of temperature ranges from 7.5°C to 55°C reveals a marked thermal activation effect. Peroxide values of 2000 me/kg or greater are obtained in 100 hours of reaction time.

85. Henley, E.J., W.P. Schiffries, and N.F. Barr.

Effect of Gamma Radiation on Aqueous Ethylene-Oxygen Solutions. A.I.Ch.E. Journal, 2, 211-14(1956).

Mixtures of ethylene and O<sub>2</sub> dissolved in water under pressures ranging from 200 to 700 psi were irradiated with Co 60 gamma-rays at a dose rate of 180,000 r./hr. G values as high as 200 were observed for aldehyde production. Increasing total pressure and dose

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were found to decrease these G values. Alcohols, acids,  $H_2O_2$ , and organic peroxides are also products of the reaction; however, the yields are much smaller.

86. Proskurnin, M. A., E. V. Barelko, and L. V. Abramova.

Oxidation of Organic Compounds. Sbornik Rabot Radiatsionnoy Khim., Akad. Nauk S.S.S.R., 106-10(1955).

Gamma radiation from Co 60 acting on the systems  $H_2O, O_2, BuOH$  and  $H_2O, O_2, PhCH_2OH$  causes an oxidative attack, which yields  $H_2O_2$  and the corresponding aldehydes, as well as BzOH in the last case. The yield of  $H_2O_2$  is constant at 3.1 molecules per 100 ev. The kinetic curves of accumulation of the aldehydes and the acid are shown. In addition an unknown phenolic substance is formed from benzyl alcohol.