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THE EFFECT OF RADIATION ON CHEMICAL REACTIONS

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PREFACE

For the past five years a research group at The University of Michigan has been studying the effect of high-energy radiation on chemical reactions. The activities of that group during the last half of 1955 are the subject of this report.

The primary support for this work has been from the United States Atomic Energy Commission through its sponsorship of a project in the Engineering Research Institute of the University. Support for research in the same field has also been received from Michigan Memorial-Phoenix Project No. 98, with funds contributed by the Chrysler Corporation. This report represents a collaborative effort of the personnel from both projects. These personnel have shared the same equipment and facilities in the Fission Products and Phoenix Project laboratories and have cooperated with each other in carrying out the overall objectives of the program.

In addition to acknowledging the financial support of the Atomic Energy Commission and the Michigan Memorial-Phoenix Project, the opportunity is taken here to express appreciation to several other organizations which have been most helpful. The Engineering Research Institute itself, through a director's grant, supplied approximately five thousand dollars worth of new laboratory equipment that made it possible to conduct a number of experiments which could not have been performed otherwise. The gift of equipment included an Aminco high-pressure reactor bomb, a Magna-Dash magnetically stirred reactor, a Brown recorder-controller, a Flexopulse electronic timer, a gas booster pump, and miscellaneous high-pressure stainless-steel piping and fittings. The Dow Chemical Company supplied a large cylinder of oxygen-free ethylene, together with a chemical analysis of the cylinder's contents. The Continental Oil Company supplied samples of nonene and dodecene which were used in several reactions. The Koppers Company, Inc., supplied an interesting comparison of the physical properties of polyethylene produced by gamma radiation here at the University with those of polyethylenes produced by commercial processes.

Special appreciation should also go to Dr. David E. Harmer, formerly with this project and now with the Dow Chemical Company, who gave generously of his own time in aiding some of the present laboratory assistants to master the techniques of conducting chemical reactions in gamma radiation fields.

Some of the material included in this report was presented at the International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, August 8-20, 1955. It is expected that most of the remainder of the subject material will be offered for publication in current scientific journals.

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ABSTRACT

During the period of this report investigations have been conducted on a half-dozen different types of reactions to determine the extent to which they are catalyzed or promoted by gamma radiation. The results of the experimental studies may be summarized briefly as follows:

A. The study of the polymerization of ethylene was continued to include a wide range of temperature and pressure. The products of polymerization ranged from liquids to waxes to solids. The radiation yields were fairly high, indicating chain-reaction mechanisms and giving some promise for eventual commercial application.

B. Various mixtures of 1,3-butadiene and styrene were copolymerized in different ways. Highest radiation yields were obtained in emulsion polymerization. The products were examined visually, but no physical properties were determined that would allow their potential use as plastics or elastomers to be clearly defined.

C. Sulfur dioxide was reacted with a number of individual olefins. Polymerization reactions generally took place very rapidly with high radiation yields. The products appeared to be plastic-like compounds with rather high melting points.

D. The Oxo reaction involving the condensation of hydrogen, carbon monoxide, and an olefin was the subject of considerable study. Solids, waxes, oils, and thin liquids were obtained as products; subsequent distillation and test of the fractions indicated the presence of aldehydes and alcohols in the product. For the runs made thus far, the radiation yields were not very high under the reaction conditions employed.

E. The chlorination of aromatic hydrocarbons was extended to include benzene, toluene, xylene, mesitylene, naphthalene, and ethyl benzene. In general, these aromatics react vigorously with chlorine at room temperature in the presence of gamma radiation. Gamma radiation tends to promote the addition of chlorine to the benzene nucleus more than the substitution of chlorine for hydrogen either on the nucleus or on a side chain.

F. Trichloroacetic acid was produced by the chlorination of chloral hydrate in the presence of gamma radiation. The reaction was fairly rapid and is being subjected to further study.

In addition to the experimental chemical reaction studies, a speculative plant design was developed to illustrate procedures which might be economically feasible for radiation chemical processing. The process chosen for study was the chlorination of benzene to produce benzene hexachloride, a well-known insecticide. The present commercial process for the latter compound utilizes ultraviolet light, so that a comparison of the approximate costs of the gamma-radiation reaction and the ultraviolet-light reaction could be made. On the basis of somewhat limited information, which required estimation of radiation costs, it was concluded that the gamma-radiation process is not impracticable and could compete with the ultraviolet process. More precise costs of gamma radiation will lead to a more firm comparison of the two processes.

INTRODUCTION

The promotion of chemical reactions by radiation is not a new field, as exemplified by the fact that ultraviolet light has long been employed in such studies. However, the use of high-energy radiation, or ionizing radiation as it is often referred to, is comparatively recent since it dates from the discovery of radium and the invention of the x-ray machine. Because of the somewhat limited amount of radiation available from radium or from x-ray machines, only a limited amount of work had been done on the influence of such radiation on chemical reactions. The advent of the atomic energy program, however, changed this situation. The vast quantities of radiation that are released either directly or indirectly as a result of nuclear fission have stimulated many research activities to discover uses for high-energy radiation, and the promotion of chemical reactions appears to be one of the more promising applications.

Neutron, gamma, and beta radiation are released directly in a nuclear reactor. Some materials which may be circulated through the reactor may deliver gamma or beta radiation. Finally, the fission products which may be recovered from the spent fuel are very copious sources of gamma and beta radiation. At the present time these highly radioactive fission products are considered a waste material which requires rather expensive storage to prevent contamination of the surroundings. If the radiation from these fission products can serve as a catalyst in useful chemical reactions, a difficult waste-disposal problem may be alleviated to some extent and overall productivity increased at the same time.

Ideally, a program to find chemical reactions promoted by fission-product radiation might well be carried out with fission-product sources; however, in the present stage of development of the atomic energy program, fission-product sources are not readily available. It has been necessary, therefore, to conduct investigations with other sources of radiation. Since beta radiation has a low penetrating power, it is not expected that this radiation from fission-product sources could be used effectively as catalysts because the fission products would have to be in almost direct contact with the chemical reactants. This could result in dispersal of the fission-product catalyst and, consequently, a very difficult contamination problem could arise. On the other hand, gamma radiation is extremely penetrating, and, therefore, chemical

reactions which are catalyzed by gamma radiation would constitute very favorable uses for the fission products. The fission products could be isolated in sealed stainless-steel containers which would transmit the radiation and the fission products then could be kept completely isolated from the chemical reactants. In the absence of fission-product sources and because of the expected use of gamma radiation, the experimental work at Michigan has been conducted with cobalt-60 sources. Although the gamma radiation from cobalt-60 has a somewhat shorter wavelength than that from fission products, it is believed on the basis of considerable scientific evidence that the chemical effects will be very similar.

The Fission Products Laboratory is equipped with two powerful cobalt-60 sources. One of these is nominally rated at ten kilocuries and has an actual strength of about three kilocuries; the other is nominally rated at one kilocurie and has an actual strength of about 300 curies. The Phoenix Project has acquired a new cobalt-60 source which is estimated to have a strength of about four kilocuries, though no accurate calibrations have yet been made. The reactions described in the subsequent sections were all carried out in the presence of one or more of these sources. The intensities of radiation were determined at the location of the chemical-reaction equipment by means of ferrous sulfate dosimetry and electronic ionization type instruments. These procedures have been described in previous reports along with a number of other chemical reactions which have been investigated. The reader is referred to the Bibliography for a complete description of the earlier work.

EXPERIMENTAL WORK

A. POLYMERIZATION OF ETHYLENE

The study of the effect of gamma radiation on the polymerization of ethylene was initially reported by Lewis.¹⁷ This work has been extended with the primary emphasis upon the effect of temperature variation at pressures in the region of from 75 to 100 atmospheres. A portion of this work was reported in Progress Report 7⁴ of this laboratory and the work reported here is a continuation of these earlier experiments.

Two grades of ethylene were used in this investigation. The first study involved commercial ethylene as available in cylinders from several industrial concerns; later, the ethylene was a special grade having a very low oxygen concentration.

1. Equipment Used.—The majority of the runs were conducted in the

high-pressure stainless-steel reactor designed and reported by Lewis.¹⁷ A set of heaters built by Lewis was placed around the bomb, even when heating was not required, in order to insure that the radiation flux would be the same in all cases. Some difficulty was encountered at high temperatures with gas leakage through the thermocouple junction at the head of the bomb. This thermocouple was inserted into the pressure region through a port that was sealed with a Teflon gasket. After several hours irradiation at high temperatures and pressures, leaks developed in the gasket and vented the ethylene to the atmosphere. To correct this situation, a new reactor head was designed with an external entry thermowell. The thermowell extended into the center of the bomb to the same relative region as previously, but there were now no high-pressure seals to contend with. At steady-state conditions the temperature measurement was the same as previously.

The design specifications for the new reactor head are found in Fig. 1. The head was turned from a solid piece of A.I.S.I. 304 stainless steel. The thermowell was constructed of 1/4-inch high-pressure A.I.S.I. 316 stainless-steel tubing welded to the head with A.I.S.I. 316 stainless-steel welding rod. The design conditions were 2000 psi at 200°C. All dimensions are to be found in Fig. 1. The new head has been used satisfactorily at the design conditions under radiation. The original head and reactor body have been completely described by Lewis.

Some of the runs were made in a Standard Aminco reactor supplied by a grant from the Engineering Research Institute. An American Instrument Company 4-3/8-inch series reaction vessel constructed of 316 stainless steel (Cat. No. 406-25J3), 3-5/16-inch internal diameter by 10-inch internal height, was purchased for this work. This reactor was used in runs where pressures higher than 2000 psi were encountered. A pressure gage was attached to the head of the reactor for pressure readings. The bomb was equipped with a thermowell for thermocouple temperature measurements. The reactor was equipped with a heater for high-temperature work. A photograph of the disassembled reactor is to be found in Fig. 2.

2. Experimental Procedure.—The same loading and cleaning procedure was followed for each run. The reactor was cleaned with boiling xylene and rinsed with acetone and distilled water. The vessel was sealed mechanically and was pressure tested with nitrogen overnight at a pressure of 1000 psi or greater. On the day of loading, the nitrogen was vented to the atmosphere and the bomb was evacuated to a pressure of less than one millimeter of mercury. The ethylene was loaded to a desired pressure computed beforehand to give the approximate pressure condition desired at the reaction temperature. The reactor was placed in the source cave and brought to the desired temperature with the source in the well. When this predetermined temperature was reached, the source was raised into the irradiation position for

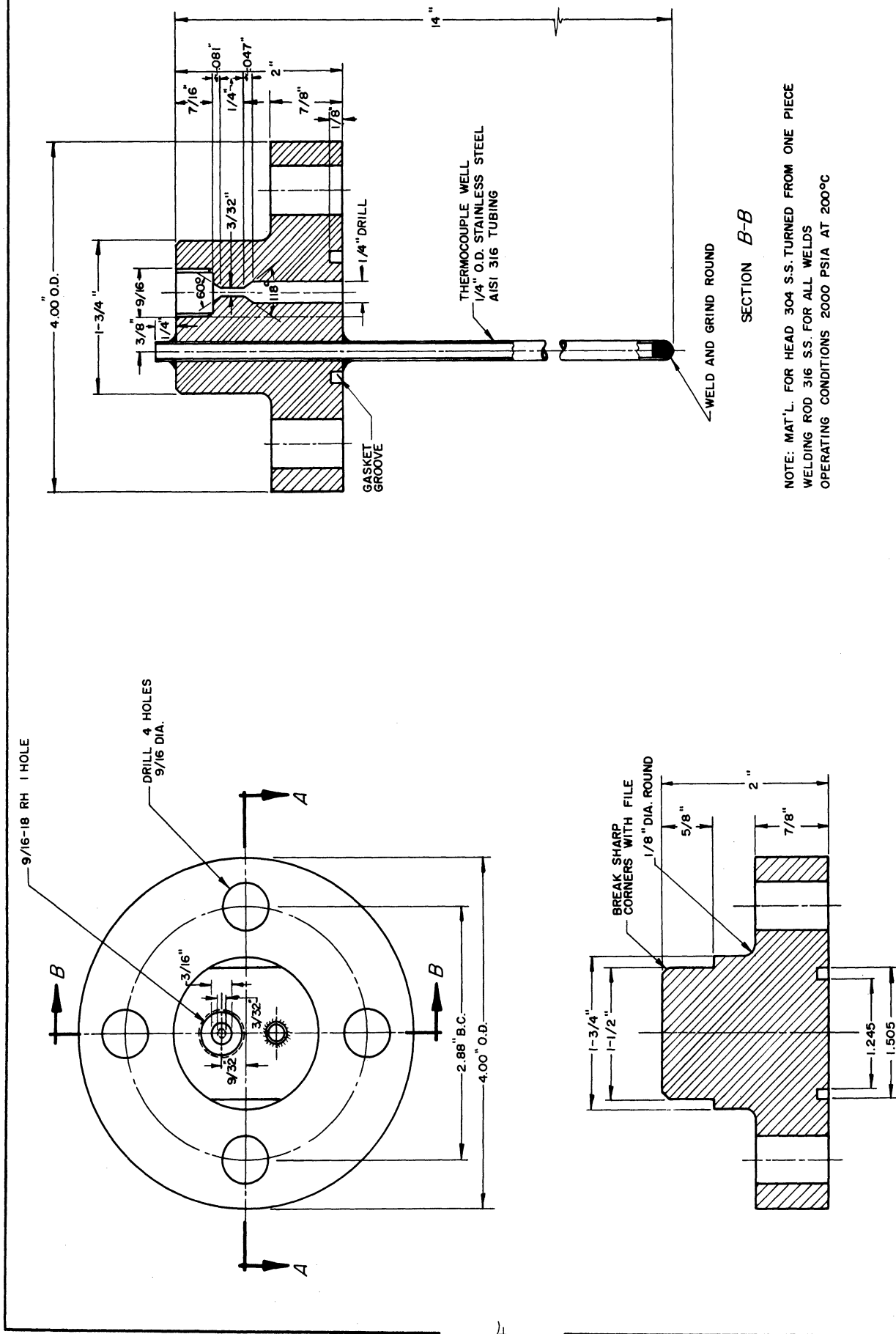


Fig. 1. Working drawing of the new reactor head for the Lewis reactor.

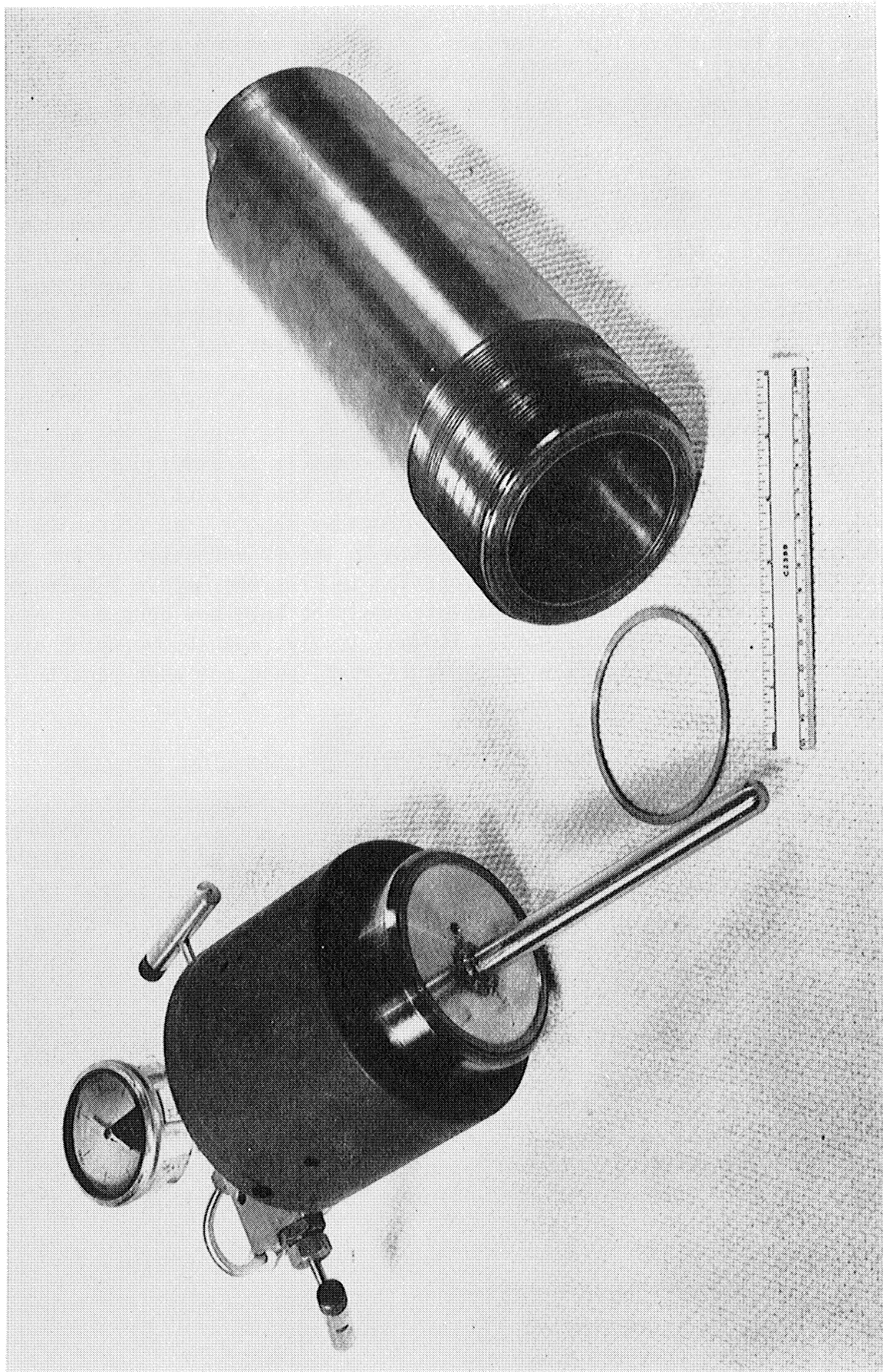


Fig. 2. Disassembled view of the Aminco reactor.

a specific time. During this irradiation period, temperature and pressure readings were made at various intervals. After the desired accumulated dose had been obtained, the excess ethylene was vented from the reactor. The reactor was then disassembled and the product was recovered and stored for further analysis.

3. Experimental Results.—A complete summary of the reaction conditions and polymer yields from the irradiation of commercial ethylene is given in Table 1. White, curdy, solid polymers were formed at reaction temperatures from 6° to 130°C. A white wax formed at about 160°C, and above this temperature the product was an opaque liquid that separated into two layers after standing for several hours. The top layer was colorless and the bottom layer contained a finely divided solid. The yield of polymer is presented as the A value,¹⁷ gm moles of ethylene reacted/ (metric ton of ethylene charged) (megarep of gamma radiation). The rep is based on the absorption of 93 ergs per gram. From the scatter of the data it is difficult to determine the effect of temperature on the yield since the largest yields were at 39° and 217°C. A portion of Table 2 from Progress Report 7 is presented here in Table 1. The reason for this duplication in the presentation of the data is that the analyses of the products reported in Progress Report 7 were not complete at the time of writing. Complete analyses have now been made and are presented here. Runs 145839, 145833, 145845, 154712, and 145858, which are low-temperature and intermediate-temperature runs, have not been reported before.

TABLE 1. PRODUCTS FROM THE IRRADIATION OF COMMERCIAL ETHYLENE

Run on Page	Reaction Temp. °C	Reaction Pressure Avg Psia	Radiation Dose Krep/Hr	Total Radi- ation Dose Megarep	Radiation Yield A*	Polymer State	Tensile Strength Psi
145839	6	755	61.0	4.20	1340	Solid	3050
145833	8	985	59.0	5.46	1630	Solid	3075
145800	13	1145	63.0	4.10	1530	Solid	3350
145801	13	875	63.0	5.28	2270	Solid	3100
145807	39	1380	63.0	4.47	3040	Solid	2520
145808	88	1325	26.5	1.90	490	Solid	
145812	90	1300	62.5	5.85	433	Solid	
145845	132	1700	43.0	4.05	955	Solid	
154712	160	1490	31.0	2.76	945	Wax	
145848	190	1125	25.0	2.88	1300	Liquid	
145814	217	1100	33.0	3.77	4030	Liquid	
145813	220	1175	62.5	4.86	1400	Liquid	

$$*A = \frac{\text{gm moles reacted}}{(\text{metric ton charged}) (\text{megarep})}$$

The commercial ethylene and, consequently, the gas compositions are the same as presented by Lewis.¹⁷ This approximate analysis is found in Table 2 with the analysis of oxygen-free ethylene as supplied by the Dow Chemical Company for this work.

TABLE 2. COMPOSITIONS OF ETHYLENE USED

Material	Percent O ₂	Percent CO	Percent CO ₂	Percent N ₂	Combustibles
Commercial	.02	.05	.37	1.7	.8% Pentane
Oxygen Free	<10 ppm	Nil	Nil	Nil	<10 ppm Acetylene 1.5% Ethane

A summary of reaction conditions and polymer yields from the oxygen-free ethylene is presented in Table 3. The product had the same appearance as that from the commercial ethylene. In general, the A values are higher than the A values for commercial ethylene at the same temperatures. Harmer¹⁴ showed that small amounts of oxygen inhibited the reaction of chlorine with aromatic hydrocarbon. A comparison of Tables 1 and 3 indicates that oxygen may inhibit the polymerization reaction of ethylene in a similar manner.

TABLE 3. PRODUCTS FROM THE
IRRADIATION OF OXYGEN-FREE ETHYLENE

Run Number	Reaction Temp. °C	Reaction Pressure Avg Psia	Radiation Dose Rate Krep/Hr	Total Radiation Dose Megarep	Overall Radiation Yield A*	Polymer State
154039	8	1800	24.2	9.38	3340 ^a	Solid
154038	13	810	54.0	7.46	1990 ^a	Solid
154011	26	1000	24.4	3.98	3280	Solid
154034	63	1370	25.0	3.08	2450	Solid
154032	103	1310	27.5	2.90	970	Solid
154007	210	2400	10.5	2.40	13,000	Liquid

*
A =
$$\frac{\text{gm moles reacted}}{(\text{metric ton charged}) (\text{megarep})}$$

a. Not believed true indication as excessive radiation was given.

4. Evaluation of the Polymer Product.—Table 4 is a summary of the physical properties of the polyethylene produced from commercial ethylene under gamma radiation. Melting points of the solid and waxy products were taken on a melting-point bar as described in previous reports.^{17,7} Melting points of the liquids were observed in small tubes of the polymer which were allowed to warm up after being frozen in a dry-ice bath; two measurements were made on most samples and both values are listed in Table 4. It should be emphasized that only the lower limit of the melting-point range is presented. Because each product was a composite of polymers of varying molecular weights, a range of melting points was always observed. In general, the larger the dose of radiation applied, the larger the range of molecular weights because of the greater amount of cross linkage of polymer molecules in a high radiation field. The points at which melting could be detected first have been plotted in Fig. 3 as a function of reaction temperature.

Solid products which were produced in appreciable quantity were pressed in a one-compartment mold at 1500 psi and 150°C for five minutes. Specimens were punched from the molded polymer sheet and placed in an Instron Tensile Test Machine. The tensile strengths were determined at a head and/or jaw speed of ten inches per minute. These tensile strengths are presented in Table 1.

Specimens were also punched from the molded polymer sheet for the determination of melt viscosity. The melt viscosities of these solid polymers were obtained in a parallel-plate plastometer at about 137°C. Viscosities of the liquid products were determined in a modified Ostwald pipette. Molecular weights were estimated from the viscosities by the method of Dienes and Klemm⁹ and are shown in Fig. 3 as a function of reaction temperature. Because there is a range of molecular weights formed in the polymerization process, the molecular weights presented in Table 4 and Fig. 3 are only approximate, but a general trend is indicated.

Densities of the solid polymers were determined by the Archimedes principle, while those of the liquids were measured by weighing in a calibrated pipette. The numerical values of the densities are found in Table 4. Figure 4 is a plot of the densities as a function of the reaction temperatures. The crystallinities or the degree to which the molecules are arranged in parallel positions were determined from the densities by the method of Kirk-Othmer.¹⁶ These crystallinities are found in Fig. 4 as a function of the reaction temperature.

A portion of the polymer product from run no. 145833 was supplied to Koppers Company, Inc., for analysis and comparison with their own polyethylene products. The comparative analysis as run by the Koppers Company appears in Table 5. It is felt, however, that a range of melting points and molecular

TABLE 4. PHYSICAL PROPERTIES OF POLYETHYLENE
PRODUCED BY GAMMA RADIATION OF COMMERCIAL ETHYLENE

Run Number	Reaction Temp. °C	Lower Limit Melting Range °R	Density gm/cm ³	Crystallinity Percent	Approximate Molecular Weight
145839	6	724 734	0.953	77.5	25,200
145833	8	723 737	0.945	69	26,500
145800	13	718	0.950	77	24,150
145801	13	723 719	0.943	73.5	34,500
145807	39	717 720	0.940	72	37,100 and 38,600
145808	88	682	0.937	70	Samples
145812	90	677	0.930	66	Too small
145845	132	648 653	0.912	56	Too small
154712	160	487 499	0.879	36	Too small
145848	190	393 388	0.849	Liquid	8,840
145814	217	371 382	0.725	Liquid	5,690
145813	220	395 391	0.860	Liquid	8,950

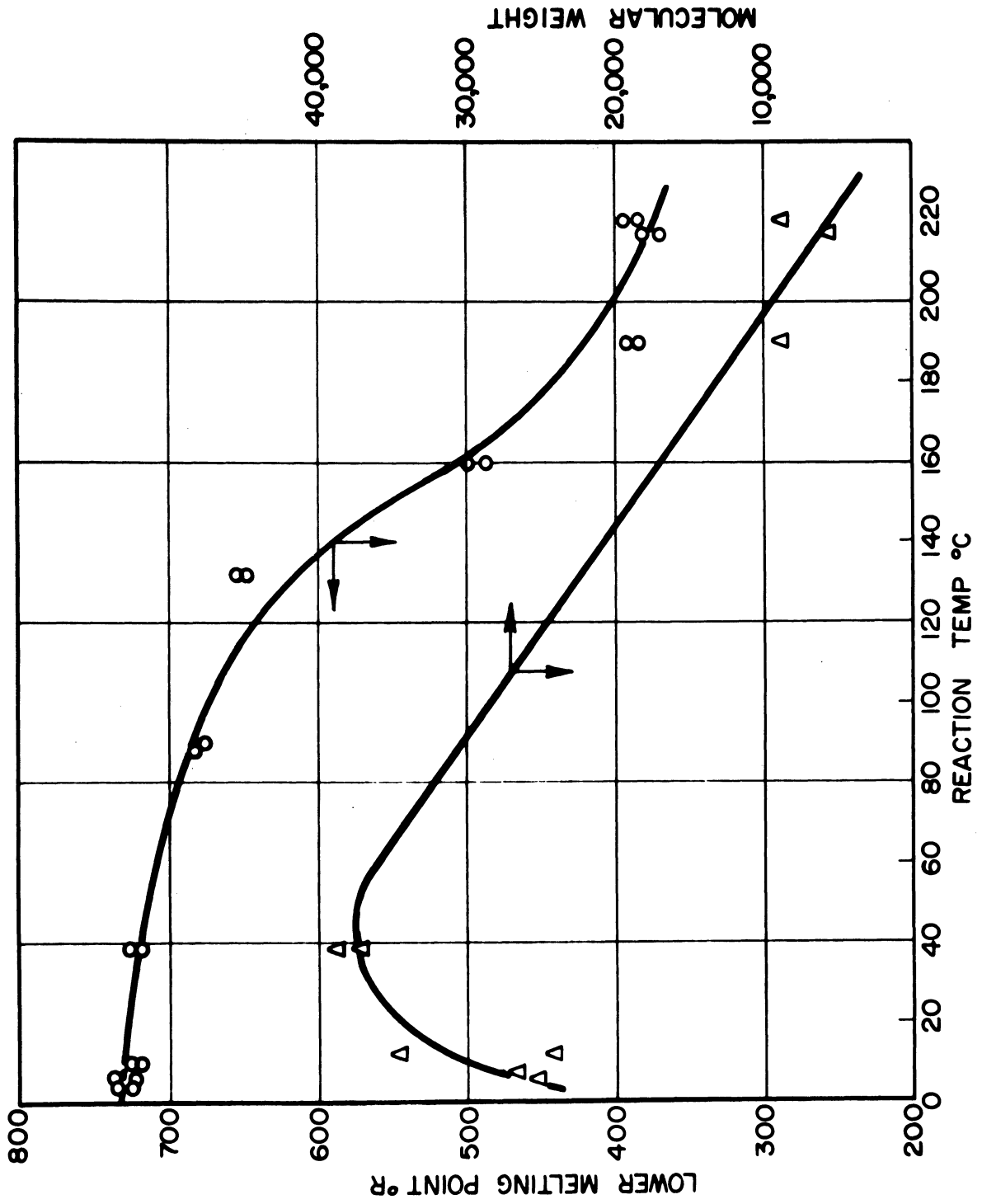


Fig. 3. Melting point and molecular weight of polyethylene.

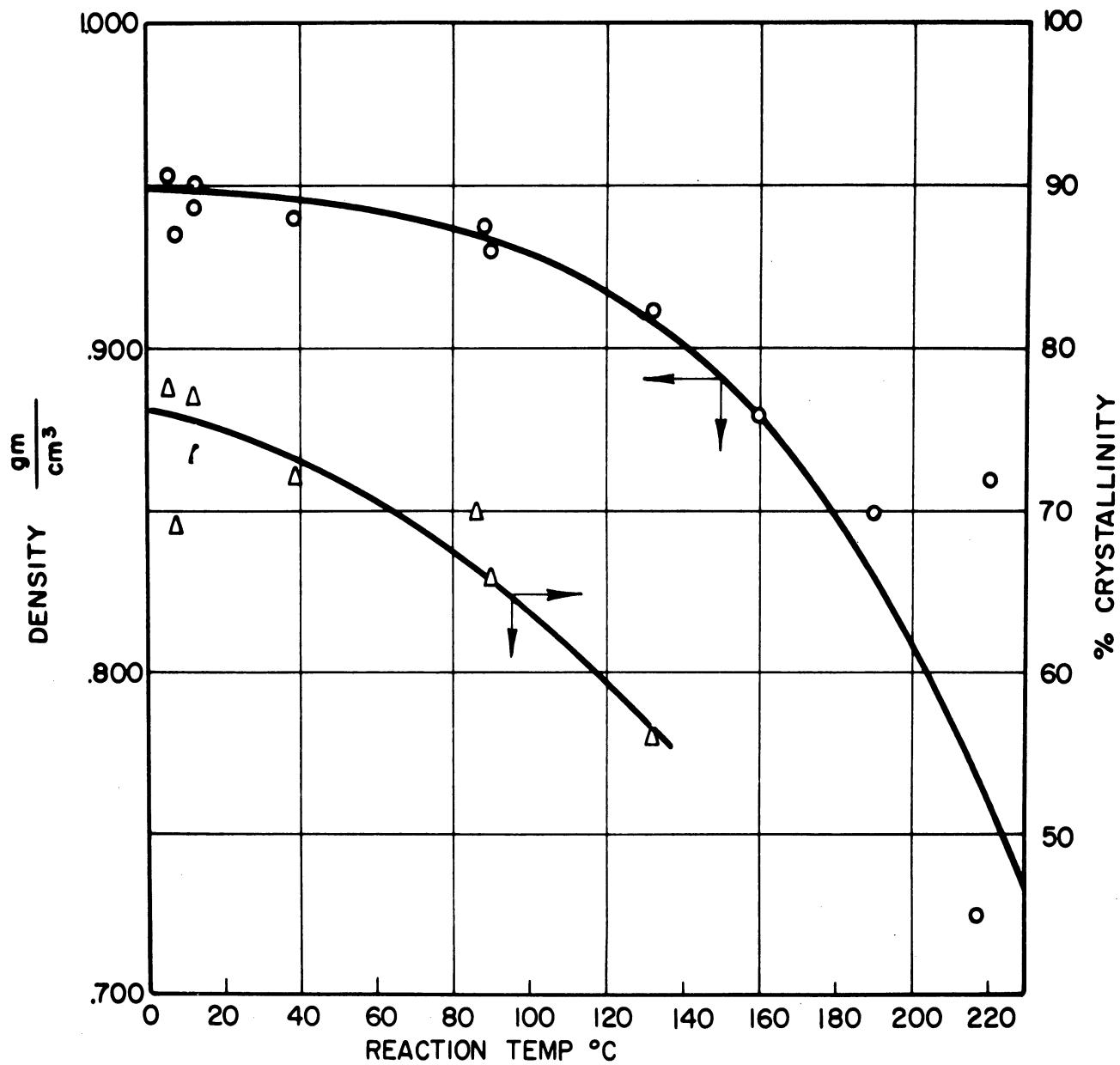


Fig. 4. Density and crystallinity of polyethylene.

weights were present in the gamma-initiated polymer instead of the single values that are indicated. This is shown in the case of the melting-point data for the same run taken in this laboratory and found in Table 4.

TABLE 5. COMPARISON OF SOME PROPERTIES OF GAMMA-INITIATED AND CONVENTIONALLY PRODUCED POLYETHYLENES

Polyethylene	Sp Gr	MP, °C ^(c)	Molecular Weight ^(d)
Gamma initiated ^(a)	0.9459	124.5	42,800
"Super Dylan" ^(b) (Ziegler)	0.95-0.98	135-139	40,000-120,000
"Dylan" ^(b) (conventional)	0.91-0.92	114-116	20,000-30,000

(a) Run 145833.

(b) Koppers trade marks.

(c) Crystalline melting point under crossed Nicol prisms.

(d) Determined from viscosity of decalin solutions at 135°C.

$$\text{Intrinsic viscosity} = 1.141 \times 10^{-3} \times (\text{mol. wt})^{0.66}.$$

The physical properties of the polyethylene produced from oxygen-free ethylene have not been completely evaluated as yet. For this reason the presentation is delayed until complete analyses can be made.

From the results presented in Tables 1, 3, and 4 it is clear that a wide variety of polymers of ethylene were produced in the radiation reaction. From the results of oxygen-free ethylene polymerization it was seen that oxygen had a definite inhibiting effect upon the reaction. The yields were sufficiently high to consider the process feasible for commercial applications. At this stage, economic studies are in order for the determination of the possible competitive position of polyethylenes produced by radiation processing with respect to the position of those produced by conventional processes.

B. COPOLYMERIZATION OF BUTADIENE-STYRENE MIXTURES

Preliminary investigations have been made on the effect of gamma radiation upon the copolymerization of 1,3-butadiene and styrene and upon emulsions of 1,3-butadiene and styrene in various soap solutions. These

preliminary experiments involved small quantities of reacting materials in glass vials which were given various doses of gamma radiation. The amount of reactant used in the preliminary experiments was relatively small and no attempt, beyond a mere visual inspection, was made to evaluate the products obtained.

1. Equipment Used.—All these investigations were carried out in heavy-walled vials blown from thick pyrex tubing. Figure 5 is a diagram of the vials used and the average dimensions of the vials; when sealed, they will safely withstand pressures up to 400 psi. In this work the pressures encountered with 1,3-butadiene are of the order of 50 psia.

A schematic diagram of the gas-loading rack, which was constructed of heavy pyrex tubing to facilitate loading the vials, is shown in Fig. 6. The rack was equipped with three loading lines, one of which was used as an emergency vent to a hood. A gas-scrubbing column and a gas-drying column, which were incorporated in one of the load lines, could be used to remove any impurity that was thought to be present in the gas, and a cold trap to condense vapors that might have harmed the vacuum pump was also included. The standard high-vacuum "Duo-Seal" pump capable of producing a vacuum of less than 100 microns of Hg was used in this work. Dry ice in a 60-40% mixture of chloroform and carbon tetrachloride provided a temperature of -75°C for the condensing baths in both the cold trap and the cold bath around the vial.

2. Chemicals Used in the Reactions.—Some of the chemicals used in these preliminary experiments were obtained from commercial sources and others were prepared in this laboratory. The analyses and methods of preparation were as follows:

1,3-butadiene

Grade A: 0.4% butane and/or butene
0.5% acetylene
0.1% phenyl β -naphthylamine inhibitor
1,2-butadiene also present in unknown amount

Grade B: 99.77% 1,3-butadiene

Normal butane, butenes, and possibly a trace of acetylenes (0.23%).

Styrene

500 ml distilled under vacuum from stabilized reagent-grade styrene, rejecting initial 50 ml and final 150 ml.

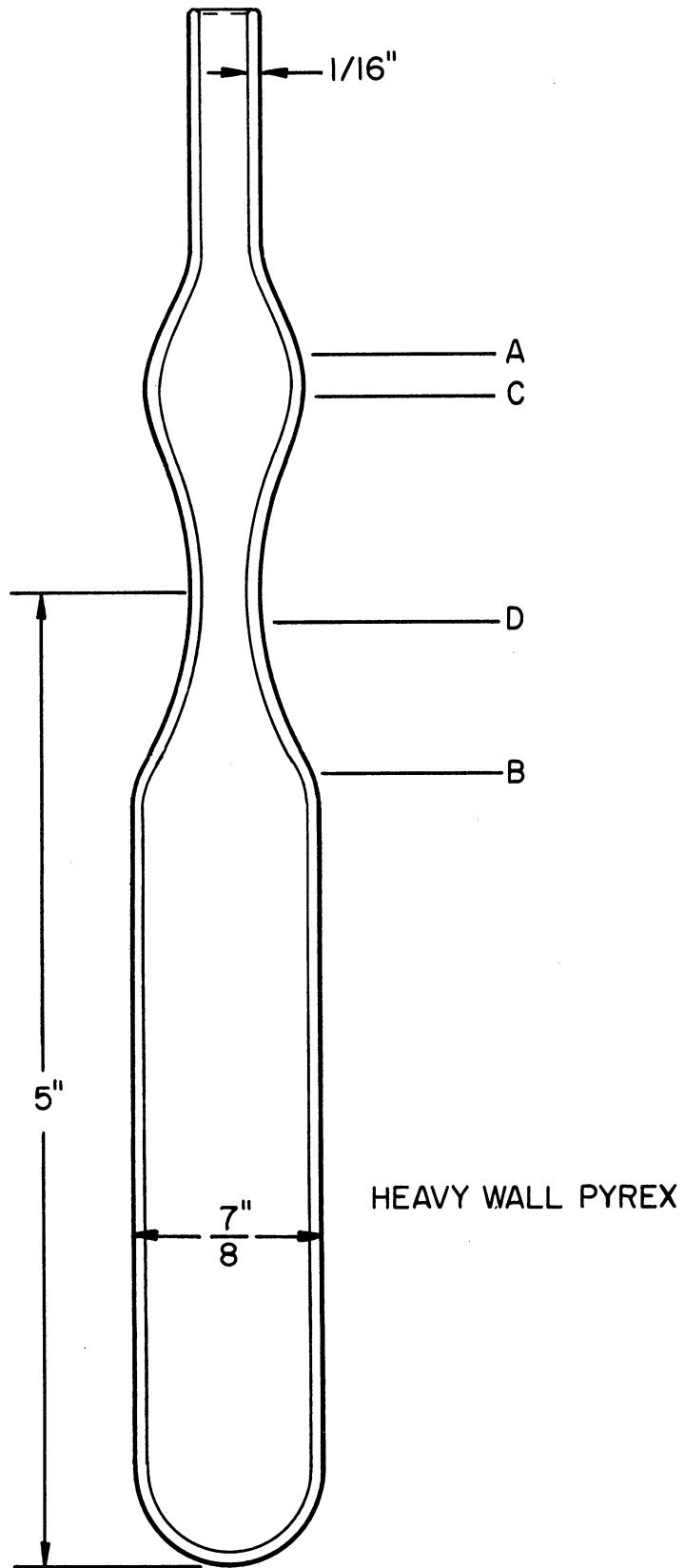


Fig. 5. Heavy wall pyrex vials used in small batch experiments.

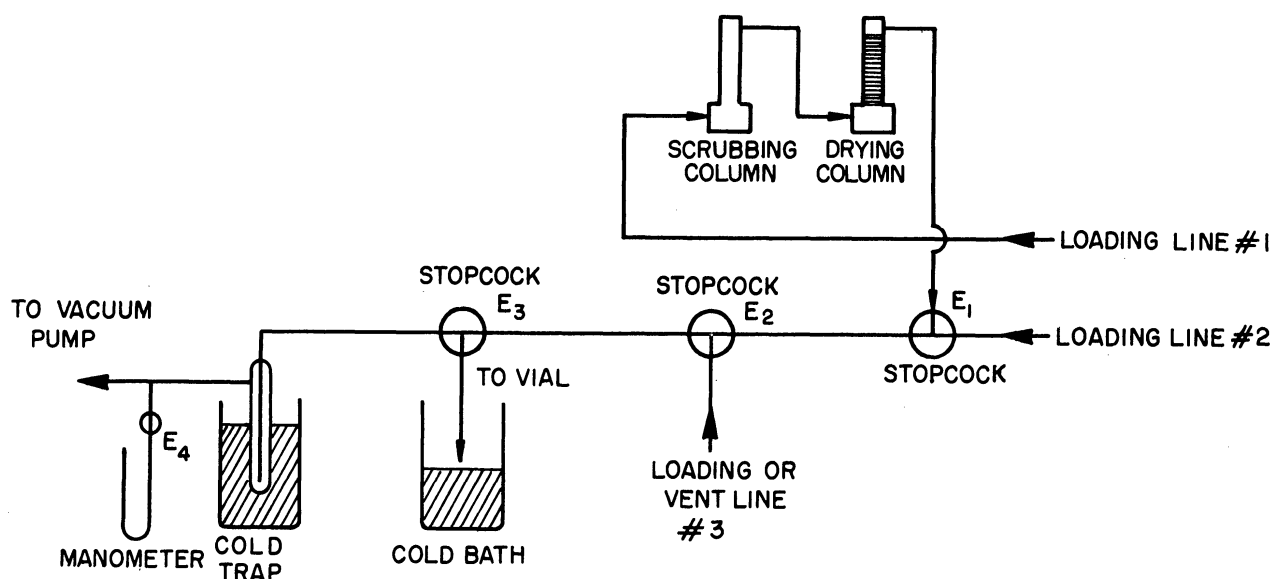


Fig. 6. Schematic diagram of vial-loading equipment.

Nacconal and Alconox Solutions

Saturated solutions in distilled water were prepared in the laboratory and used throughout the experiments.

Other Soap Solutions

Solutions of sodium stearate, calcium stearate, zinc stearate, and lead oleate were prepared from reagent grades and used throughout the experiments.

3. Experimental Procedure.—A standard method for loading, irradiating, and handling the vials was adopted and followed in all cases. This procedure was as follows.

Emulsifying solutions and liquid reactants at room temperature were introduced into the vial by pipette, weighed by difference, and frozen in the cold bath. The vial was connected to the system by means of high-pressure tubing and placed in the cold bath. The whole system was evacuated to less than 1-mm-Hg pressure; a high vacuum was necessary to avoid possible inhibition of the reactions by the oxygen of the air.

In the first eight runs the Grade A 1,3-butadiene was loaded directly to the vial through loading line 2 shown in Fig. 6. In subsequent runs an attempt was made to remove the amine inhibitor thought to be present in the

gas by using loading line 1. The gas was bubbled through a 6 Normal sulfuric acid solution and dried in a calcium chloride tower before it was condensed in the vial. The Grade B 1,3-butadiene and all other gases used in later experiments were loaded directly to the vial through loading lines 2 and 3.

After introduction of the desired reactants, a check was made on the line pressure by connecting the vial to the vacuum-pump manometer. The temperature of the cold bath was low enough so that if sufficient time was allowed for complete condensation to take place, the vapor pressure of butadiene was below atmospheric pressure and the vial was ready for sealing.

Stopcock E₃ was then closed and the cold bath lowered to permit heating by the natural-gas—oxygen torch of the region AB on the vial, as shown in Fig. 5. After uniform heating of this region to a temperature close to the softening point, the tip of the flame was concentrated on the region CD, which rapidly became soft. Due to the weight of the vial, the region CD elongated and, since the external pressure was higher than the internal pressure, the wall collapsed upon itself, the end result giving a fine tip capable of withstanding high pressures.

The vial was exposed to radiation at room temperature for various predetermined periods of time. After removal from the source of radiation, the vial was cooled to -75°C and broken at the tip. The vials were then placed in the hood and allowed to warm to room temperature to permit escape of unreacted gases. The product was then recovered and processed to eliminate the soap, water, and unreacted styrene. It was then weighed and stored.

4. Experimental Results.—The results of the copolymerization of 1,3-butadiene and styrene are presented in Tables 6 and 7. The two grades of butadiene used are presented separately. No evaluation of the polymer products was attempted beyond mere visual inspection. The observed state of the polymer is described on the tables in the last column under remarks. The yields are recorded with the total doses of radiation received by each vial. These values, together with the molecular weight, permit a standard A value to be calculated. The A value is the same as that described previously for the polymerization of polyethylene.¹⁷ It is calculated from the expression:

$$A \frac{\text{gram moles reacted}}{(\text{metric ton charged}) (\text{megarep})} = \frac{\% \text{ yield} \times 10^6}{(\text{mol. wt}) (\text{dose, megarep})}$$

When two reactants were charged, the weight average molecular weight used in the above formula was determined by the relation:

$$\text{Mol. wt}_{\text{avg } 1,2} = \frac{(\text{mol. wt}_1) (\text{wt } 1 \text{ charged}) + (\text{mol. wt}_2) (\text{wt } 2 \text{ charged})}{\text{wt } 1 \text{ charged} + \text{wt } 2 \text{ charged}}$$

TABLE 6. GRADE A 1,3-BUTADIENE-STYRENE COPOLYMERIZATION AT 10°-15° CENTIGRADE

Components	Run on Page	Run	Total Weight Charged gm	Weight of Product gm	Percent Yield	Dose Rate Rep/Hr	Dose Megarep	A Value	Remarks
B	154832	9	3.5	0.2	5.7	166,000	37.4	28.2	sticky substance
S	154832	6	4.0	5.5	-	125,000	28.1	-	viscous-creamy-polystyrene
B + S	145831	2	2.3	trace	≈ 0	120,500	30.44	0	yellow-cream flakes, could be fibrous
B + S	145831	5	2.2	0.15	6.8	95,000	20.78	43.9	yellow-crystalline
B + S	145831	1	2.4	trace	≈ 0	0	control	0	
B + S + K ₂ S ₂ O ₈ + H ₂ O	145831	3	4.1	0.3	7.3	115,000	26.92	38.6	yellow-curdy-waxy
B + S + K ₂ S ₂ O ₈ + H ₂ O	145831	4	4.4	0.9	20.4	138,000	31.57	94.0	milky liquid (So)
B + S + Na ₂ CO ₃	145832	7	6.6	0.9	13.6	148,000	33.3	61.7	white-granular solid (So)
B + S + Na ₂ CO ₃	145835	14	7.5	1.3	17.3	133,000	3.26	793.3	rubbery-white-spongy substance
B + S + Na ₂ CO ₃	145838	34	4.9	0.5	10.2	148,000	6.99	198.1	white precipitate (So)
B + S + Na ₂ CO ₃	145835	15	8.3	0.9	10.8	0	control	-	yellow-waxy
B + S + Alconox soln.	145835	12	7.4	1.0	15.5	148,000	3.63	576.2	brown-curdy
B + S + Alconox soln.	145835	13	5.4	< 0.1	≈ 0	0	control	-	flaky white (So)

TABLE 7. GRADE B 1,3-BUTADIENE-STYRENE COPOLYMERIZATION AT 10°-15° CENTIGRADE

Components	Run on Page	Run	Total Weight Charged gm	Weight of Product gm	Percent Yield	Dose Rate Rep/Hr	Dose Megarep	A Value	Remarks
B + S	145840	41	2.7	0.05	1.85	140,000	8.88	31.1	cream-yellow-fibrous-some crystals
B + S	145840	40	1.6	trace	≈ 0	0	control	-	
B + S + Alconox soln.	145840	42	7.7	1.2	15.6	127,000	8.04	299.2	spongy white polymer
B + S + Alconox soln.	145840	43	8.5	0.3	3.5	0	control	-	yellow hard polymer
B + S + Na Stearate soln.	145842	46	5.6	0.8	14.3	140,000	3.7	576.8	milky liquid (So)
B + S + Na Stearate soln.	145842	47	5.6	trace	≈ 0	0	control	-	
B + S + Na Stearate soln.	145843	52	4.7	0.5	10.6	155,000	4.3	330.6	curdy white polymer (So)
B + S + Na Stearate soln.	145843	53	7.3	0.3	4.1	0	control	-	cream-crystalline-flaky
B + S + Zn Stearate soln.	145842	50	6.7	trace	≈ 0	140,000	3.87	0	
B + S + Zn Stearate soln.	145842	51	6.5	trace	≈ 0	0	control	-	
B + S + Zn Stearate soln.	145844	59	5.9	2.2	37.3	155,000	6.75	839.1	milky white liquid (So)
B + S + Zn Stearate soln.	145844	58	7.0	trace	≈ 0	0	control	-	
B + S + Ca Stearate soln.	145842	48	6.0	1.0	16.7	155,000	4.29	604.6	milky white liquid (So)
B + S + Ca Stearate soln.	145842	49	6.3	trace	≈ 0	0	control	-	
B + S + Ca Stearate soln.	145844	57	8.0	2.7	33.8	155,000	6.75	804.2	curdy white solid (So)
B + S + Ca Stearate soln.	145844	56	7.1	trace	≈ 0	0	control	-	
B + S + Pb Oleate soln.	145843	54	5.8	2.7	46.5	163,000	4.51	1,489.1	yellow layer lighter than water (So)
B + S + Pb Oleate soln.	145843	55	5.1	< 0.1	< 2	0	control	-	brown-flaky

Abbreviations: B = 1,3-butadiene
 S = styrene
 So = possible soap and water left

A perusal of the first equation indicates that conclusions as to the rate or extent of a reaction, based solely on A values, could be misleading. When the yield approaches 100% in a finite reacting mixture, large quantities of radiation may be applied with small change in yield. Thus, an infinite dose conceivably could be given to a 100%-completed reaction, resulting in a zero A value. Dosimetry calibrations presented by Lewis *et al.*¹⁸ were used throughout this work in calculating radiation doses.

Table 6 presents the results of a number of experiments performed with the Grade A butadiene and styrene. Except for the butadiene-styrene-Nacconal and the butadiene-styrene-Alconox products, which showed interesting elastomeric properties, the amount and quality of the products obtained were generally low.

The results obtained with Grade B inhibitor-free 1,3-butadiene are presented in Table 7. In some runs the soap and water were not completely removed from the products and it is believed that the higher yields obtained are partly due to this fact.

Comparing the results shown in Table 6 and in Table 7 for the butadiene-styrene and for the butadiene-styrene-Alconox copolymerizations, it appears that the effect of the amine inhibitor contained in the Grade A 1,3-butadiene was slight. Although the yields obtained in the 1,3-butadiene-styrene copolymerization reactions were not particularly high, it may be seen that generally the percent yields of the controls were relatively insignificant when compared to those of the irradiated samples.

C. COPOLYMERIZATION OF SULFUR DIOXIDE WITH VARIOUS OLEFINS

The copolymerization of sulfur dioxide with olefins has been of interest for many years. The resulting polysulfone is a thermoplastic resin having many physical properties similar to those of some major commercial plastics. There are inherent deficiencies that require correction before they are substituted for conventional plastics, but the large quantities of SO₂ and olefins available at modest cost have led to considerable research on the polysulfone resins.

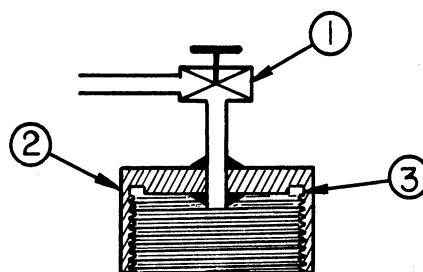
The reactions between SO₂ and olefins proceed under additive catalysts such as peroxides, nitrates, and other oxidizing agents,²⁷ and it has also been found that actinic light will catalyze the reaction.²⁷ Preliminary studies in this laboratory by Lewis¹⁷ showed that gamma radiation catalyzed the copolymerization of SO₂ and ethylene.

In the past year much work has been done on the copolymerization of

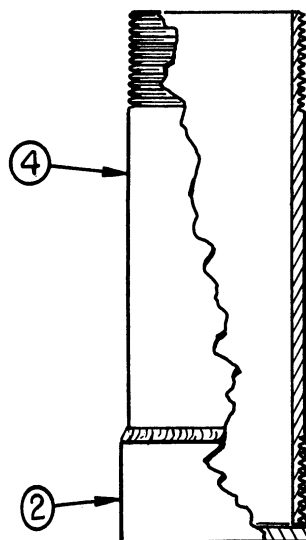
sulfur dioxide with other olefins. Preliminary experiments have been carried out in glass vials, and in larger-scale experiments a stainless-steel reaction vessel was used. The olefins that have been employed are propylene, butene-1, butene-2, isobutylene, 1,3-butadiene, nonene, dodecene, and styrene. The reactions have been carried out primarily at room temperature and under the vapor pressures of the mixtures.

1. Equipment Used.—In the preliminary experiments heavy-walled, pyrex-glass vials were charged with SO_2 and the olefin by condensation. These vials and the gas-loading rack are the same as those described for the butadiene-styrene experiments. The vials are shown in Fig. 5 and the gas-loading rack is shown in Fig. 6.

The larger-scale reactions were conducted in a stainless-steel reaction vessel constructed of A.I.S.I. 304 stainless steel shown in Fig. 7.



- ① Hoke angle pattern valve type PY 275
- ② 304 stainless-steel bar stock, threads:
standard pipe
- ③ Groove for poured lead gasket
- ④ Body: 304 stainless steel, schedule-80 pipe
Length: 8 in.
ID: 1-9/16 in.
Thickness: 5/32 in.



All welds are fillet welds; 316 stainless-steel welding rod used for all welds.

Fig. 7. Diagram of the stainless-steel reactor used in SO_2 copolymerizations.

The body of the bomb was constructed of schedule-80 pipe. The heads, turned from bar stock, and body were threaded to provide a means of closing the bomb. The bottom head was placed on the body and welded with 316 stainless-steel welding rod. The top head was machined for a lead gasket to provide a pressure seal. The inlet provided in the top head for loading consisted of high-pressure stainless-steel tubing welded to the head. A standard Hoke valve was attached to this inlet tube. The maximum working pressure of this bomb was 1500 psi. Although 200 psi was the maximum pressure used in this work, the bomb was hydrostatically tested before use at the maximum pressure.

A high-pressure steel loading system was constructed for loading gases into the reaction vessel. A photograph of the system is shown in Fig. 8. All lines were made of 6000-psi 316 stainless-steel pressure tubing, except for the two ends which were fitted with flexible steel hoses rated at 2000 psi. The valves were standard Hoke valves rated at 2000 psi. The equipment was provided with four pressure gages of various ranges for pressure measurement. The high-vacuum pump and cooling mixture were the same as those used in the preliminary experiments.

2. Chemicals Used in the Reactions.—The chemicals used in both the preliminary and large-scale experiments were standard commercial grades, except as indicated. No individual analyses were made on gas cylinders and the following analyses were indicated by the commercial suppliers.

Ethylene-0.02% O₂, 0.05% CO, 0.37% CO₂, 1.7% N₂, 0.8% pentane, 97.06% C₂H₄.

Propylene-C.P. grade: 99.0% C₃H₆. Principal impurity was propane.

Butene-1-C.P. grade: 99.0%. Principal impurities were isobutane and small amounts of normal butane and butene-2. No isobutylene was known to be present.

Butene-2-C.P. grade: 99.0%, both "cis" and "trans" forms. Principal impurity was butene-1; 0.1% acetylenes and lesser amounts of diolefins and other hydrocarbons were present.

Isobutylene-C.P. grade: 99.0%, butene-1 was the most probable impurity.

1,3-butadiene-99.77% 1,3-butadiene. Impurities were normal butane, butenes, and possibly a trace of acetylenes (0.23%).

Sulfur dioxide-C.P. grade: 99.988% SO₂, 0.002% moisture, 0.010% non-condensable gases.

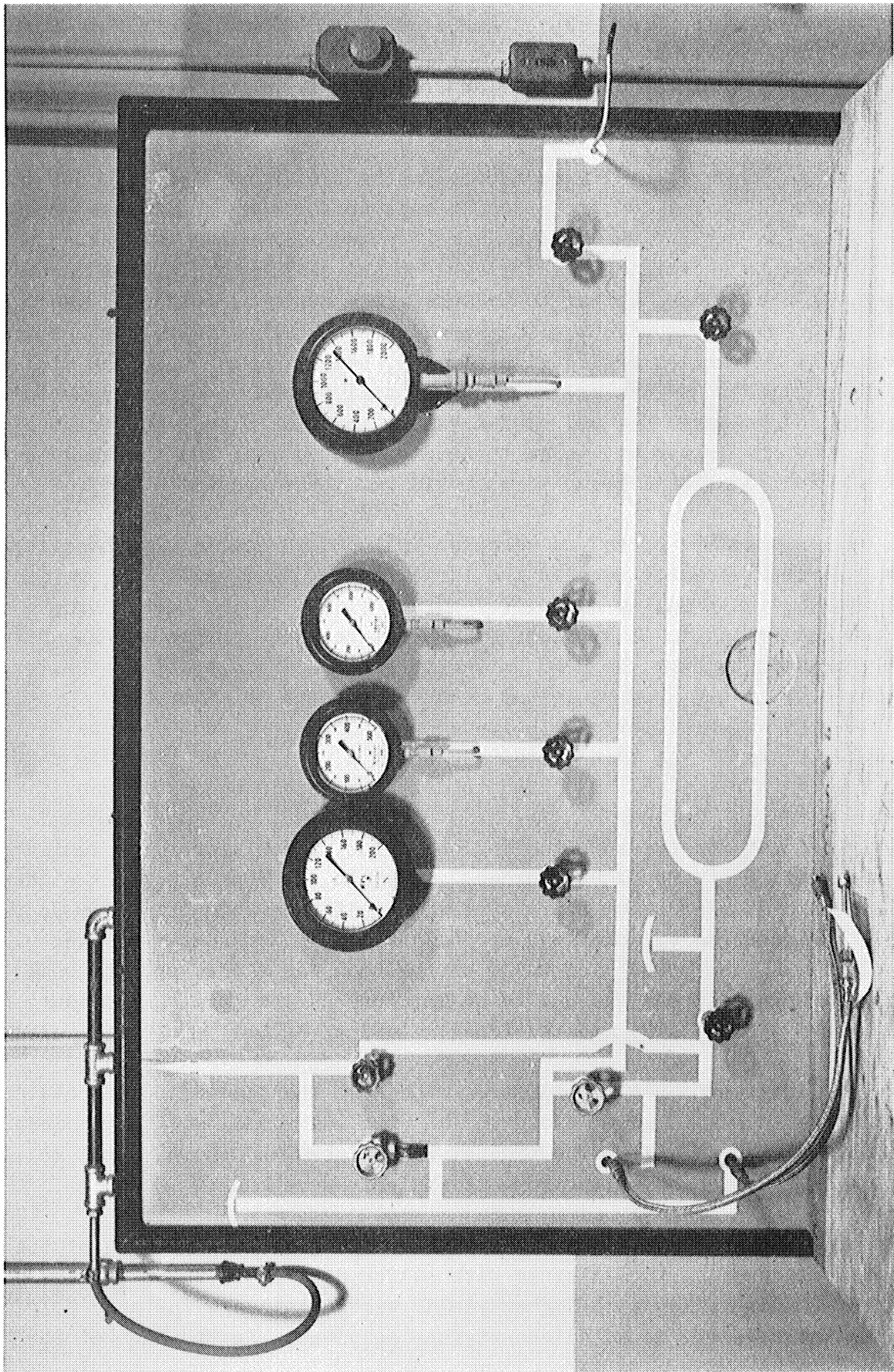


Fig. 8. High-pressure gas-loading rack.

Nonene and dodecene-500 ml were distilled under vacuum from research-grade reagents supplied by Continental Oil Company.

Styrene-500 ml were distilled under vacuum from stabilized reagent-grade styrene, rejecting initial 50 ml and final 150 ml.

3. Experimental Procedure.—In the preliminary experiments the standard experimental loading procedure set up for the butadiene-styrene polymerization was followed, with one exception. When two gaseous components were charged to a vial, as was the case in the olefins of lower molecular weight, it was thought better to measure the amounts of condensed vapor by volume rather than by weight. The weighing procedure had two serious drawbacks: (1) the lines filled with air and, hence, oxygen when the vial was disconnected from the system, and (2) the vial warmed up slightly during weighing and released SO_2 and olefin vapors into the room. The volumes were computed by comparison with a calibrated graduated vial and the weights were obtained from densities found in standard reference handbooks.

A standard procedure was also followed in loading and handling the stainless-steel reactor used in the larger-scale experiment. To provide the bomb with a tight seal, a strip of lead was placed in the gasket groove of the cap and melted in it by means of the natural-gas-oxygen torch, while care was taken to have the head perfectly horizontal to provide a uniform thickness of lead. When cool, the head was screwed onto the body of the bomb and the threads were coated with leaded pipe dope to give additional assurance of seal. Nitrogen was then introduced up to a pressure of 800 psig and the bomb placed in water and inspected to detect possible escape of gas.

After the pressure-testing operation, the nitrogen was vented and the tare weight of the bomb recorded. The bomb was connected to the gas-loading apparatus and the entire system evacuated to less than 1-mm-Hg pressure. The feed gas cylinder was opened and the desired amount of gas allowed to condense in the bomb. The valve of the bomb was closed and the bomb weighed. When a second gas had to be introduced, the loading procedure outlined above was repeated and the final weighing made.

After exposure to radiation, the bomb was placed in the hood and its gaseous contents allowed to escape. The bomb was opened and the product was removed mechanically. The product was weighed and stored until melting-point measurements and sulfur-content analysis were made.

4. Experimental Results.—Table 8 presents the results of the copolymerization of various alkenes with sulfur dioxide in the preliminary experiments. Generally, much higher yields were obtained with these polymers than in the case of the butadiene-styrene polymers. In the case of the

TABLE 8. COPOLYMERIZATION OF VARIOUS ALKENES WITH SULFUR DIOXIDE AT 8° to 15° CENTIGRADE AND 153,000 TO 162,000 REP PER HOUR

Components	Run on Page	Run	Total Weight Charged gm	Weight of Product gm	Percent Yield	Dose Megarep	A Value	Remarks
SO ₂ + 1,3-Butadiene (B)	145846	62	6.3	5.3	84.0	3.85	3,184.7	white-creamy-hard polymer—melts above 310°C—color changes to brown
SO ₂ + 1,3-Butadiene (B)	145846	63	6.6	3.3	50.0	control	-	white crystalline
SO ₂ + Butene-1	145847	64	3.8	2.5	65.8	3.85	2,771.8	white and gray polymer—porous—melting range: 234°-259°C
SO ₂ + Butene-1	145847	65	1.9	0.4	21.0	control	-	
SO ₂ + Butene-1	145849	66	5.0	2.1	42.0	5.56	1,217.0	white-some colorless polymer—melting range: 232°-262°C
SO ₂ + Butene-1	145849	67	4.1	0.2	4.9	control	-	yellowish white film polymer
SO ₂ + Butene-2	154700	68	2.6	2.4	82.5	5.56	2,404.5	colorless hard polymer—melting range: 231°-260°C
SO ₂ + Butene-2	154700	69	5.0	4.3	86.0	control	-	colorless hard polymer
SO ₂ + Nonene	154705	71	11.0	trace	≈ 0	3.48	0	
SO ₂ + Nonene	154705	70	4.4	0.0	≈ 0	control	-	
SO ₂ + Dodecene	154706	81	3.7	0.3	8.1	3.68	2,065.3	golden brown liquid-black precipitate
SO ₂ + Dodecene	154706	80	4.4	trace	≈ 0	control	-	
SO ₂ + Styrene	154707	91	5.9	2.0	34.0	3.48	1,258.2	fibrous white polymer—melting range: 248°-284°C
SO ₂ + Styrene	154707	90	5.7	2.0	35.0	control	-	hard white polymer
SO ₂ + i-butylene	154708	101	6.1	0.3	4.92	3.69	218.7	spongy white polymer
SO ₂ + i-butylene	154708	102	5.8	< 0.1	< 1.7	control	-	fine white polymer

1,3-butadiene, styrene, butene-1 and butene-2—sulfur dioxide copolymerizations, the percent yield of the controls was also high, though consistently less than those of the irradiated samples. This relatively high yield in the control samples was believed due to the fact that the control vials were stored in the light during the time that the other vials were being irradiated. The literature²⁸ reports that sunlight or light in the region of 3000 to 3800 Å catalyzes the reaction. The yields of polymer in the larger-scale control experiments conducted in the absence of light in stainless-steel vessels were negligible. Dodecene, nonene, and 1-butylene—sulfur dioxide copolymerizations generally gave poor results. The products of the alkene-sulfur dioxide copolymerizations from the preliminary vial experiments are described below. A more accurate evaluation of the effects of gamma radiation upon the reaction is shown later in the discussion of the larger-volume experiments.

Butene-2—sulfur dioxide: The irradiated sample gave a transparent product which has the appearance of mica; the only visible difference between the control and the irradiated sample was that the control product was colorless. The inside wall of the vials was covered by a thin, brittle layer of product which was white in the case of the irradiated sample and colorless in the case of the control.

Butene-1—sulfur dioxide: Both the control and the irradiated samples gave a white-gray, crystalline, and porous product.

1,3-butadiene (Grade B)—sulfur dioxide: The irradiated sample gave a white product which turned brown on standing; the control was a pure-white crystalline substance.

Styrene-sulfur dioxide: A yellowish product with a fibrous appearance was obtained. The control gave a product which had an initial elasticity but became hard on standing, due to further polymerization of the excess styrene.

Table 9 presents the results of the large-scale experiments carried on with mixtures of various alkenes and sulfur dioxide. Generally, much smaller doses were used in these experiments than in the preliminary ones. The reactions with nonene and dodecene were not investigated further. The reaction with 1-butylene and styrene gave comparatively mediocre results and their further study was relegated to a later time. Propylene-sulfur dioxide copolymerization was found to be quite successful.

Most reactions were carried on at ambient room temperature. A few low-temperature runs were made in an attempt to determine the possible influence of temperature on the yield or physical aspect of the product. As yet, these reactions have not been studied at high temperatures.

TABLE 9. LARGE-SCALE COPOLYMERIZATION OF VARIOUS ALKENES WITH SULFUR DIOXIDE

Alkene Used	Run Page	Temp. of Run °C	Moles Charged Organic	Total Weight Charged gm	Weight of Product gm	Percent Yield	Dose Rate Krep/hr	Dose Krep	A Value	Melting-Point Range °C	Percent SO ₂ in Product	Molecular Arrangement SO ₂ :Organic
Butene-2	154801	-74	0.36	46	17.6	38.3	39.4	489	12,900	Chars and boils at 244	54.1	1:1
Butene-2	154749	20	0.07	24	16.5	68.8	40.6	2,540	4,190	240-316	51.4	1:1
Butene-2	154815	28	0.55	51	1.5	2.6	0	0	-	Melts and decomposes at 268	49.5	1:1
Butene-2	154823	32	1.30	75	~0	0	68.8	4,510	0			
Butene-1	154802	20	0.38	40	0.3	0.75	32.8	541	232			
Butene-1	154804	-75	0.13	26	0.6	2.1	6.3	225	1,340			
Butene-1	154808	-75	0.18	33	25.8	78.2	25.7	575	22,000		52.2	1:1
Butene-1	154814	26	0.21	37	0.1	0.3	0	0	-			
Butene-1	154822	27	1.77	39	0.4	1.0	68.8	4,800	14.9			
1,3-Butadiene	154810	21	0.54	98	73.0	74.5	29.0	498	24,600	292	54.0	1:1
1,3-Butadiene	154811	-75	0.44	75	45.3	60.5	14.0	258	38,200	305, chars	53.9	1:1
1,3-Butadiene	154813	30	0.41	82	21.0	25.6	0	0	-	Sublimes	52.8	1:1
1,3-Butadiene	154825	28	1.54	83	1.7	2.1	68.8	4,366	84.8			
i-Butylene	154816	26	0.48	61	~0	~0	55.1	2,385	~0			
i-Butylene	154824	31	1.94	109	~0	~0	68.8	4,760	~0	>312		
Styrene	154819	28	0.34	113	31.0	27.4	60.2	3,050	1,175	Chars at 150		
None	154826	27	0.0	74	~0	~0	68.8	2,945	~0	>316		
None	154827	29	0.0	110	~0	~0	60.9	5,200	~0	>316		
Propylene	154817	26	0.88	68	~0	~0	0	0	-	>316		
Propylene	154818	27	0.93	79	71.5	90.5	68.8	2,713	6,280	283	59.0	1:1
Propylene	154820	-75	0.76	68	59.0	86.8	24.0	2,073	7,830	273-316, chars	58.5	1:1
Propylene	154821	27	1.55	65	0.6	0.9	51.2	3,095	71.4	Chars above 148		
Propylene	154828	29	1.19	82	44.8	54.7	61.4	1,080	10,000	271-decomposes at 311	59.6	1:1
Propylene	154829	25	1.07	106	91.1	85.9	61.8	462	34,000	287	66.3	5:4
Propylene	154830	26	1.54	135	31.8	23.6	46.5	63.4	69,700	284	58.2	1:1
Propylene	154833	27	1.18	128	3.9	3.0	68.8	32.1	17,080	Chars below 167	63.2	1:1
Propylene	154834	27	2.28	223	90.0	40.4	68.8	180	41,220	285	58.1	1:1
Propylene	154837	28	1.07	99	87.3	88.1	68.8	1,021	15,990		58.4	1:1
Propylene	154839	19	1.53	108.4	~0	~0	68.8	399	0			
Propylene	154840	25	1.08	116.8	54.8	47.0	68.8	375	22,580		59.6	1:1
Propylene	154841	20	1.41	151.5	140.0	92.5	68.8	719	25,240			
Propylene	154842	17	1.13	126.5	106.9	84.0	68.8	542	27,800		58.2	1:1
Propylene	154115	14	1.40	162.6	118.9	73.1	68.8	406	32,100			
Propylene	154843	18	2.63	110.5	<.4	<.35	68.8	3,754	22			
Ethylene	145817	25	2.36	70	15.1	21.6	37.8	3,720	2,170	Decomposed	24.7	2:19
Ethylene	145824	25	.48	45.1	33.9	75.0	62.5	4,000	3,770	Decomposed	62.3	2:3
Ethylene	145826	100	0.97	89.2	57.0	64.0	37.0	3,630	3,680	316	65.1	1:1
Ethylene	145827	212	.65	21.8	4.3	19.7	37.0	3,360	1,705			

For each set of reactions, except for the styrene-sulfur dioxide copolymerization, a control was made for the alkene alone and for the alkene with sulfur dioxide. All but the 1,3-butadiene—sulfur dioxide control gave small yields. The melting point of the controls sometimes showed marked differences when compared to the irradiated samples. This was due to the higher range of molecular weights found in the polymers produced under gamma radiation. Two runs were made with sulfur dioxide alone, both under exposure to radiation.

A brief description of the characteristics of the polymers formed in the larger-volume experiments and significant observations made during the runs are indicated below. Run numbers refer to specific runs presented in Table 9.

1-butylene—sulfur dioxide copolymerization gave no result in spite of the comparatively larger doses used. This was due to the fact that at room temperature we are above the "ceiling" temperature for the reaction.

Styrene-sulfur dioxide copolymerization gave a low radiation yield and has not been investigated beyond the one run reported.

Butene-2—sulfur dioxide copolymerization data tend to show the characteristic exponential curve of the percent yield vs dose; it was felt, however, that the number of data obtained were not sufficient to plot a reasonably accurate curve.

The compact, homogeneous, and transparent solids obtained with the butene-2 in the preliminary investigations were not obtained in the larger-scale runs, except to some extent in Runs 154749 and 154801. Because the products were caked in the bottom of the bomb, they had to be broken up before they could be extracted. This handling, together with the fact that the products of the bomb polymerization were not allowed to stand for long periods of time, as was the case in the preliminary experiments, probably accounts for this lack of reproducibility.

The melting-point range of the butene-2—sulfur dioxide copolymers was between 240° and 316°C. The average percent sulfur dioxide of the butene-2 product was found to be 51.6%, which indicated a one-to-one molecular arrangement.

Butene-1—sulfur dioxide copolymerizations yielded white, hard powders; the percent sulfur dioxide calculated on the analysis of Run 154808 was 52.2% and indicated a molecular proportion identical to that of the butene-2 product.

1,3-butadiene (Grade B)—sulfur dioxide copolymerization yielded a

white product having the appearance of chalk. The product was very dry and difficult to grind by ordinary means. The lower limit of the melting-point range was in the vicinity of 292° to 305°C. The product charred before the upper limit was attained. The sulfur dioxide content was found to average 53%, which also indicated a one-to-one molecular arrangement.

Propylene-sulfur dioxide copolymerization was by far the most successful mixture. Two outstanding features were: (1) the importance of the relative amounts charged and (2) the sharp rise of the percent yield for a comparatively small increase in radiation.

When the propylene to sulfur dioxide ratio of moles charged was close to 1, much higher A values were obtained than with propylene-rich mixtures. For instance, in Run 154818 6,280 kilorep were needed for a 90.5% yield with .927 mole of propylene to .624 mole of sulfur dioxide charged, while only 719 kilorep sufficed to obtain a 92.5% yield with the 1.41 moles of propylene and 1.42 moles of sulfur dioxide mixture in Run 154841.

The other feature was best brought out by the graphical representation in Fig. 9, indicating that the percent yield rose from zero to 90% within a dose of 700 kilorep.

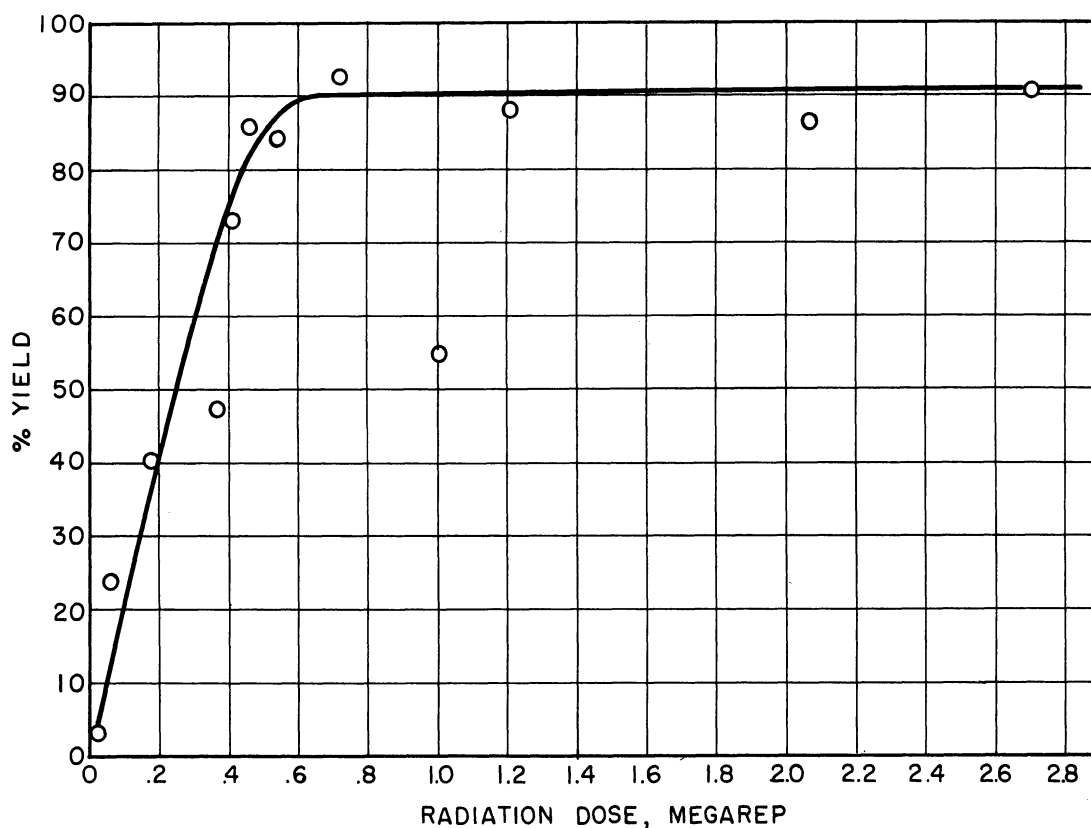


Fig. 9. Propylene-sulfur dioxide copolymerization at room temperature.

One point (Run 154828) was considerably off the curve. This was believed to be due to the initial composition of the reaction mixture. The reaction probably reached completion on a sulfur dioxide basis, leaving unreacted propylene, and this would tend to indicate a low overall completion of reaction.

In some cases very low doses were used in attempts to determine the existence or nonexistence of an induction period; however, with a dose as low as 32 kilorep, some product was obtained. This indicated very little induction period to the reaction.

The product obtained in all cases was a hard and dry white substance which could be ground to a fine powder. In all cases but one, the lower limit of the melting-point range was in the vicinity of 280°C and the upper limit at 310°C or higher. Charring usually occurred before any fluidity could be detected in the sample to be melted.

The sulfur dioxide analysis showed that on the average the products contained 59.9% sulfur dioxide, from which the molecular arrangement was deduced to be one to one, as previously indicated for other alkene-sulfur dioxide copolymers.

Ethylene-sulfur dioxide copolymerization: Analyses of the products were made on the two runs reported in Progress Report 7⁴ and these are included in Table 8 with two runs made since that time. The product was a finely divided white powder. The yields may be somewhat obscured by the fact that polyethylene may have been formed in the runs. This was thought to be the case in Run 154817, where the ethylene-sulfur dioxide ratio is higher than ordinarily expected. Run 145827 was above the "ceiling" temperature for ethylene and sulfur dioxide, but polyethylene may still be formed. In general, the polymer decomposed before melting. This is a common phenomenon associated with all polysulfones of this type.

5. Evaluation of the Product.—Product yields are presented as the A value, as is customary for this work. A complete analysis of this quantity is to be found in the literature.¹⁷ The A value and the molecular-weight calculations were the same as presented for the butadiene-styrene experiments. Melting points were taken on the laboratory melting-point bar described previously.

Sulfur analyses were made in the laboratory by standard methods. The procedure followed was that outlined in the Parr Booklet 104⁸ for the analysis of sulfur in vulcanized rubber. For the products at hand, it was found more convenient to increase slightly the amount of potassium chlorate (0.6 gm in lieu of 0.5 gm) and replace the 0.5 gm of sugar by 0.7 gm of benzoic acid. Approximately 0.2 gm of the finely ground product was weighed and thoroughly

mixed in the Parr bomb with the above-mentioned amounts of benzoic acid and potassium chlorate, and 10 gm of sodium peroxide. The mixture was then covered with an additional 4 gm of sodium peroxide and the bomb was sealed and fired.

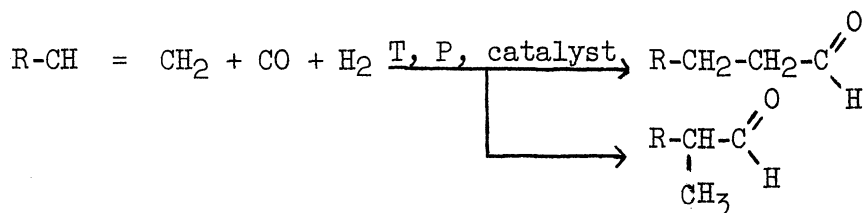
The contents were dissolved in warm distilled water and processed for further analysis as outlined in Willard and Furman.³² The procedure consisted in making the solution acidic with hydrochloric acid, neutralizing with ammonium hydroxide, and boiling for 30 minutes after addition of 15 gm of ammonium carbonate.

The precipitate was filtered and rinsed with a dilute sodium carbonate solution. The filtrate was then made acidic with hydrochloric acid and boiled free of carbon dioxide. After an addition of 5 cc of hydrochloric acid in excess, the solution was diluted to 400 cc and barium sulfate was precipitated by slowly adding 20 cc of a 10% solution of barium chloride. After checking for complete precipitation, the solution was kept warm for an hour. The precipitate was then filtered and washed with distilled water, ignited and weighed, and the last two steps were repeated until a constant weight was obtained. From the weight percents of organic constituents and sulfur dioxide in the products, a molecular composition was calculated. These values are presented in Table 9.

In nearly all instances the molecular ratio was one to one. This corresponded to the molecular compositions found in the literature for the polysulfone products produced with conventional catalysts.²¹

D. OXO-TYPE REACTION

Since World War II the Oxo reaction has been of some interest in the United States. This hydroformulation reaction, as it is sometimes called, consists of the addition of carbon monoxide and hydrogen to an olefin, producing an aldehyde of one carbon atom greater than the original olefin. In general, a mixture of aldehydes are formed. The equations for the reactions involved are:



The reaction has been investigated under a wide range of external conditions.

The present commercial industrial operation takes place at a temperature of from 120° to 190°C at from 100 to 250 atmospheres of pressure in the presence of a cobalt carbonyl catalyst.²⁵ A complete review of the history, conditions, and operation of the reactions is presented by Orchin and Schroeder.²³

Various mechanisms have been suggested for the reaction. Evidence has been presented for cyclopropanone, carbonium-ion, hydrogenation, and free-radical type mechanisms.²³ It is this last mechanism that apparently is involved in the use of gamma radiation to promote chemical reactions, and for this reason it was considered of interest to study the promotion of the Oxo reactions under gamma radiation.

Ethylene, butene-1, butene-2, propylene, and isobutylene were subjected to Oxo conditions under the influence of gamma radiation from the cobalt-60 source. No cobalt carbonyl catalyst was used in the reacting mixture. Different temperatures, pressures, and radiation doses were studied with varying success. The data that are reported are to be considered preliminary in nature, as no effective scheme was followed in varying the conditions. It was deemed advisable first to obtain a product and prove the reaction feasible before systematically controlling the variables present.

1. Equipment Used.—Several reactors were utilized in the study of the Oxo reaction in the laboratory. The reactor designed by Lewis¹⁷ was used in the case of the ethylene and butene-1 Oxo reactions. Here, gas-phase reactions were studied at moderate pressures and the reactor was well suited to this work. In the high-temperature work involving higher pressures, the American Instrument Company reactor presented by the Engineering Research Institute was used. This reactor has been described in the section on polymerization of ethylene and is shown in Fig. 2 of this report. It has a larger volume and is more capable of withstanding high pressures at high temperature than is the Lewis reactor.

In those systems where two phases were present in the reacting mixture, an Autoclave Engineer's "Magna-Dash" reactor with a variable magnetic stirrer was utilized. This reactor was purchased by the Engineering Research Institute for high-pressure two-phase work in this laboratory. The two-phase reacting system consisted of the liquid olefin and gaseous carbon monoxide and hydrogen at temperatures below the critical temperature of the olefin. The magnetic stirring mechanism provided violent agitation in the vessel, allowing greater surface contact between the two phases. Figure 10 is a photograph of the disassembled Magna-Dash reactor. The reactor was the standard Autoclave Engineer's Magna-Dash licensed by Standard Oil of Indiana. The reactor was constructed of 18-8 stainless steel with a capacity of 500-ml. The stirring mechanism consisted of an external solenoid acting upon an internal shaft to which the stirring plates were attached. There were no packing glands or

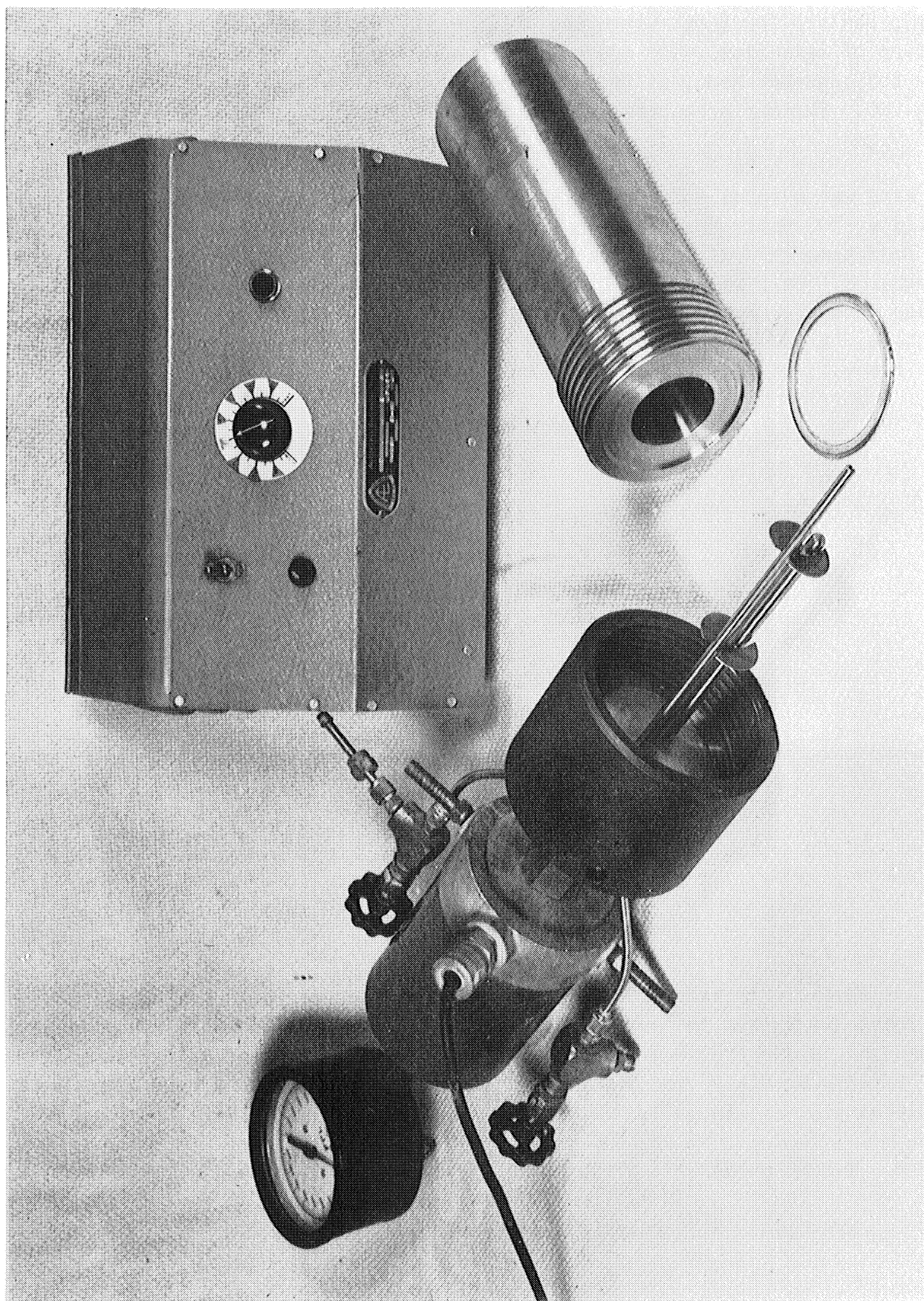


Fig. 10. Disassembled view of the Magna-Dash reactor and agitator timer.

external ports which might allow gas leakage. The reactor was equipped with strip heaters for temperature variation and an adjustable timer to vary the amount of agitation. The operating pressure range was from 0 to 5000 psi. The body, gasket head, stirring mechanism, and adjustable timer are shown in Fig. 10. The strip heaters and stand are not shown.

One butene-2 Oxo-reaction run was made in a large-volume tank obtained as army war surplus. The vessel had a capacity of 8.5 liters and was pressure rated at 500 psi. The reaction was run in the vapor phase at a low pressure at room temperature. The tank had two 3/8-inch-pipe openings for loading and discharge. Only reactions which went from vapor-phase reactants to liquid-phase products were conducted in the tank, since cleaning was otherwise a problem. A product-collection well was added to the tank to facilitate product removal and cleaning of the vessel. The tank is shown in Fig. 11.

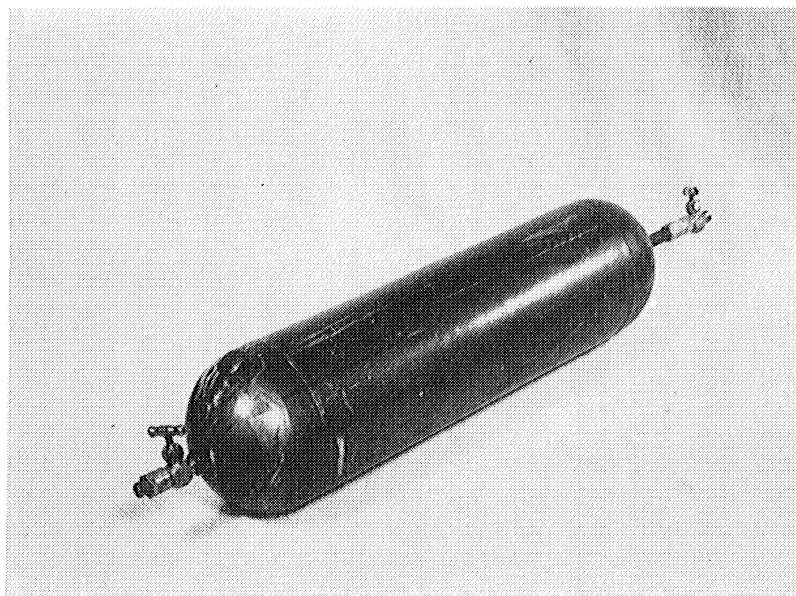


Fig. 11. Large-volume reaction tank.

2. Chemicals Used in the Reactions.—The olefins used in these experiments were from the same cylinders and had the same chemical analyses as presented in the previous section on the copolymerization of sulfur dioxide and various olefins. The analyses of the carbon monoxide and hydrogen are as follows:

Carbon monoxide: 97.5% CO, 0.2% CO₂, 0.2% O₂, 1.0% H₂, 1.1% N₂

Hydrogen: Electrolytic grade, 99.8% H₂, 0.2% H₂O.

The percent oxygen in the carbon monoxide is higher than desired for this work because oxygen may have an inhibiting effect upon the reaction; however, this was the best carbon monoxide obtainable in large quantities at the time. In some cases, the poor experimental results were thought to be due to the presence of this oxygen inhibitor.

3. Experimental Procedure.—The same experimental procedure was followed in all cases for all reactions in all reactors. The reactors were cleaned with various solvents, dried, and sealed for pressure testing. Nitrogen was used in the pressure-testing operation and was left in the reactors at a specific pressure for at least 12 hours. After venting the nitrogen, the vessels were evacuated to less than 1-mm Hg before introduction of the reactants. The olefin was charged first by immersing a portion of the reactor in a -75°C cold bath of CCl_4 and CHCl_3 . A specific amount of olefin was added and determined either by direct pressure measurement, weighing, or by heating to above the critical temperature and making a pressure measurement. The carbon monoxide and hydrogen were then charged separately to specific predetermined pressures to give approximately a one-to-one mole ratio of CO to H_2 . The exact proportions of all components were then calculated from standard tables of thermodynamic properties.

The reactor was brought to the desired reaction temperature in the radiation-source room and the source was raised into irradiation position for a specific time. On completion of the run, the bomb was removed from the radiation and allowed to cool. Duplicate Orsat analyses were taken of the gases remaining in the reactor. An analysis was made for the olefin and carbon monoxide present and hydrogen was taken by difference. The rest of the gases were vented to the hood and the reaction vessel was opened for product recovery. The reactor was then cleaned for the next run while the product was stored for further analysis.

4. Experimental results.—In general, poor results were obtained from the Oxo reaction with most olefin reactants investigated. Table 10 is a summary of all reaction conditions and product yields obtained. The yields were so low and, in general, the doses were high enough that the calculation of A values was not warranted. The total dose and yield are presented, showing the relative values leading to this calculation.

In the Orsat analyses made on the reactor off gas, no account was taken of the possible alkane formation by hydrogenation of the alkene. It is not known whether or not this can account for the low product yields. Another effect thought, but not proved, to be present is the oxygen inhibition of the reaction due to oxygen in the carbon monoxide feed stock. Harmer¹⁴ showed that oxygen inhibits other reactions in the presence of gamma radiation. Oxygen seems to inhibit the ethylene polymerization reaction, and the Oxo reaction is quite similar in many respects.

TABLE 10. REACTION CONDITIONS AND PRODUCT YIELDS
FOR THE OXO REACTION INVOLVING VARIOUS OLEFIN REACTANTS

Page No.	Average Temp. °C	Average Press. Psig	Organic Used	Mole Percent Charged		Radiation Dose Rate Krep/Hr	Total Dose Megarep	Product Yield gm	Product Description	
				CO	H ₂					
154001	7	1120	ethylene	45	29	26	30.5	2.39	1.133	mp 137°C, light, fluffy, powder polymer
154003	143	1450	ethylene	40	31	29	29.3	1.89	0.066	waxy, brown polymer
154005	17	1065	ethylene	56	21	23	37.0	3.43	2.071	mp 114°C, light, fluffy, powder polymer
154008	58	1375	ethylene	55	12	33	19.5	1.24	0.50	light, fluffy, powder polymer
154010	108	900	butene-1	11	44	45	33.5	2.85	sm. amt 0.1	dark-brown, waxy polymer
154013	189	1235	butene-1	24	38	38	31.5	3.87	sm. amt	tan, viscous, oily liquid
154015	30	690	i-butylene	86	2	12	17.0	3.09	sm. amt ≈0.2	brown, viscous, oily liquid
154018	181	2260	i-butylene	68	17	15	11.0	2.16	19.1	yellow liquid, pungent odor
154029	20	718	i-butylene	51	29	20	10.8	5.53	0.2	tan, oily liquid
154020	30	910	propylene	70	16	14	16.3	3.12	2.8	brown, viscous, oily liquid
154037	14	546	propylene	77	14	9	16.3	7.58	9.7	clear, tan, viscous wax-solid
154027	190	1960	butene-2	49	27	24	11.1	4.74	14.0	clear, yellow liquid, pungent odor
154030	231	2020	butene-2	78	14	8	0	0	13.5	clear, yellow liquid, low viscosity, pungent odor
154036	14	180	butene-2	14	44	42	36.1	13.4	2.0	dark-brown liquid, low viscosity

Visual appearances of the products are included in Table 10. In general, the product yields were so low that this was the only measurement made. The small quantities of polymer and oil product were not sufficient for analyses of most physical properties. Melting points were taken where sufficient product was available. These are presented on Table 9 under product description. Melting points were taken on the laboratory melting-point bar as has been described previously.

As is to be seen on Table 10, the majority of runs yielded polymer products. Solids, waxes, and heavy oily liquids were obtained in most cases rather than the expected liquid aldehydes. In general, these products were obtained in rather low yields. In three cases, 154018, 154027, and 154030, light, low-viscosity, pungent liquids were obtained in appreciable quantity. These products are being analyzed at the present time. Distillation curves have been run on Run 154018 and a variety of products are assumed to be present. Aldehydes, alcohols, and condensation products of the aldehydes are thought to be present from observation of the boiling-point curve. These data will be presented at a future time when complete analyses have been made.

In the case of high product yields in runs with butene-2, it should be noticed that Run 145030 was a control run with no radiation. The product obtained was the same as that from Run 145027, where radiation was present. This leaves doubt of the effect of radiation upon the reaction. The reaction is to be investigated further to eliminate this question.

E. CHLORINATION OF SOME AROMATIC HYDROCARBONS

In general, chlorination of an aromatic hydrocarbon may result in three possible reactions: (1) substitution of chlorine for hydrogen in the benzene ring, (2) substitution of chlorine for hydrogen in an alkyl group attached to the ring, and (3) addition of chlorine to the ring. Friedel-Crafts catalysts promote substitution in the ring; high temperature in the absence of a catalyst favors substitution in the alkyl group, and radiation appears to favor addition to the ring. Ultraviolet,^{11,12} roentgen rays,¹⁹ alpha radiation,¹ and gamma radiation^{13,14} have been employed to promote the addition reaction. In this laboratory, Harmer¹⁴ initiated a study of the chlorination of benzene and toluene in the presence of gamma radiation. This has been extended to include xylene, mesitylene, ethyl benzene, and naphthalene.

1. Equipment Used.—In general, the glass reaction equipment designed and built by Harmer¹⁴ was used for all runs. Some difficulty was encountered with breakage of the chlorine-flow tubes in the part between the second-floor analysis laboratory and the first-floor radiation cave where the reactor was located. The removal, repair, and replacement of this glass

tubing took a great deal of time, since the port to the radiation chamber contained a right-angle bend in the center to insure no radiation hazard to the workers in the second-floor laboratory from the radiation source below. It was found that Teflon tubing was a suitable replacement for this glass tubing through the port and the angle bend in the port. Teflon becomes brittle under gamma radiation, and so a Teflon-to-glass seal was made in the radiation cave. Glass tubing was still used where the lines came in contact with radiation. The Teflon-to-glass tubing seal is a standard shrink fit of plastic to glass covered by De Khotinsky cement at the junction to insure a full vacuum seal.

During the runs it was noticed that the inlet chlorine rotameter float had a tendency to oscillate through a small range. The cause of this behavior was attributed to the bubbling of the chlorine gas through the reaction liquid in the reactor. Attempts to eliminate this oscillation were only partially successful. Dry traps were inserted in the flow lines before and after the rotameter to cushion the gas flow and pressure differential due to bubbling.

The cooling-system tanks were enlarged and provided a much more accurate temperature control. A mixture of methyl alcohol and water was used as the primary coolant around the reactor. An ether, chloroform, methyl alcohol, and dry-ice mixture was used as the secondary coolant in the low-temperature tank. The temperature was brought to any predetermined run value within a few minutes, allowing initial analyses samples to be taken sooner than was possible previously.

A control valve was installed between the vacuum pump and the equipment proper to control the rate of evacuation. It was found that too rapid evacuation would collapse the rubber connections used in the lines and, consequently, reactor contents would be drawn into the lines and traps before start of the run. Previously it was necessary to have an observer in the source room at all times during the evacuation of the lines preceding a run.

2. Chemicals Used in the Reactions.—The analysis of the chemicals used in the reactions is presented here as an aid to the reader.

Chlorine: 99.8% Cl_2 , trace of chloroform, hexachloroethane, carbon tetrachloride, air, and tetrachloroethylene

Benzene: Reagent grade, distilled in the laboratory

Toluene: Reagent grade, distilled in the laboratory

Ethyl benzene: Reagent grade, distilled in the laboratory

Mesitylene: Reagent grade, as obtained

Naphthalene: Reagent grade, as obtained recrystallized from ethyl alcohol

Nitrogen: Prepurified, 99.9% N_2 , no H_2O , .001% O_2 , .001% H_2 , remaining inert.

3. Experimental Procedure.—A standard experimental procedure devised by Harmer¹⁴ was followed in all runs. Before the run, the reactor and all auxiliary glassware were washed, cleaned for several hours in hot chromic acid cleaning solution, steamed out in a specially constructed tower, and dried thoroughly at 150°C on glass in an oven. The lead lines were washed with acetone between runs. The liquid reactants to be used were placed in the reactor and the head sealed on with De Khotinsky cement and the whole assembly placed in the steel cooling jacket in position in the source room. The lines to the second-floor analysis laboratory were connected and the run was ready to start. The whole system was successively evacuated and refilled with nitrogen three times to displace air and, hence, oxygen present.

Then temperature control and chlorine flow were started and the cobalt-60 source was raised into the radiation chamber. The reaction time was measured from the moment the source was raised and to the midpoint of the period during which a sample of gas was collected. Radiation dosages were determined by the time and dosimetry calibrations mentioned previously.

Rates of reaction between chlorine and the aromatic hydrocarbons were determined by chlorine balance. The amount of chlorine into the system was measured with a rotameter. Excess chlorine was passed through the reactor at all times to maintain saturated conditions. At certain intervals samples of the exit gas were absorbed in a solution of 0.2 Normal sodium arsenite and 3.0 Normal potassium hydroxide. The amount of free chlorine was determined by titrating the excess arsenite with ceric sulfate and total chloride ion was measured by the Volhard method. In this way the amount of substitution and addition could be determined. The complete analysis procedure is described by Harmer.¹⁴

4. Experimental Results.—The results of the chlorination of xylene, mesitylene, ethyl benzene, and naphthalene are presented in Table 11, with the temperature and radiation conditions involved. In general, individual products were not isolated, but kinetic data were taken on an overall chlorine balance on the system. The data on the chlorination of benzene and toluene have appeared in previous progress reports^{14,17} and are presented in Table 11 for comparison purposes.

Benzene, toluene, xylene, and mesitylene reacted vigorously with chlorine in the presence of gamma radiation. Addition of six chlorine atoms

TABLE 11. CHLORINATION OF AROMATIC COMPOUNDS WITH GAMMA RADIATION

Run on Page	Aromatic Chlorin- ated	Temp. Reaction °C	Dose Rate Krep/Hr	Cl ₂ Add. moles/ liter	Cl ₂ Sub. moles/ liter	Average G ^(b) Addition	Average G ^(b) Sub- stitution
129767	30% Benzene	20	61.0	35.20	---	234,000	---
129770	20% Benzene	20	61.0	32.60	---	252,000	---
129771	10% Benzene	20	61.0	33.30	---	90,000	---
129774	30% Benzene	-10	61.0	13.70	---	90,000	---
129773	10% Benzene	-10	61.0	32.70	---	57,000	---
150450	Toluene	20	14.0	17.42	7.54	523,000	226,000
150463	Toluene	- 5	14.0	14.12	6.59	900,000	420,000
150456	Toluene	35	14.0	10.35	6.12	812,000	480,000
150479	Toluene	20	None	3.23	0.85	---	---
154561	Xylene	20	13.7	5.90	3.48	462,000	272,000
154570	Xylene	- 5	13.7	7.45	2.94	448,000	177,000
154573	Xylene	20	None	3.20	2.63	---	---
154590	Xylene	- 5	None	0.41	0.175	---	---
154270	Mesitylene	- 5	12.5	2.86	12.0	380,000	945,000
154585	Mesitylene	20	13.7	4.20	15.10	210,000	827,000
154558	Ethyl Benzene	20	13.7	1.81	0.47	137,000	35,000
154555	Ethyl Benzene	20	None	1.61	0.13	---	---
154276	Ethyl Benzene	- 5	12.5	2.22	0.233	360,000	42,600
154595	Ethyl Benzene	- 5	None	0.61	1.71	---	---
154250	Naphthalene	21	None	---	0.415(a)	---	---
154259	Naphthalene	20	12.5	1.27(a)	0.815(a)	893,000	647,000
154264	Naphthalene	- 5	12.5	1.48(a)	0.615(a)	906,000	273,000

(a) Based on a 10% naphthalene, 90% carbon tetrachloride solution by weight.

(b) $G = \frac{\text{molecules reacted}}{100 \text{ e.v. absorbed}}$, based on chlorine.

to the ring and alkyl substitution appeared to be the primary reactions. The ratio of addition to substitution was different than that obtained in chlorination reactions without radiation. In general, this ratio appeared to be increased by radiation and decreased by increasing the temperature. The radiation yield is reported as G value (molecules chlorine reacted per 100 e.v. of radiation absorbed) in Table 11. For some reason radiation had little effect on the reaction with ethyl benzene. Whether this is due to inherent inactivity or to inhibiting impurities is not known. Harmer¹⁴ demonstrated the inhibiting

properties of small amounts of benzyl chloride and oxygen in the chlorination of benzene and toluene.

Any alkyl substitution product may have a similar inhibiting effect upon the reaction. The product formed in the chlorination of naphthalene has not been determined as yet. It is not known whether the compound produced is wholly or partially saturated by the chlorination. Further work will be done on the reaction and product analysis in the future. The G values of addition for the naphthalene reaction based on chlorine are high; the G values based on naphthalene would be lower, depending on the amount of saturation to the rings. For example, if the product from Run 154264 was wholly saturated, the G value for addition based on the naphthalene would be: $906,000/5 = 181,200$, where 5 is the mole ratio of chlorine to naphthalene involved in the reaction. Similarly, the G values for substitution will be lower if based on the aromatic compound rather than the chlorine.

Radiation chlorination of benzene took place so quickly that temperature control was difficult. Also the production of the solid addition product tended to plug up the reactor unless the benzene was diluted with carbon tetrachloride. Toluene, xylene, and mesitylene did not react quite so fast and were charged to the reactor in a pure condition. Naphthalene was dissolved in carbon tetrachloride to give a liquid-phase reaction. Some solid product precipitated in the reactor during the run and the carbon tetrachloride provided a slurry medium to prevent plugging the reactor tubes. However, in all cases, reaction under gamma radiation takes place so rapidly as to make it very attractive for commercial application. This is particularly true where the addition product might be desired, for radiation favors the addition reaction.

5. Equipment Changes.—At the termination of the series of runs presented above, it was necessary to dismantle the rack for cleaning and repair. In the course of this dismantling, it was decided to redesign the rack and cooling system to give a wider versatility of operation and a greater ease of operation. In general, the same schematic system employed by Harmer¹⁴ was followed. The changes mentioned previously were incorporated into the system more economically. Other aids in operation were employed. Figure 12 is the schematic diagram of the redesigned chlorination equipment. A photograph of the completed rack is to be found in Fig. 13.

Essentially the changes involved were: (1) location of all cylinders on the rack proper, (2) central location of all stop cocks, (3) central location of measuring devices, (4) fewer rubber connections, (5) more systematized flow pattern on the rack, and (6) incorporation of new equipment.

The N₂ cylinder to purge the system and the O₂ cylinder to cut off

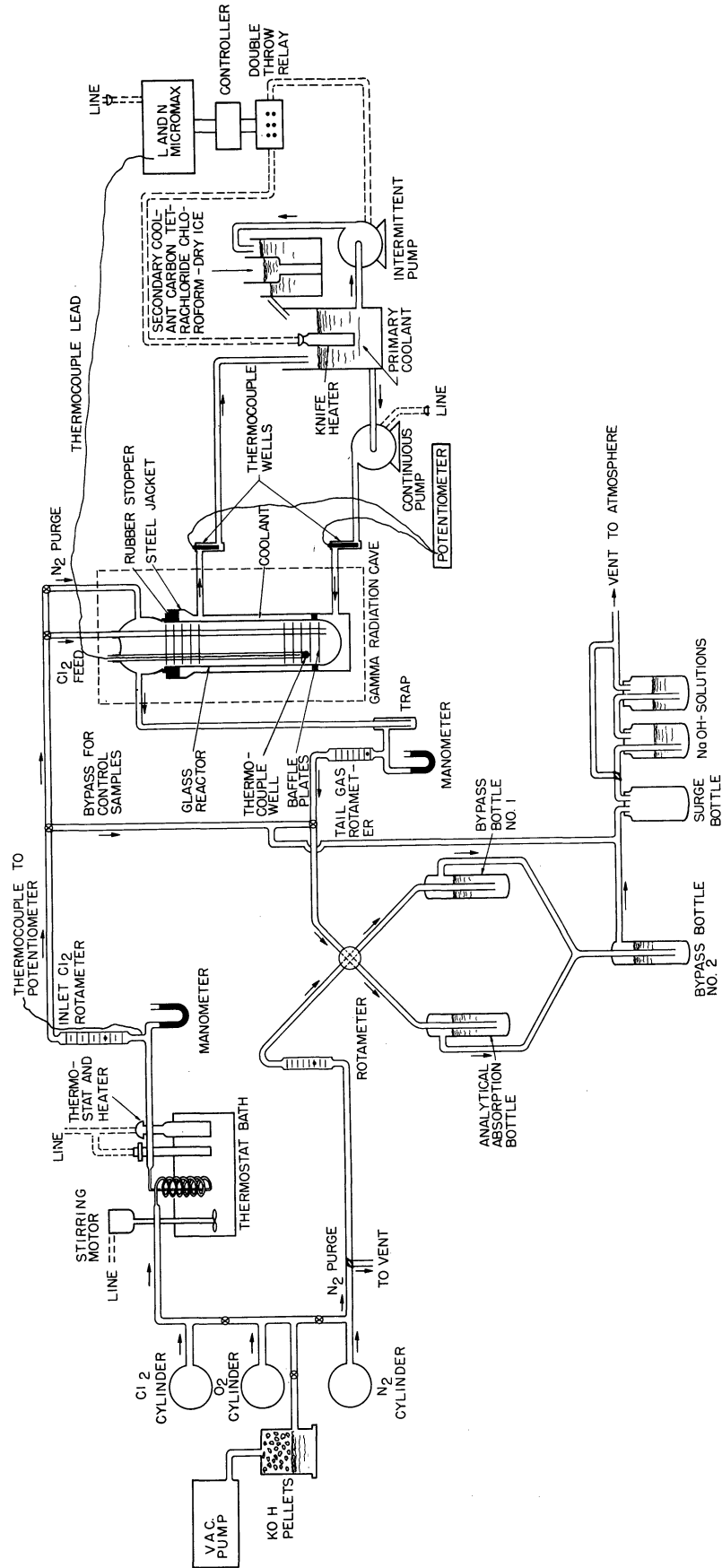


Fig. 12. Schematic diagram of laboratory equipment used in aromatic chlorinations.

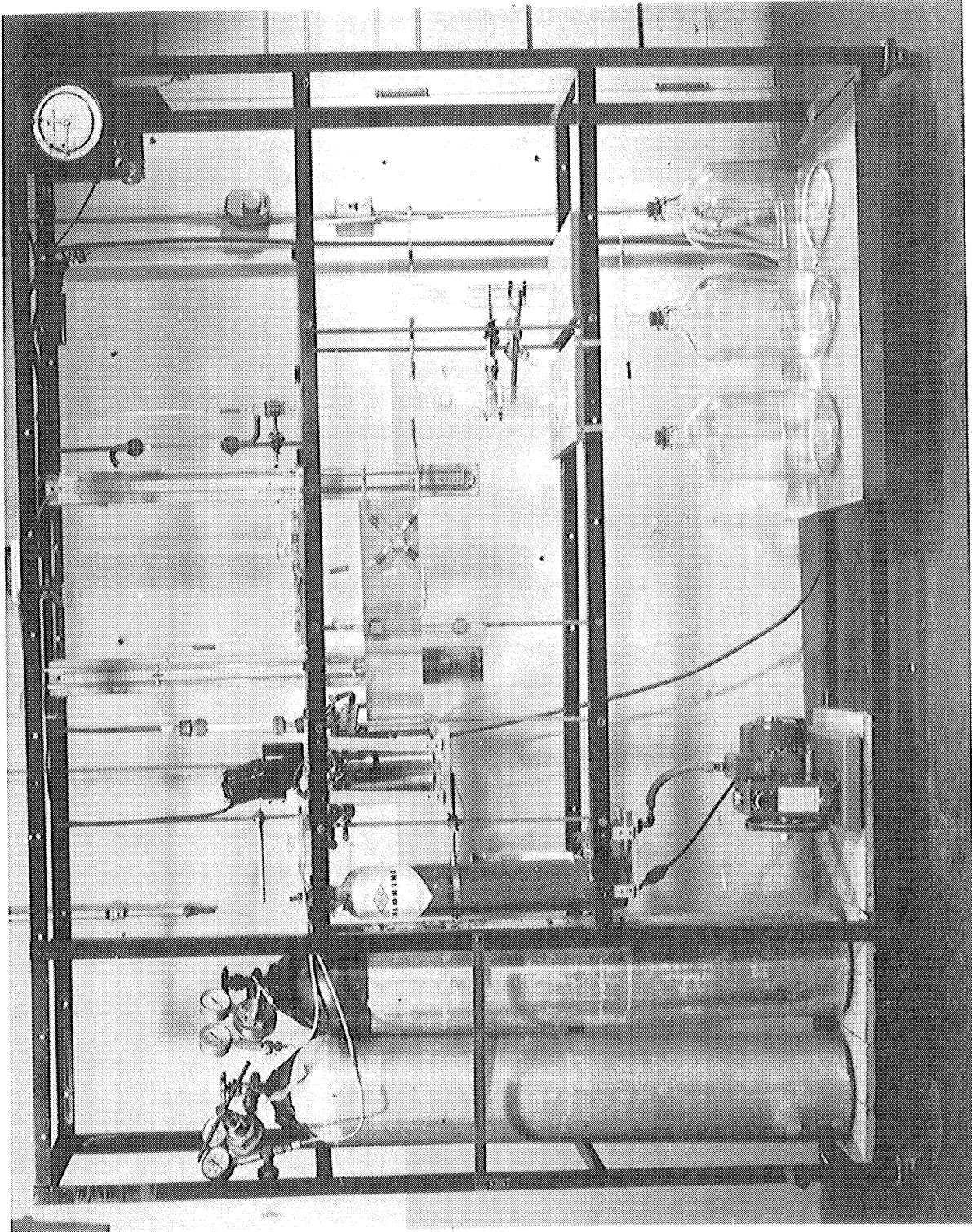


Fig. 13. Redesigned gas rack used for measurement and control of reactant and tail gases in the chlorination experiments.

the reaction at completion of the run were previously located on individual carts external to the rack proper. They took up needed space in the operation area and were awkward to move around the laboratory. In the new rack facility they are located with the chlorine cylinder on the rack proper, as shown in Fig. 13. This eliminated external tubing connections to the rack as well as providing more operation area in front of the rack.

The more central location of stopcocks and measuring devices provided for greater ease of operation. The operator now may make all measurements and adjustments from one position. Any unexpected behavior taking place in the system may be compensated for immediately without major movement on the part of the operator.

The number of rubber-to-glass connections has been reduced by two- or threefold. In general, this eliminated evacuation problems. It also cut down the possibility of chlorine leakage into the analysis laboratory during operation. Glass manifolds were used instead of individual glass stopcocks.

In general, the flow pattern on the rack was more systematized so that the inexperienced operator would have no problem in tracing lines. The gas flow was indicated, stopcocks were numbered, and the number of lines was reduced to a minimum for ease in operation. As indicated in Fig. 12 and shown in Fig. 13, gases enter the system on the left side of the rack, pass through control and measuring devices, enter the reaction area from the center, pass back to the rack in the center, and are absorbed for analysis on the right. The cooling system and the temperature recorder-controller are not shown in Fig. 13. The cooling unit was located in the first-floor laboratory, near the door to the radiation cave. The temperature recorder-controller is located just to the left of the rack during an actual run.

Some new equipment and aids to operation were installed on the rack at the time of rebuilding. A new Flexapulse electric timer was purchased by the Engineering Research Institute for this work. A new Duo-Seal Model 1400B vacuum pump was purchased and installed on the rack. As shown in Fig. 12, new rotameters were installed in the tail-gas line from the reactor and the N_2 purge line to the absorption bottles. These were aids in operation when running plots of the gas data were kept. They also provided accurate control of gases not immediately involved in the chlorine-balance measurements.

A complete operation manual for the new redesigned gas rack has been written for the laboratory and for the aid of any new operator working on the chlorination equipment.

ECONOMICS OF RADIATION CHEMICAL PROCESSING

The laboratory studies on the polymerization of ethylene and the chlorination of aromatic hydrocarbons have demonstrated the feasibility of promoting chemical reactions with gamma radiation. It is of interest to examine the costs of such radiation processes. The chlorination of benzene is well suited to cost estimation and comparison because the reaction is presently conducted on a commercial scale, using ultraviolet radiation.

The addition product of benzene and chlorine is technically known as 1, 2, 3, 4, 5, 6 hexachlorocyclohexane, but it is usually referred to as benzene hexachloride. The gamma isomer of this compound is a powerful insecticide^{15,26} which is sold under various trade names. In the usual radiation reaction this isomer constitutes about 12% of the total addition product. The present commercial process utilizes small quartz equipment necessary for transmission of the ultraviolet. The following calculations are made for the gamma-radiation process using a single larger reaction vessel made of nickel alloy. Costs are estimated for four different gamma-radiation sources derived from fission products.

A design for a similar facility was presented by this laboratory in Progress Report 7.⁴ The reactor designed there consisted of tubes passing close to a radiation source. The reactor design presented here involves a cylindrical vessel surrounding a radiation source located concentrically within it. The vessel and the reacting mixture act as a shield for the gamma radiation. The design here uses a gamma source more efficiently than the design presented previously. Many of the calculations are the same in both cases and for more completely detailed calculations reference should be made to Progress Report 7, pages 26 to 51. The complete data for the chlorination of benzene are reported in that reference and by Harmer *et al.*¹³ The plant design here has been made on the same overall yield basis as that previously reported.

A. DESIGN OF A CHLORINATION PROCESS USING GAMMA RADIATION

In a typical batch run at 20°C and 62 kilorep/hr of radiation, Harmer *et al.*¹³ obtained 63.6 gm of benzene hexachloride in 0.333 hr from a charge of 20 ml of benzene and 80 ml of carbon tetrachloride. The theoretical yield is 65.6 gm, based on the benzene density of 0.88 gm/ml. Neglecting the actual increase in volume of the reactor contents, the benzene concentration decreased from 20 to 0.6% by volume. Assuming the reaction is first order

with respect to benzene concentration C , the rate is $dC/d\theta = -kC$, with k being the reaction velocity constant and θ the time. Integrating this from the beginning to the end of the batch reaction gives $\ln(20/0.6) = -k(0.333)$, or $k = 10.6 \text{ hr}^{-1}$.

As a basis it will be assumed that a plant is to be designed to produce 454 kg/day of the gamma isomer. This corresponds to a production of 541 gm moles/hr of mixed isomers. A cylindrical agitated-flow reactor is to be employed with a uniform benzene concentration of 80%. The gamma source is to be placed in a center hole, according to the scheme shown in Fig. 14. The source is to be of such strength that the mean reaction velocity constant is 1.0, so the reaction rate is $(1.0)(0.8) \text{ ml benzene/hr-ml solution}$. This is equivalent to 9.02 gm mole benzene/hr-liter solution. Since a gm mole of benzene makes a gm mole of product, the volume of the reactor is $541/9.02$ or 60 liters. This volume may be realized in a cylinder 50 cm high and 50 cm in diameter, with a hole 20 cm in diameter for the radiation source and cooling coils circling the inside of the walls.

The reaction velocity constant is assumed to vary directly with radiation intensity I (Harmer¹⁴ showed the chlorination of toluene to vary as \sqrt{I}), which is conservative for intensities less than that of the laboratory experiment. Thus, $k = mI$, or $k = 0.171 I$, from the fact that $k = 10.6$ at $I = 62$. For rough estimation, assume the cylindrical reactor is the equivalent of a 25-cm-radius sphere with a point source of radiation at the center. There will be a spherical hole of 10-cm radius at the center to account for the volume occupied by the actual source. If the radiation intensity on the surface of the hole at 10 cm from the center is 50 kilorep/hr, and if the intensity decreases according to the inverse-square law and the exponential-absorption law, the average k throughout the reactor volume may be calculated as

$$k_{\text{avg}} = \int_{10}^{25} \frac{0.171(50)(10)^2 e^{-0.064(0.88)(r-10)} (4\pi r^2) dr}{r^2 (4/3)\pi [(25)^3 - (10)^3]} = 1.0 .$$

Here 0.064 is the gamma absorption coefficient and 0.88 is the density of the benzene. In order to obtain an intensity of 50 kilorep/hr at 10 cm from the center for a fission-product source, about 1250 curies would be required.²⁰ This is multiplied by a factor of four to account for self-absorption, absorption by the wall and the agitator between the source and the benzene, and losses of radiation from the cylinder through the hole. Therefore, 5000 curies will be taken as a conservative estimate.

The radiation chamber housing the reactor will be made 3 meters square to provide adequate working space. To insure that the intensity of radiation is less than 0.5 millirep/hr outside this chamber with a 5000-curie

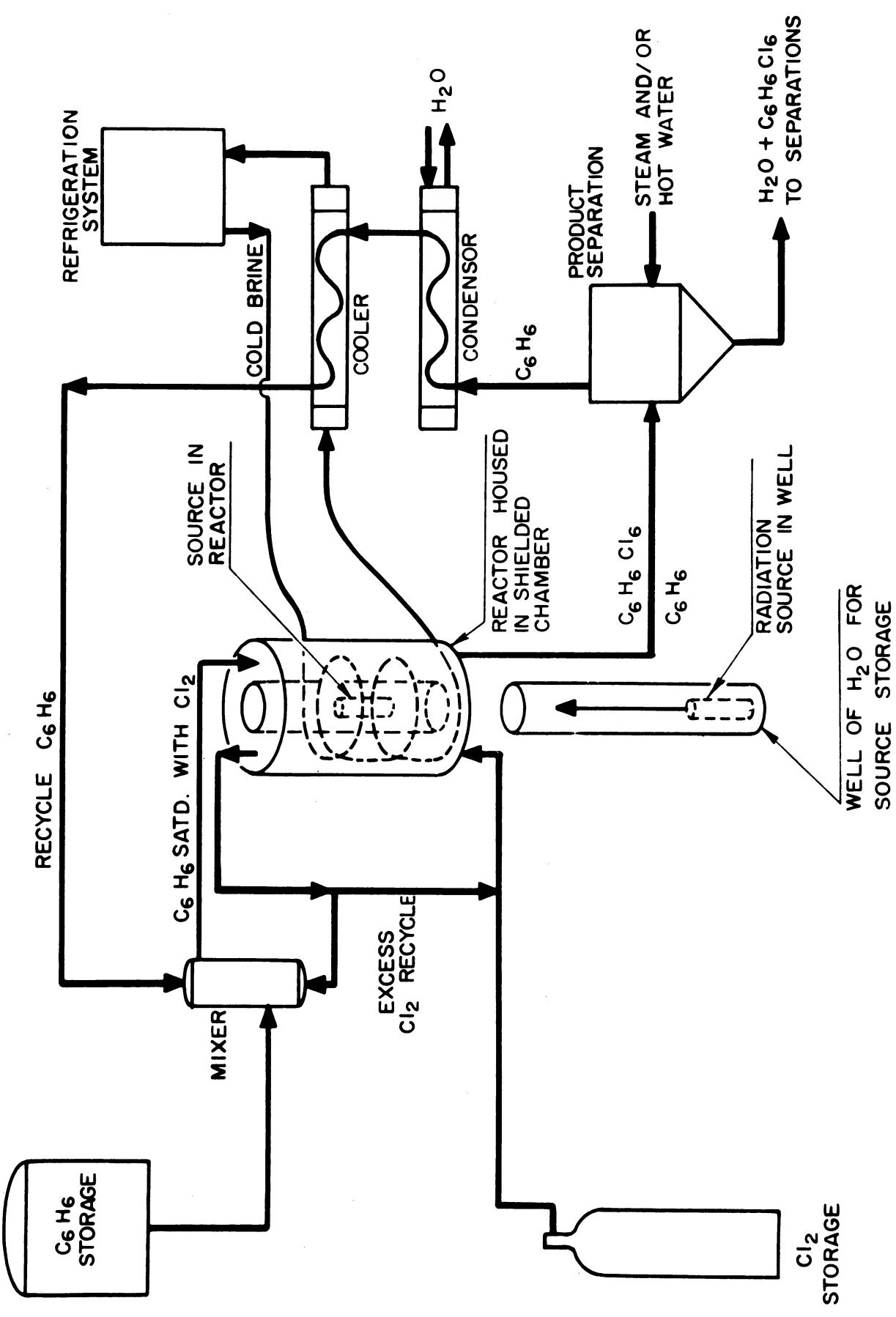


Fig. 14. Flowsheet of proposed plant design for producing benzene hexachloride.

source, the concrete walls must be 85 cm thick.²² The other units in the system are calculated by conventional means. The process is straight-forward, with the benzene being saturated with chlorine before entering the reactor and excess chlorine bubbling through the reactor to keep the contents saturated. The product from the reactor is flashed to separate out the solid benzene hexachloride. The benzene is condensed and returned to the chlorine saturator. Refrigerated coolant is required to maintain the reactor feed and contents at 20°C.

B. COST ESTIMATIONS

The costs of fission-product sources are not yet available. Therefore, estimations are made for a range of values that seem reasonable. Because of varying half-life of different sources, it will be assumed that charges are made approximately according to the radiant energy delivered. Since the energy E of a radioactive source is given by $\int I_0 e^{-\lambda\theta} d\theta = I_0(1 - e^{-\lambda\theta})/\lambda$, at large values of time θ the energy varies inversely as the disintegration constant λ . But λ is the reciprocal of the half-life, so the energy varies directly as the half-life. The costs will therefore be selected in proportion to the half-life. The cost of long half-life sources is to include shipping. Short half-life sources would involve excessive shipping costs and are assumed to be used in the vicinity where they are produced. If the source intensity is not to fall below, say, 80% of its initial strength, short half-life materials will require frequent replacement. These factors have been considered in Table 12, where the costs of producing the mixed isomers of benzene hexachloride are given as a function of the type of radiation source. In estimating the total radiation required, the source is to be composed of five sections. Whenever the intensity falls off 20%, one section is replaced with fresh radioactive material. In the case of cesium-137, it is apparent that no replacements are necessary. In fact, at the end of a five-year period, the cesium activity is still more than 90% of its initial value. In selecting costs for radiation sources, tenfold ranges were estimated for each case, but only the highest value is given in the table. It is noted that the variation in costs of radiation actually has only a small effect on the product cost.

The costs of benzene and chlorine are taken from the latest trade journals. These also give the cost of commercial benzene hexachloride as \$1.90 to \$3.00 per kg of gamma isomer in 12% mixture with the other isomers. The gamma-radiation process evidently can compete with the ultraviolet process for making this compound. Of course, the true comparison between the two should be made on the basis of the comparative costs of the reactors and radiation sources, since all other equipment is the same. What this comparison does show, however, is that gamma-radiation processing is not out of line with other processing methods and that it should be given serious consideration by industry.

TABLE 12. COST ESTIMATE FOR PRODUCING 454 kg/DAY OF
GAMMA ISOMER OF BENZENE HEXACHLORIDE WITH FOUR RADIATION SOURCES

	Radiation Source			
	Gross Fission Product 0.5-yr.	Gross Fission Product 1 - yr.	Gross Fission Product 2 - yr.	Cesium- 137
Half-life, years.	0.2	0.3	1.1	33
Total Curies Req'd.-5 years.	84,000	57,000	19,000	5,000
Selected High Cost/Curie, \$.	0.05	0.10	0.25	5.00
Radiation Cost-5 yr, \$.	4,200	5,700	4,800	25,000
Initial Investment in Radi- ation Source.	250	500	1,250	25,000
Radiation-Chamber Cost, \$.	22,000	22,000	22,000	22,000
Process-Equipment Cost, \$.	49,000	49,000	49,000	49,000
Total Investment, Including Radiation.	71,250	71,500	72,250	96,000
Annual Charges on Investment at 80%, Depreciation, Taxes, Interest, Maintenance, Etc.	57,000	57,200	57,800	76,800
Annual Radiation-Replacement Cost.	800	1,000	700	0
Salaries of Workers, \$/yr.	21,000	21,000	21,000	21,000
Chlorine and Benzene, \$/yr.	109,000	109,000	109,000	109,000
Utilities, \$/yr.	3,000	3,000	3,000	3,000
Sales and Marketing, \$/yr.	8,000	8,000	8,000	8,000
Total Annual Cost, \$.	199,000	199,000	200,000	218,000
Annual Production, 290 Working Days, kg Gamma Isomer.	131,500	131,500	131,500	131,500
Cost/kg Gamma Isomer, in 12% Mixture, \$.	1.51	1.51	1.52	1.66

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PREPARATION OF TRICHLOROACETIC ACID

Clerement⁵ reported that trichloroacetic acid was obtained in 63% yield by the oxidation of chloral hydrate with fuming nitric acid. The same author also reported the synthesis of the trichloro acid by oxidizing chloral hydrate with KMnO_4 .⁶ Other investigators were able to prepare the acid through the oxidation of an aqueous solution of chloral hydrate with KClO_3 ²⁴ or CaOCl_2 .²⁹

Ralph E. Plump³⁰ stated in his patent that trichloro acid was obtained in over 60% yield by the oxidation of the corresponding trichloroaldehyde or the aldehyde hydrate with an aqueous solution of chlorates during agitation. The reaction is initiated at lower temperature in presence of a promotion catalyst such as NH_4VO_3 or $\text{Ce}(\text{SO}_4)_2$.

Stauff Schumache,³³ in an attempted photochemical oxidation of chloral with O_2 at 70° to 90° , found that $\text{COCl}_2 + \text{CO} + \text{HCl}$ were the decomposition products obtained.

Charles Strosacher¹⁰ studied the preparation of trichloroacetic acid by the direct chlorination of acetic acid in the presence of a chlorinating catalyst such as S chloride; the monochloro acid was first formed, and when the chlorination was continued successively at high temperature up to 160° the trichloro compound was formed.

In our chemistry laboratory, repeated experiments at different temperatures gave no conversion of chloral hydrate to trichloroacetic acid by the action of chlorine alone.

At room temperature there was no reaction of chlorine on anhydrous chloral, but at high temperature the chain reaction involving the formation of COCl_2 , CO , and HCl occurred at a very high reaction rate. When sealed tubes of chloral hydrate and liquid chlorine were subjected to gamma radiation, excellent yields of trichloroacetic acid were obtained. Attempts have been made to carry on the conversion as a continuous process; thus far there are not enough data available to indicate the necessary radiation doses, temperature, chlorine concentration, and other factors that affect the reaction. This work is being continued because the product of the reaction has real value, a process of this type merits considerable study, and its mechanism and kinetics should be investigated.

A typical experimental run is outlined below:

Chloral hydrate, 5.5 gm (0.33 moles), and liquid chlorine, 16 ml (.3 mole), were irradiated for 15 hours in a sealed tube at a rate of 41,000 rep/hr at an average temperature of 8° to 10°. The tube was opened and the chlorine was allowed to evaporate at room temperature. The semi-solid residue was extracted from the tube with petroleum ether (60° to 75°). The solvent was evaporated and the residue was fractionated in a small column and .9 gm of unreacted chloral hydrate distilled at 90° to 96°. The residual viscous oil in the distilling flask was subjected to sublimation and 3.8 gm of trichloroacetic acid sublimed at 70° to 74° at 2-mm pressure (80% yield). The colorless crystalline trichloroacetic acid melted at 55° to 57° and gave no depression when admixed with an authentic sample. The methylaniline salt came down quantitatively by mixing equimolecular quantities in a little benzene and leaving the warmed-up solution to cool. The salt crystallizes in colorless needles from CCl₄. The crystalline needles have a melting point of 97°. ³¹ The trichloroacetic acid could be isolated from the reaction mixture by extracting the reaction products with dry benzene and adding the proper amount of freshly distilled methylaniline. The methylaniline salt crystallizes when the mixture is allowed to stand overnight.

Chlorine does not react with chloral hydrate in the absence of radiation. Chloral hydrate (5.5 gm) and liquid chlorine (16 ml) were mixed together in a sealed tube and allowed to stand in the dark for three weeks. When the reaction mixture was subjected to the treatment outlined above, chloral hydrate was recovered unchanged.

CONCLUSIONS AND PROPOSALS FOR FUTURE WORK

On the basis of the work completed and reported here, recommendations as to future work can be made.

The work here, combined with the work by Lewis,¹⁷ gives a generalized picture of the polymerization of ethylene influenced by gamma radiation. The data are sufficient to indicate general trends of temperature, pressure, radiation, and oxygen concentration on the reaction. The yield of polyethylene under gamma radiation is high enough to warrant investigation of the commercial feasibility of the radiation process. A preliminary plant design similar to the design presented for the chlorination of benzene will be made.

The data on the copolymerization of butadiene and styrene show that, in general, the radiation reaction is not as favorable as the present emulsion

polymerization being employed commercially. However, because this compound has such a high commercial value, possibly a few runs will be made at other ranges of reaction conditions than those presented here. No major emphasis will be put upon this future work and the runs will be made at widely divergent reaction conditions. The number of runs will be kept at a minimum.

The data taken on the copolymerization of sulfur dioxide with various olefins indicate that the reactions proceed in a fairly straightforward manner under radiation. The yield is a direct function of the radiation applied. There is little or no induction period as is present in many polymerization reactions under radiation conditions. The reaction proceeds fast enough to warrant commercial investigation. For these reasons the kinetics of reaction will be investigated further to determine the combined radiation and temperature effects upon the copolymerization of sulfur dioxide with a complete series of olefin hydrocarbons. Some olefins not considered in this report will be investigated to give a complete picture of the reaction under radiation conditions.

The data on the Oxo-type reaction are, in general, poor. It is not clear what effect the radiation has upon the reaction. Several more runs will be made under different pressure and temperature conditions in the radiation field to try to answer this question. Olefins of higher molecular weight will be used in some of the future reactions.

General trends are shown in the chlorination reactions for the effects of the addition of methyl groups to the benzene ring. No future runs are contemplated with toluene, xylene, or mesitylene. The effect of longer side chains on the benzene ring is not clear from the runs on the one compound (ethyl benzene) investigated. It is anticipated that runs with higher homologues of the same series will help clear up the question. Several runs will be made with propyl benzene and higher alkyl aromatics. The chlorination of higher ring structures, like naphthalene and possibly anthracene, is to be investigated further. These latter compounds will be run in a solution inert to chlorine such as carbon tetrachloride.

Other gas-liquid reactions will receive literature study and some experimental work. Reactions involving ammonia and hydrogen sulfide as the gaseous reactants are of some interest and will receive attention. The glass reaction equipment is well suited to the measurement and control of these gases and therefore a minimum of equipment changes will have to be made. Analysis procedures must be investigated before any such reactions are carried out.

Batch and flow bromination and iodination should receive some attention during the future period. These reactions should proceed in much the same manner as the chlorination reactions already investigated.

The preparation of trichloroacetic acid from the chlorination of chloral hydrate will be subjected to further study. The kinetics of reaction involving radiation is to be studied further by the group from the Michigan Memorial-Phoenix Project.

In general, a variety of reactions will be studied in the immediate future. Both polymerization and gas-liquid reactions are well suited to the facilities and equipment available in the laboratory. It is in these general fields where most of the work will be carried out.

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