

## **Radiation-Induced Polymerization. I. A Pyrotechnic Binder**

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### **Synopsis**

In the past, binder systems had to be limited to systems where the catalytically initiated polymerization exotherm was low. With radiation-initiated polymerization, this is not a problem, and the number of monomers which can now be investigated is unlimited. Based upon the styrene-benzoyl peroxide system, addition of peroxide sensitizers significantly decrease the radiation dose required for 100% conversion.

### **INTRODUCTION**

A major problem which has confronted pyrotechnic research is the development of an effective binder. The binder must be safe to use, provide good composition to ease bonding, have desirable burning characteristics, and lend itself to rapid mass production techniques. These factors have long been recognized and plague production of most binder systems. Presently, there are two production methods in use: (1) casting,<sup>1</sup> which suffers from high binder concentrations, and (2) pressing,<sup>2</sup> which does not lend itself to continuous processing methods. Both methods suffer from problems, such as hydrogen production from moisture attack on the magnesium, poor bonding of the composition to the casing, and chunking of the candle during burnings.

The search for new binders and production methods has been the subject of much research. One interesting method presently under investigation is the extrusion of mixes similar in composition to those used in cast systems. Typically, these systems involve precipitation of polymers such as Viton A or Estane 5702 with a nonsolvent like 2-propanol to coat the fuel and oxidizer.<sup>1,2</sup>

Another technique tried in this facility microencapsulates magnesium and sodium chloride with poly(methyl methacrylate). The encapsulated particles are dry mixed in an atmosphere of the monomer, pressed, and the absorbed monomer is polymerized by cobalt-60 gamma irradiation. Since the coated particles are in intimate contact after pressing, radiation-induced polymerization bonds the particles together. Doses of approximately 2 megarads are required to produce the maximum strength for the system.

This procedure meets the requirements that the coated particles be moisture resistant, easy to handle, and suitable for continuous processing.<sup>3</sup> Although the ideal of radiation-induced bonding of microencapsulated flare components is new, microencapsulation of fuels with liquid oxidizers has been reported previously.<sup>4</sup> It was found that this method has inherent difficulties in microencapsulating the sodium nitrate and particularly the magnesium.<sup>5</sup>

Although the method of production of pyrotechnic binders by radiation-induced polymerization is still under investigation, several applications which have commercial potential, have been examined. For example, development of concrete-polymer materials<sup>6</sup> is an interesting application where the concrete specimen is loaded with approximately 6% monomer and polymerized with either gamma irradiation or catalytically. Monomers that have been used to date are methyl methacrylate, styrene, acrylonitrile, and copolymers with trimethylolpropane trimethacrylate. The resultant is 300% to 500% stronger than standard concrete.

Another example of the use of gamma radiation is to polymerize monomer-impregnated wood. Commercial production of wood-plastic began in the U.S. in 1969. Three companies (American Novawood Company, Atlantic Richfield Company and Lockheed Georgia Company) are currently using gamma radiation to cure monomer-impregnated wood.<sup>7</sup>

These examples illustrate that commercial applications of ionizing radiation to polymerize vinyl monomers when applied to the proper system can be economically sound. The economics of the production of wood-plastic materials indicate that the cost of curing (radiation cost) are no more than 10% of the total processing cost.<sup>8</sup>

The work described in this report discloses a process which readily lends itself to an irradiation curing process, viz., the production of pyrotechnic materials. As mentioned previously, present production methods suffer from the lack of automation and present many inherent safety hazards, which stem from production operations where personnel must handle the composition (the batch mixing processes). It is the intent of the work described here to illustrate that (1) this method of producing pyrotechnic materials is feasible and (2) these methods can be applied to a continuous process.

## EXPERIMENTAL

### Materials

The monomers used in this study were of standard commercial purity. Removal of inhibitors by distillation would add to the cost of manufacturing and to the inconvenience of the method. Therefore no attempt was made to remove the inhibitors added by the manufacturer, so that actual production conditions could be simulated.

The magnesium and sodium nitrate used were standard production materials. The magnesium sieve size was 30/50 mesh, and the sodium nitrate

was  $32 \pm 10$  microns. These materials were not pretreated before preparation of either the test candles or the ampoules.

### Irradiation Facility

All irradiations in this investigation were carried out in a nominally 10,000-Curie cobalt 60 source at the Radiation Laboratory of Indiana State University.<sup>9</sup> This facility is a "cave type" design with water well source storage. An automatic source-lowering system also was installed which would remove the cobalt 60 from the irradiation chamber in the event of a fire, thus preventing a radiation hazard.

The radiation dosimetry was based on the Fricke ferrous sulfate method with a  $G(\text{Fe}^{+3}) = 15.5$ .<sup>10</sup>

### Conversion Studies

All samples reported here were prepared under ambient conditions in a sealed vial. A mixture, consisting of 60%  $\text{NaNO}_3$  and 40% Mg, was added to the monomer system. In most cases,<sup>3</sup> a polymer was added to the monomer to increase its viscosity. The polymerization sample usually consisted of 15% of the monomer system and 85% of the pyrotechnic mix. Methods of analysis of polymers varied but generally consisted of gravimetric techniques.

**Styrene.** The starting binder contained a 15% mixture of polystyrene and styrene. A simulated flare was prepared with 10.9% binder, 54.4% sodium nitrate, and 35.7% magnesium. Approximately 4 g of this mixture was placed in a glass vial and sealed at ambient pressure. The ampoules were irradiated at  $3 \times 10^5$  rad/hr, and the polymer was analyzed by dissolving the monomer-polymer system in toluene which contained 0.1% hydroquinone. This mixture was then filtered to remove the magnesium and sodium nitrate. The toluene solution was concentrated to a volume of 25 ml. Then 300 ml methanol was added to the solution to precipitate the polymer as a fine suspension. This polymer suspension was heated and then set aside for 24 to 36 hr so that the polymer could agglomerate. The polymer was isolated by filtering into a tared filter crucible and weighed. The per cent conversion of monomer to polymer was recorded.

**Styrene-Benzoyl Peroxide.** The binder contained 2.1% benzoyl peroxide, 12.1% polystyrene, and 85.8% styrene. The simulated flare mixture contained 17.7% binder, 46.5% sodium nitrate, and 34.1% magnesium. Approximately 5 g of this mixture was added to the sample vials and irradiated. The polymer work-up was similar to the one used for styrene.

**Styrene Oxide-Benzoyl Peroxide.** The binder contained 5.0% benzoyl peroxide, 15% polystyrene, and 80% styrene oxide. The simulated flare mixture contained 19.7% of the monomer mixture along with 48.2% sodium nitrate and 32.1% magnesium. The polymerization and polymer work-up of this system were similar to those of the styrene system.

**2-Nitro-2-methylpropyl Methacrylate (2N2MPMA).** The polymerization and polymer work-up for this system were somewhat different from the

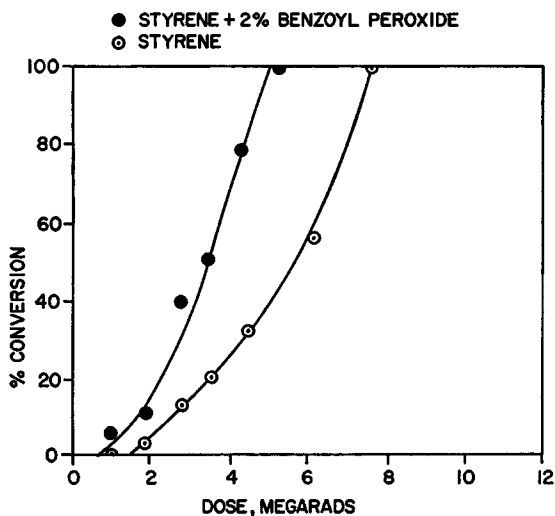


Fig. 1. Per cent conversion of styrene and styrene with benzoyl peroxide vs. radiation dose.

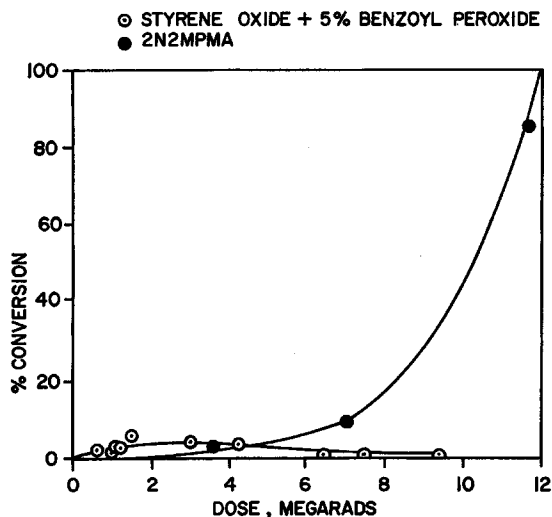


Fig. 2. Per cent conversion of styrene oxide with benzoyl peroxide and 2-nitro-2-methylpropyl methacrylate vs. radiation dose.

styrene and styrene oxide systems. A mixture of 17.5% monomer, 50.0% sodium nitrate, and 33.4% magnesium was prepared. Approximately 5 g of this mixture was added to glass vials for irradiation. Two methods of analysis were used since low-converted material was soluble in acetone, and the higher-converted material was not. For conversions less than 10%, approximately 200 ml acetone which contained 0.1% hydroquinone was

added to each sample. This system was stirred for 1 hr, and then the magnesium and sodium nitrate were removed by filtration. The filtrate was concentrated to 25 ml, and then 300 ml of methanol was added to this solution. The polymer precipitated as a white solid and was isolated by filtration in a tared filter crucible. The yield was determined by standard gravimetric techniques. The higher-converted samples were analyzed by dissolving the magnesium and sodium nitrate in 300 ml of a 10% solution of hydrochloric acid. After stirring for 2 hr, the polymer-monomer mixture was isolated by filtration. This precipitation was washed with methanol, a solvent for the monomer. The remaining white solid was isolated and per cent conversion was determined by standard gravimetric techniques.

TABLE I  
Data Summary<sup>a</sup>

Summarized from		C.P.	B.T. sec	Efficiency, C.P. sec/g	B.R., sec/in.
Table II	Control	171,400	62	46,000	18.63
	Styrene	332,900	35	50,100	9.97
	Styrene oxide	240,400	37	47,800	11.78
Table III	Control #1	159,700	63	43,400	17.29
	Control #2	175,200	56	42,400	15.38
	DER 321	217,100	47	44,100	12.78
	Styrene + B.P.	296,800	35	44,600	9.68
	Styrene oxide + B.P.	248,900	40	43,700	11.16
	2N2MPMA	321,800	32	45,000	8.87
Table IV	Control	184,300	55	43,900	15.48
	Styrene	327,600	34	48,000	9.34
	Styrene oxide	251,200	41	44,700	11.08
	Formrez F-17-80	226,100	47	46,600	13.54

<sup>a</sup> C.P. = Candlepower; B.T. = burning time; B.R. = burning rate.

**DER 321.** A mixture of 11.4% DER 321 (a Dow Chemical Co. epoxy resin), 53.5% sodium nitrate, and 35.1% magnesium was prepared. Approximately 5 g of this mixture was added to glass sample vials for irradiation. There was some indication that the sample had polymerized, but the extent could not be quantitatively measured.

**Formrez F-17-80.** This monomer is a carbonate-terminated unsaturated polyester prepolymer with a molecular weight of approximately 1500, supplied by the Witco Chemical Corp. A mixture of 15.3% Formrez, 51.2% sodium nitrate, and 35.5% magnesium was prepared. Approximately 5 g of this mixture was added to sample vials for irradiation. In the dose range used, no significant conversions were observed; however, this could be owing to the lack of a satisfactory polymer isolation method. The only real change was a loss of tackiness above 2.5 megarads.

TABLE II  
Experimental Data

Candle no.	C.P.	B.T., sec	C.P. sec/g	B.R., sec/in.	B.R., g/sec
Controls					
1	153,000	63	41,900	18.92	3.65
2	171,000	63	46,800	18.92	3.65
3	165,000	64	45,900	19.22	3.59
4	176,000	63	48,200	18.92	3.85
5	192,000	57	47,600	17.18	4.04
Ave.	171,400	62	46,000	18.63	3.72
Styrene					
1	226,000	40	39,300	11.43	5.75
2	301,000	36	47,100	10.29	6.39
3	306,000	34	45,100	9.71	6.76
4	379,000	34	56,000	9.71	6.76
5	359,000	34	53,100	9.71	6.76
6	360,000	34	53,200	9.71	6.76
7	321,000	35	48,800	10.00	6.57
8	368,000	33	52,800	9.43	6.97
9	376,000	34	55,600	9.71	6.76
Ave.	332,900	34.9	50,100	9.97	6.61
Styrene Oxide					
1	247,000	43	46,200	12.29	5.35
2	250,000	34	37,000	9.71	6.76
3	256,000	43	48,000	12.29	5.35
4	277,000	44	53,000	12.57	5.23
5	296,000	43	55,000	12.29	5.35
6	262,000	43	49,000	12.29	5.35
7	237,000	42	43,000	12.00	5.48
8	288,000	38	47,600	10.86	6.05
9	291,000	41	59,900	11.71	5.61
Ave.	240,400	37.1	47,800	11.78	5.62

### Experimental Candles and Controls

**Preparation of the Monomer.** Polystyrene (15% by weight) was mixed with styrene and styrene oxide monomers to obtain a more viscous material which could easily be mixed. The other monomers and prepolymers were viscous enough to be mixed as purchased. The standard production binder, DER 321 resin and DEH 14 catalyst purchased from the Dow Chemical Co., was used for the control candles.

**Preparation of the Candles.** The composition used for the control and experimental candles was magnesium 58%, sodium nitrate 38%, and binder 4%. This composite was mixed in a Hobart blender which had been converted to air drive. The composition was pressed into fishpaper tubes at 8500 psi. The finished candles were approximately 2 in. in diameter, 3 in. long, and contained approximately 230 g.

## RESULTS

**Conversion Studies.** Results of the conversion studies for styrene, styrene plus 2.1% benzoyl peroxide, styrene oxide plus 0.5% benzoyl peroxide, and 2-nitro-2-methylpropyl methacrylate are illustrated in Figures 1 and 2. Conversion data for DER 321 and Formrez have not been included because of the difficulty in obtaining quantitative data.

**Candle Data.** The results of the candle data obtained are shown in Tables II to IV and are summarized in Table I. It should be noted that the length of each candle was measured; however, some variances in burning time and rate should be expected. One or two sets of controls were burned with each set of experimental candles to determine the burning tunnel characteristics.

## DISCUSSION

### Radiation Yields

Examination of the results of the polymerization of styrene indicate that 100% conversion to polymer is obtained after approximately 7.5 megarads; while upon the addition of 2% of benzoyl peroxide, this is lowered to a value of approximately 5 megarads. In addition, the benzoyl peroxide appears to have two effects: it tends to shorten the induction period and increase the rate of polymerization.

The polymerization of styrene oxide plus 0.5% benzoyl peroxide is illustrated in Figure 2. Here, it can be seen that there is no significant conversion of the styrene oxide for doses as high as 9 megarads. The polymerization of 2N2MPMA, also illustrated in Figure 2, shows that 100% conversion is obtained only for doses in excess of 11 megarads. There appears to be a significant induction period which may last to doses as high as 5 megarads.

The polymerization of Formrez F-17-80 and the analysis of polymer did not lend themselves to standard analytical methods; however, there was indication of an insoluble material that was not soluble in acetone, a known solvent for the prepolymer. Since Formrez F-17-80 is an unsaturated polyester with a molecular weight of approximately 1500, there is the ever-present possibility that conversion to a higher molecular weight polymer via a crosslinking-type mechanism as opposed to the conventional additional polymerization methods. This could account for the change in the viscosity observed in the range of 1 to 2 megarads.

The polymerization of DER 321 also suffered from the difficulty of analyzing the resultant polymer. Attempts to remove the magnesium and sodium nitrate only lead to hydrolysis of the polymer known to be present based on solvent extracts with toluene. However, since this solvent is not completely effective in dissolving the polymer, it could not be used in an analytic method.

Polymerization of styrene in wood-plastic combinations indicates that 100% conversion should be obtained after a dose of approximately 5 mega-

rads. One very interesting feature of the wood-plastic combination studies is the fact that the dose required for 100% conversion is a function of the irradiation intensity. For example, in the polymerization of methyl methacrylate, the dose for 100% conversion at an intensity of  $1 \times 10^4$  rads/hr is approximately 0.6 megarad, while at an intensity of  $8 \times 10^4$  rads/hr, the dose required is 1.8 megarads. Thus, a decrease in intensity by a factor

TABLE III  
Experimental Data

Candle no.	C.P.	B.T., sec	C.P. sec/g	B.R. sec/in.	B.R. g/sec
Control #1					
1	159,200	60	41,350	16.58	3.83
2	169,000	62	45,556	17.13	3.71
3	158,000	64	43,965	17.68	3.59
4	154,800	63	42,401	17.40	3.65
5	154,000	67	44,860	18.50	3.43
6	512,200	64	42,351	17.68	3.59
7	166,000	61	44,026	16.85	3.77
8	153,300	63	41,990	17.40	3.65
9	155,300	62	41,863	17.13	3.71
10	175,000	60	45,652	16.58	3.83
Ave.	159,700	62.6	43,400	17.29	3.68
Control #2					
1	167,900	57	41,610	15.75	4.04
2	179,300	51	39,757	14.11	4.51
3	181,000	57	44,856	15.75	4.04
4	168,900	55	40,389	15.19	4.18
5	175,000	58	44,130	16.00	3.97
6	182,700	53	42,100	14.63	4.34
7	176,000	57	43,617	15.75	4.04
8	172,700	56	42,048	15.47	4.12
9	173,700	57	43,047	15.75	4.04
Ave.	175,200	55.7	42,400	15.38	4.14
DER 321					
1	211,700	48	44,180	13.01	4.79
2	224,200	46	44,840	12.47	5.00
3	218,700	48	45,641	13.01	4.79
4	226,600	46	45,320	12.47	5.00
5	220,500	47	45,058	12.74	4.89
6	213,200	50	46,347	13.55	4.60
7	218,600	48	46,620	13.01	4.79
8	207,000	49	44,100	13.27	4.69
9	211,300	46	42,260	12.47	5.00
10	224,200	45	43,856	12.20	5.11
11	207,900	46	41,580	12.70	5.00
12	212,100	47	43,342	12.98	4.89
13	221,900	45	40,520	12.42	5.12
14	222,000	46	44,400	12.70	5.00
Ave.	217,100	47	44,100	12.78	4.91

(continued)



TABLE III (continued)

Candle no.	C.P.	B.T., sec	C.P. sec/g	B.R. sec/in.	B.R. g/sec
Styrene + 0.5% Benzoyl Peroxide					
1	305,000	34	45,086	9.40	6.76
2	312,000	35	47,478	9.67	6.57
3	305,000	34	45,086	9.40	6.76
4	324,000	34	42,730	9.40	6.76
5	322,000	35	49,000	9.67	6.57
6	289,000	36	45,234	9.96	6.39
7	294,000	34	43,460	9.40	6.76
8	269,200	36	42,135	9.96	6.39
9	282,000	36	44,139	9.96	6.39
10	266,000	36	41,666	9.96	6.39
Ave.	296,800	35	44,600	9.68	6.57
Styrene Oxide + 0.5% Benzoyl Peroxide					
1	264,000	40	115,391	11.05	5.75
2	249,000	41	44,386	11.32	5.61
3	260,000	41	46,347	11.31	5.61
4	245,700	40	42,730	11.05	5.75
5	243,200	40	42,295	11.05	5.75
6	259,000	40	45,043	11.05	5.75
7	241,500	41	43,050	11.32	5.61
8	248,500	39	42,136	10.75	5.90
9	229,000	41	40,821	11.32	5.61
10	249,000	41	44,386	11.32	5.61
Ave.	248,900	40.4	43,700	11.16	5.70
2-Nitro-2-methylpropyl Methacrylate					
1	324,000	32	45,078	8.85	7.19
2	307,000	33	45,482	9.12	6.96
3	336,000	31	45,286	8.56	7.42
4	337,000	32	46,886	8.85	7.19
5	339,000	32	47,165	8.85	7.19
6	334,000	32	46,469	8.85	7.19
7	313,000	33	44,908	9.12	6.96
8	324,000	31	43,669	8.56	7.42
9	302,100	33	43,334	9.12	6.96
10	302,000	32	42,107	8.85	7.19
Ave.	321,800	32.1	45,000	8.87	7.17

of 8 decreases the dose required to reach 100% conversion by a factor of 3. This would be an important design factor to be considered in any future commercial application of this method. Gamma radiolysis of sodium nitrate produces several radical species, and the presence of these radicals could hinder polymerization and account for the higher doses required.<sup>11</sup>

The use of peroxide to lower the dose required for 100% conversion is also illustrated in Figure 1. Here, a factor of approximately 2 was gained on the dose required for 100% conversion. This effect was previously observed in the polymer-concrete combinations.

### Comparison of Controls and Experimental Candles

From Table I it can be seen that the experimental candles exhibited higher candlepower and faster burning rates than the control candles without loss in efficiency, particularly styrene candles, which show higher candlepowers and efficiencies.

The fast burning rates observed in the experimental candles probably result from incomplete conversion of the monomer or prepolymer. If

TABLE IV  
Experimental Data

Candle no.	C.P.	B.T., sec	Efficiency, C.P. sec/g	B.R., sec/in.	B.R., g/sec
Controls					
1	193,300	58	48,745	16.38	3.97
2	197,600	59	42,956	14.12	4.60
3	188,000	59	48,226	16.66	3.90
4	191,100	58	48,190	16.38	3.97
5	186,100	54	43,693	15.25	4.26
6	182,600	58	46,046	16.38	3.97
7	174,800	55	41,800	15.54	4.18
8	170,600	52	38,750	14.69	4.42
9	183,000	50	39,782	14.12	4.60
10	175,700	54	41,251	15.25	4.26
Ave.	184,300	54.8	43,900	15.48	4.21
Styrene					
1	331,600	35	50,460	9.64	6.57
2	324,500	34	47,969	9.67	6.76
3	324,900	35	49,441	9.64	6.57
4	339,500	33	48,710	9.09	6.97
5	351,200	34	51,916	9.67	6.76
6	318,060	33	45,634	9.09	6.97
7	311,050	35	47,333	9.64	6.57
8	315,600	33	45,281	9.09	6.97
9	323,400	33	46,400	9.09	6.97
10	335,900	32	46,733	8.82	7.19
Ave.	327,600	33.7	48,000	9.34	6.83
Styrene Oxide					
1	262,700	41	46,829	11.11	5.61
2	256,000	42	46,747	11.38	5.48
3	251,000	39	42,679	10.57	5.90
4	245,800	43	45,953	11.65	5.35
5	260,300	40	45,269	10.84	5.75
6	222,900	42	40,703	11.38	5.38
7	261,500	41	46,661	11.11	5.61
8	242,400	42	44,264	11.38	5.48
9	248,100	40	43,147	10.84	5.75
10	261,600	39	44,358	10.57	5.90
Ave.	251,200	40.9	44,700	11.08	5.63

(continued)

TABLE IV (continued)

Candle no.	C.P.	B.T., sec	Efficiency, C.P. sec/g	B.R., sec/in.	B.H., g/sec
Formrez F-17-80					
1	249,200	46	49,840	13.15	5.00
2	226,000	49	48,147	14.00	4.69
3	234,600	45	45,900	12.86	5.11
4	225,500	50	49,021	14.29	4.60
5	230,800	48	48,166	13.71	4.79
6	230,400	48	48,083	13.71	4.79
7	245,000	47	50,065	13.43	4.89
8	230,000	48	48,000	13.71	4.79
9	203,000	59	44,130	14.29	4.60
10	237,400	48	49,544	13.71	4.79
11	229,000	47	46,795	13.43	4.89
12	218,300	48	45,558	13.71	4.79
13	224,400	45	43,904	12.86	5.11
14	214,100	49	45,612	14.00	4.69
15	219,400	47	44,833	13.43	4.89
16	211,800	48	44,201	13.71	4.79
17	216,200	47	44,180	13.43	4.89
18	226,130	46	45,226	13.14	5.00
19	222,700	46	44,450	13.14	5.00
20	228,900	46	45,780	13.14	5.00
Ave.	226,100	47.4	46,600	13.54	4.86

the monomers are not completely converted to polymer, there is the possibility that vaporization of the unreacted monomer would immediately precede the advancing flame front. The effect of the unreacted monomer is a matter of conjuncture, but should be investigated.

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