

# Flame-Resistant Cotton Textiles by a Continuous Photocuring Process

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## Synopsis

A continuous process for the photoinitiated copolymerization of vinyl phosphonate oligomer (MW 0.5–1.0 kg) and *N*-methylolacrylamide from aqueous solutions with cotton printcloth and a sateen fabric was investigated. The free radical reactions, initiated on the cellulose molecules by exposure of the padded cotton fabric to UV radiation gave a flame-resistant (DOC FF 3-71 test) textile product. The effects of several variables on the efficiency of oligomer and monomer conversion to polymer add-on were determined, with maximum efficiencies being 75–85%. Variables were fabric speed through the reactor (0.006–0.039 m/sec), light transmission through Pyrex or quartz windows in the tunnel, four sets of interchangeable tri-power UV lamps having different spectral distributions and relative intensities, and heat buildup within the reactor. Selected samples of these modified cotton fabrics were evaluated for flame resistance, some textile properties, and elemental phosphorus and nitrogen analysis. Copolymer and phosphorus distribution within and between the cotton fibers were illustrated by transmission electron microscopy and by energy dispersive x-ray analysis.

## INTRODUCTION

The development of new processes for the application of flame retardants and other finishing agents to cotton fabrics continues to be of interest. Processes utilizing UV light are currently receiving increased attention. Near-UV radiation has been used in unsensitized free radical reactions to initiate copolymerization of vinyl monomers with cellulose.<sup>1-9</sup> The products from these reactions can have a high degree of stability and conversion of monomer to copolymer grafts.

A process for preparing flame-resistant cotton fabrics with a water soluble mixture of a vinyl phosphonate oligomer and *N*-methylolacrylamide in an unsensitized photoinitiated reaction has been developed on a laboratory scale<sup>4</sup> with Rayonet\* photochemical reactors. Optimum conditions for the conversion of oligomer and monomer to grafted copolymer with cotton fabrics were established.

This article deals with utilizing the available data to adapt the laboratory scale process to a continuous photoinitiated process for preparing flame-resistant cotton fabrics. The effects of experimental factors on graft copolymerization, location of copolymer in the fibrous structure, and some textile properties are reported.

\* Names of companies or commercial products throughout this article are given solely for the purpose of providing specific information their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

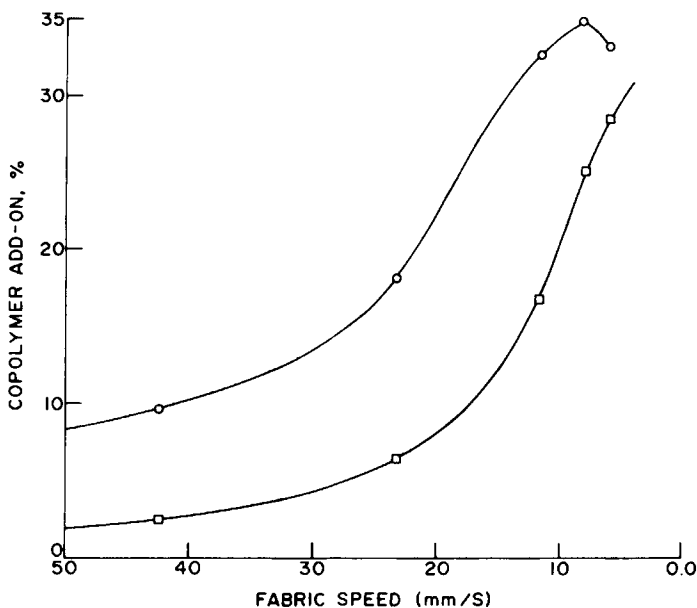


Fig. 1. Effects of fabric speed and quartz (O) vs. Pyrex (□) tunnel windows on copolymer add-on of vinyl phosphonate oligomer and *N*-methylolacrylamide (VP:NMA, 1:0.80 mole ratio, solids content on fabric, 45%, lamp set No. 1, 0.006–0.04 2 m/sec).

## MATERIALS

Cotton fabrics were a commercial grey printcloth ( $\sim 0.115$  kg/m<sup>2</sup>, 3300  $\times$  3300 threads/m) and a commercial grey sateen (about 0.254 kg/m<sup>2</sup>, 3200  $\times$  2000 threads/m). The fabrics were desized, alkali scoured, bleached, water washed, and air dried. Samples of the fabrics to be padded and irradiated were equilibrated overnight in air at about 25°C and 45% RH to constant weight for add-on calculations.

Fyrol 76 (Stauffer Chemical Co.), a water soluble, polyunsaturated, vinyl-phosphonate oligomer (VP) (MW 0.5–1 kg; 22–23 wt % phosphorus) that was made by condensation polymerization of vinyl phosphonate monomer,<sup>10,12</sup> and *N*-methylolacrylamide (NMA), a commercial product, were used as received. Other chemicals used were of reagent grade.

## METHODS

The UV light source was a modified UV Processor, model 1  $\times$  1, manufactured by PPG Radiation Polymer Co.<sup>13</sup> Modifications included installing a stainless steel tunnel through the processor chamber, having interchangeable quartz or Pyrex windows for UV light passage, and adding manifolds for uniform nitrogen purging, above and below the fabric, as well as a brush and flexible flap at each end of the tunnel to control flow of nitrogen purging and prevent UV-light leakage. The processor was equipped with two UV-lamp housings mounted horizontally within the chamber so as to irradiate both the top and bottom of the fabric. Each housing contained one lamp, 0.4572 m long. The tunnel windows were opposite each housing. The replaceable, interchangeable lamp sets

TABLE I  
Effects of Four Sets of Tri-power Lamps on Photoinitiated Conversion of Vinyl Phosphonate Oligomer and *N*-Methylolacrylamide to Copolymer Add-On on Cotton Printcloth<sup>a</sup>

Fabric speed, m/sec	Copolymer add-on for lamp sets, %			
	No. 1	2	4	5
	Low Wattage, 120			
0.0395	—	15.0	14.5	18.2
0.0236	16.1	23.2	21.4	26.3
0.0117	32.3	32.4	32.0	37.0
0.0076	35.4	36.7	34.9	37.6
0.0061	33.4	35.3	34.7	36.4
	Normal Wattage, 200			
0.0395	—	16.4	16.3	19.9
0.0236	18.2	24.1	23.1	25.7
0.0117	32.7	33.3	32.8	35.5
0.0076	34.9	35.7	37.5	36.5
0.0061	33.1	34.9	34.3	35.9
	High Wattage, 300			
0.0395	—	19.8	19.7	23.6
0.0236	22.2	27.5	26.2	30.6
0.0117	36.1	37.6	35.8	39.1
0.0076	35.0	37.6	35.4	37.1
0.0061	31.9	36.9	34.6	4.9 <sup>b</sup>

<sup>a</sup> Mole ratio of vinyl phosphonate oligomer to *N*-methylolacrylamide in solution was 1:0.80, solids content on fabric, 45%. Quartz windows in tunnel.

<sup>b</sup> Lamps off, heat effect only.

were operated at three selected levels of power (300, 200, and 120 W/0.0254 m).

The standard set was medium pressure, mercury vapor lamps. Four additional sets of "seeded" medium pressure, mercury vapor lamps with different spectral distributions were supplied with the processor. Lamp distance (upper and lower) from the fabric was 0.127 m.

Samples of fabric [0.41 × 0.99 m–(0.41 × 3.04 m)] were weighed and padded through aqueous solutions of VP and NMA at 25°C by a two-dip, two-nip process. These padded samples, after either air drying (overnight) on-line or heat drying in a tenter frame for 60 sec at 60°C, were sewn together with interspersing, unpadded spacers (0.41 × 1.83 m) and rolled on a shell. The spacers provided an interval of time in which to change lamp power and/or fabric speed between samples while the fabric continued to move with the lights remaining on. The material from the shell was threaded through the tunnel and the draw rolls of a variable-speed fabric batcher. The draw rolls pulled the material through the processor at a constant speed. Entrance ports to the chamber were closed, and the water, air, nitrogen (0.001 m<sup>3</sup>/sec), and lamps were turned on. Photoirradiation was carried out by opening the lamp shutters and pulling the fabric through the tunnel by the variable-speed fabric batcher.

After photoirradiation, the samples were removed from the shell and washed in hot water either in a washing machine (samples were separated from spacers) for 600 sec at 60°C or in a pilot-plant winch for 600 sec at 82°C to remove unreacted oligomer and monomer. Samples were dried either 1800 sec in a clothes dryer or for 180 sec at 82°C in the tenter frame. After equilibration to constant

TABLE II  
Effects of Fabric Speed and Lamp Wattage on the Mole Ratio of Vinyl Phosphonate Oligomer and *N*-Methylolacrylamide in the Copolymer on the Fabric

Fabric speed m/sec	Lamp wattage <sup>a</sup>	Lamp set	Solids content, <sup>b</sup> % on fabric	Copolymer add-on, %	VP:NMA <sup>c</sup> mole ratio in copolymer
Cotton printcloth fabric					
0.0400	<i>L</i>	5	45	18.2	1:1.75
0.0079	<i>L</i>	5	45	37.6	1:1.04
0.0395	<i>L</i>	2	45	15.0	1:1.98
0.0076	<i>L</i>	2	45	36.7	1:1.07
0.0400	<i>N</i>	5	45	19.9	1:1.57
0.0079	<i>N</i>	5	45	36.5	1:1.11
0.0076	<i>N</i>	2	45	31.5	1:1.11
0.0099	<i>N</i>	1	45	25.8	1:1.51 <sup>d</sup>
0.0099	<i>N</i>	1	45	—	1:1.71 <sup>e</sup>
0.0099	<i>N</i>	1	45	—	1:2.18 <sup>f</sup>
0.0099	<i>N</i>	1	45	—	1:2.74 <sup>g</sup>
0.0400	<i>H</i>	5	45	23.6	1:1.35
0.0079	<i>H</i>	5	45	37.1	1:1.00
0.0234	<i>H</i>	2	45	27.5	1:1.35
Cotton sateen fabric					
0.0400	<i>N</i>	5	42	10.5	1:1.50
0.0236	<i>N</i>	5	39	16.7	1:1.40
0.0119	<i>N</i>	5	37	22.1	1:0.96
0.0079	<i>N</i>	5	38	24.2	1:1.07
0.0061	<i>N</i>	5	37	24.6	1:0.85
0.0117	<i>N</i>	2	39	22.2	1:1.35
0.0076	<i>N</i>	2	37	24.5	1:1.35

<sup>a</sup> *L* = Low (120), *N* = Normal (200), and *H* = High (300).

<sup>b</sup> *M* = Mole ratio, 1:0.80 in solids content.

<sup>c</sup> = VP, vinyl phosphonate oligomer; NMA, *N*-Methylolacrylamide: mole ratio calculated on basis of nitrogen and phosphorus contents. Wash and dry cycles, <sup>d</sup> (0), <sup>e</sup> (1), <sup>f</sup> (25), and <sup>g</sup> (50).

weight at about 25°C and 45% RH, the increase in weight of the photoirradiated, modified fabric over its original weight was recorded as a copolymer add-on. The efficiency of conversion of the oligomer and monomer to copolymer add-on was calculated as (copolymer add-on)/(solids in wet pickup).

The padded fabrics, modified by photoirradiation, were laundered and dried in accordance with AATCC Test Method 124-1969, as specified in the DOC standards.<sup>14</sup> Flammability measurements were made in accordance with DOC FF 3-71.<sup>15</sup> The phosphorus contents of the samples were determined by the x-ray fluorescence method<sup>16</sup>; the nitrogen contents were determined by the Kjeldahl method.<sup>17</sup> Physical properties of the fabrics were determined by ASTM Methods for breaking strength,<sup>18a</sup> tearing strength,<sup>18b</sup> flex abrasion,<sup>18c</sup> and conditioned and wet-wrinkle recovery, Monsanto.<sup>18d</sup>

Microscopical analyses<sup>19</sup> were used to determine the interaction between cellulose and the vinyl phosphonate oligomer and *N*-methylolacrylamide and the location of the oligomer-polymer within the fibrous cross section (transmission electron microscopy); surface areas of deposits of oligomer-polymer (scanning electron microscopy); and phosphorus location within the fibrous cross section (energy dispersive x-ray analysis).

TABLE III  
Effects of Wash and Dry Cycles on Phosphorus and Nitrogen Contents of Modified Cotton Fabrics<sup>a</sup>

Copolymer add-on, %	Machine wash and dry cycles							
	0		1		25		50	
	P,%	N,%	P,%	N,%	P,%	N,%	P,%	N,%
	Printcloth							
25.8	1.86	1.27	1.57	1.20	1.19	1.16	1.04	1.28
33.2	3.07	1.50	3.10	1.52	2.90	1.54	2.73	1.54
	Sateen fabric							
19.4	2.08	1.07	1.14	1.01	0.84	0.89	0.81	1.01
23.7	2.38	1.06	2.19	1.13	2.17	1.10	1.75	1.02

<sup>a</sup> Lamp set No. 1 used, normal wattage (200), solids content on fabric, 45%.

## RESULTS

The effects of the speed at which the fabric is passed through the UV processor and the tunnel window material on the photoinitiated conversion of VP and NMA to copolymer add-on on cotton fabrics are shown in Figure 1.

With the set of standard lamps (identified as lamp set No. 1 in Table I operating at 200 W/0.0254 m, as the speed of the fabric passing through the reactor is reduced from 0.042 to 0.006 m/sec, and copolymer add-on increases from 9.7 to 34.9% for the quartz windows and from 2.5 to 28.5% for the Pyrex windows. For this set of lamps, the maximum conversion of oligomer and monomer to copolymer graft was 75.2% for the quartz and 67.8% for the Pyrex windows.

The effects for four sets of tri-power lamps on the photoinitiated conversion of VP and NMA to copolymer add-on on cotton printcloth are shown in Table I. Results from lamp sets 2, 4, and 5 show little change in percent add-on when compared to standard lamp set No. 1, even though the lamps were manufactured to enhance some wavelengths while inhibiting others in the spectra. Spectra for these lamps range from 238–580 nm with no calibration curve available to establish what percentage of light is within a certain wavelength range.

The effects of the speed at which the fabric passes through the reactor, lamp set, and lamp wattage on the mole ratio of VP:NMA in the copolymer on the fabric are shown in Table II. Samples of printcloth were padded through

TABLE IV  
Effects of Wash and Dry Cycles on Flame Retardance of Modified Cotton Fabrics<sup>a</sup>

Copolymer add-on, %	Char length, m <sup>b</sup>				
	Machine wash and dry cycles				
	0	1	10	25	50
	Cotton printcloth				
25.8	64	89	145	Bel	Bel
33.2	61	79	64	61	66
	Cotton sateen fabric				
19.4	51	99	155	Bel	Bel
23.7	28	28	33	53	48

<sup>a</sup> Lamp set No. 1 used, normal wattage (200), solids contents on fabric, 45%.

<sup>b</sup> DOC FF 3-71 flammability test: char lengths less than about 0.177-m pass: Bel, burned entire length, 0.254 m.

TABLE V  
Effects of Photoinitiated Polymerization of Vinyl Phosphonate Oligomer and *N*-Methylolacrylamide on some Textile Properties of Cotton Fabrics

Lamp set No.	Lamp <sup>a</sup>	Fabric speed, m/sec	Copolymer add-on, %	Breaking strength, N	Tearing strength, N	Flex abrasion (cycles)	Wrinkle recovery stiffness		
	watt-age, 0.254 m						angle, °(W + F)		mN m
Cotton printcloth									
—	—	—	—	164	8.1	694	194	169	0.017
—	—	6.1	—	151	7.6	583	219	159	0.017
5	<i>L</i>	40.0	18.3	153	5.1	228	178	267	0.141
5	<i>N</i>	40.0	19.9	168	4.7	204	180	268	0.138
5	<i>N</i>	23.6	25.7	160	4.2	147	181	257	0.125
5	<i>H</i>	23.6	30.6	155	3.8	132	184	270	0.197
5	<i>L</i>	11.9	37.0	132	2.5	102	213	272	0.286
5	<i>N</i>	7.9	36.5	136	2.2	95	233	278	0.296
2	<i>L</i>	39.5	15.0	164	5.8	334	203	240	0.059
2	<i>H</i>	23.7	27.5	163	4.3	168	164	274	0.099
2	<i>L</i>	7.6	36.7	134	2.4	111	232	254	0.292
2	<i>N</i>	7.6	35.7	129	2.6	145	233	270	0.174
Cotton sateen									
—	—	—	—	494	62.8	1813	202	132	0.090
2	<i>N</i>	11.7	22.2	462	43.2	575	179	221	0.441
2	<i>N</i>	7.6	24.5	445	25.5	639	177	263	0.870
5	<i>N</i>	11.9	22.1	471	43.8	499	181	252	0.452
5	<i>N</i>	7.9	24.2	408	32.0	523	204	242	0.893

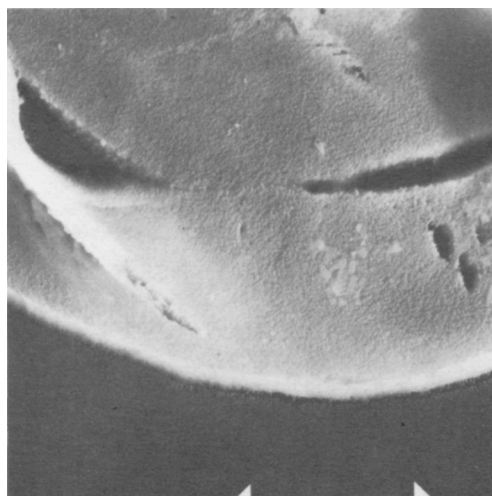
<sup>a</sup> *L* is low (120), *N* is normal (200), and *H* is high (300)/0.254 m.

Note: Only in lamp wattage column does *N* stand for normal. In other columns, *N* is the prefix for Newton.

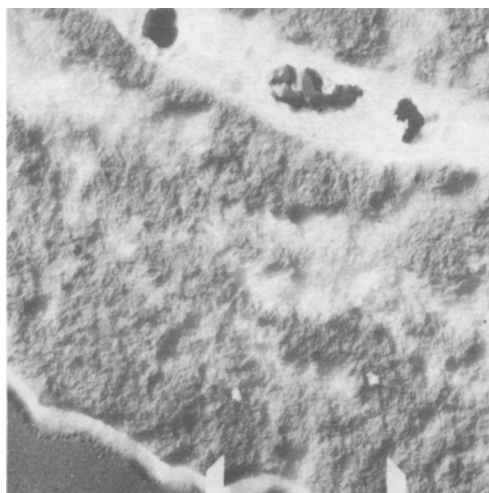
aqueous solutions containing 50% solids of VP:NMA (mole ratio in pad solution of 1:0.80) to a wet pickup of 90%. When the fabric speed through the reactor was reduced from 0.040 to 0.0079 m/sec with lamp set No. 5, the concentration of VP in the copolymer increases from a VP:NMA mole ratio of 1:1.75 to 1:1.04 at low wattage, 1:1.57 to 1:1.11 at normal wattage, and 1:1.35 to 1:1.00 at high wattage. Similar effects were noted for the other lamp sets, with the concentration of VP in the copolymer increasing as the lamp wattage is increased at the higher fabric speed.

The durabilities of the VP and NMA copolymers on the irradiated, treated fabrics to machine wash and dry cycles are shown in Table III. The treated fabrics were irradiated with standard lamp set No. 1 on normal wattage. The retention of nitrogen in the modified cotton fabrics through 50 wash and dry cycles varied from 95 to 103% of the original. Under the same conditions, the retention of phosphorus was not as great, showing that the vinyl phosphonate oligomer is less durable. In Table II this difference in retention of nitrogen and phosphorus contents is shown by the mole ratio of VP:NMA, which decreased from 1:1.51 (0 wash and dry cycles) to 1:2.74 after 50 wash and dry cycles.

The effects of machine wash and dry cycles on flame resistances of VP-NMA-modified cotton fabrics (printcloth and sateen) are shown in Table IV. A series of each of the two cotton fabrics, with a range of VP-NMA add-on from 10.4 to 35.4% for the printcloth and 11.3 to 24.6% for the sateen fabric, was tested



(a)

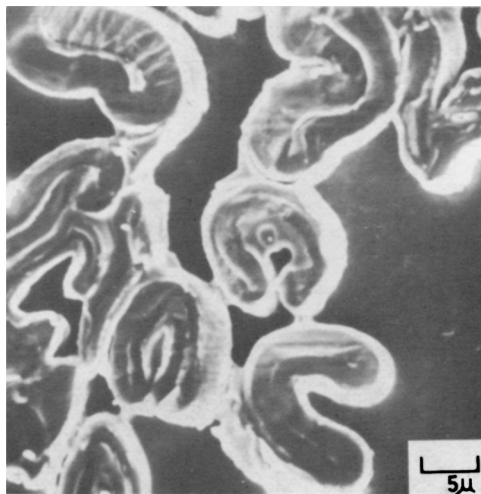


(b)

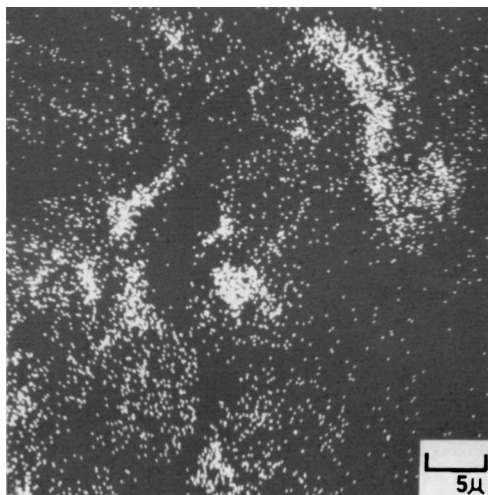
Fig. 2. TEM cotton-fiber cross section from cotton sateen fabric treated with vinyl phosphonate oligomer and *N*-methylolacrylamide (VP:NMA, 1:0.80 mole ratio padded on fabric, solids content on fabric, 45%, lamp set No. 5, 0.0079 m/sec, copolymer add-on, 24.2%, VP:NMA, 1:1.07 mole ratio in polymer on fabric). (a) Portion of fiber cross section. (b) Cross section extracted with 0.5M cupriethylenediamine dihydroxide.

for flame resistance. Two samples (one that failed the DOC test after 25 wash and dry cycles and one that passed the DOC after 50 wash and dry cycles) were selected from each series to illustrate the amount of VP-NMA required to impart flame resistance. See Table III for the phosphorus and nitrogen contents of these samples.

The effects of VP-NMA photoinitiated polymerization on some textile properties of cotton printcloth and sateen fabrics are shown in Table V. The results obtained for the treated fabrics are compared with those of a control fabric



(a)



(b)

Fig. 3. EDX map showing location of phosphorus in cotton fiber cross sections. See Fig. 2(a) for preparation of sample. (a) Fiber cross sections. (b) Phosphorus location in Fig. 3(a).

with the tearing strength and flex abrasion being significantly reduced in most cases. Stiffness of the treated fabrics increased from 3 to 17 times over that of the control fabric, giving the fabrics a harsh textile hand. Stiffness of the fabrics may be reduced, as previously reported,<sup>4</sup> by machine washing and drying. Conventional flame-retardant treatments of cotton fabrics usually cause similar changes in the textile properties of fabrics.

Microscopical analysis of VP-NMA-modified cotton-sateen fabric that has acceptable flame retardance are shown in Figures 2 and 3. A transmission electron micrograph (TEM) of a portion of an ultrathin cross section of the modified fiber [Fig. 2(a)] shows its structure to be similar to that of an unmodified



fiber cross section. When sections from the modified fibers were immersed in 0.5M cupriethylenediamine dihydroxide [Fig. 2(b)], they swelled but showed only minor solubility as compared to an unmodified control, indicating the presence of polymer within the fiber. Scanning electron microscopy (SEM) of these VP-NMA modified fibrous cross sections showed deposits of polymer between the fibers. Energy dispersive x-ray (EDX) analysis was used in conjunction with SEM to show the presence of phosphorus in the yarn and fiber structure. Figure 3(a), thick fiber cross sections from the modified fabrics, shows externally deposited polymer. EDX analysis of these sections [Fig. 3(b)] showed a heavy phosphorus content in the polymer coating and less phosphorus within the fiber. Similar results are obtained by microscopical analysis for VP-NMA-modified cotton printcloth fabric that has acceptable flame retardance, except the polymer deposition is greater between the fibers.

### SUMMARY

Utilizing the data available on laboratory scale photoreactors, a continuous unsensitized photoinitiated process for preparing flame-resistant cotton fabrics was developed. The results obtained with the PPG UV processor (after modification) were comparable with results obtained with the smaller laboratory scale units. In general, the results showed that, for either set of lamps with either cotton fabric, the degree of copolymerization increased with reduced fabric speed and/or increased lamp wattage.

Elemental phosphorus and nitrogen analysis show that *N*-methylolacrylamide polymerizes at a faster rate initially as illustrated by the change in VP:NMA mole ratios. A greater efficiency in the polymerization of VP occurs at reduced fabric speeds and/or higher lamp wattages.

The technical assistance of Jarrell H. Carra is gratefully acknowledged.

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Received March 27, 1980

Accepted May 14, 1980