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### Electron-Beam-Initiated Grafting of Flame Retardants to Fabrics Containing Cellulose. I. Reaction Rate Studies

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## **Electron-Beam-Initiated Grafting of Flame Retardants to Fabrics Containing Cellulose. I. Reaction Rate Studies**

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### **A B S T R A C T**

Triallyl phosphate (I), bis( $\beta$ -chloroethyl) vinyl phosphonate (II), and a multi-functional condensate of II were grafted to cotton and rayon fabrics and the grafted products screened for potential flame retardancy. Grafting was initiated by a  $48 \times 6$  in. electron beam, in air, from a 550 kV, 20 mA accelerator powered by an insulated core transformer, with a dose rate of approximately 1 Mrad/sec. The monomers were either copolymerized in untreated fabric with N-methylol acrylamide as a coreactant or were copolymerized with pendant double bonds in fabric that had been acrylamidomethylated in a prior step.

### **I N T R O D U C T I O N**

In work recently published by this laboratory [1], flame retardants were attached to cellulose through radiation-induced free radical addition of saturated compounds (e.g., bromoform, sodium hypophosphite,

stannic chloride) to double bonds in cotton and rayon that had been acrylamidomethylated by a prior heat and acid-catalyzed reaction with N-methylol acrylamide. Postreaction bromination of the remaining double bonds was necessary for adequate flame retardancy in most cases, a process which gave good results but which would be decidedly awkward on a practical scale. The work reported here represents progress toward the elimination of this step and preliminary success in also eliminating the acrylamidomethylation step.

The approach to the former goal was to copolymerize unsaturated, phosphorous-containing monomers with the double bonds in cotton or rayon that had been previously reacted with N-methylol acrylamide (MAM). The acrylamidomethylation step was then by-passed by polymerizing one of the monomers in untreated cellulosic fabric or by copolymerizing it with N-methylol acrylamide in a manner similar to that used in the work of Miles and Delasanta [2].

## EXPERIMENTAL

Fabrics used were a 4 oz/yd<sup>2</sup> rayon shirting from Stonecutter Mills, an 8 oz/yd<sup>2</sup> cotton twill from Cone Mills, a 9 oz/yd<sup>2</sup> 50/50 rayon-polyester twill from Deering Milliken, and 50/50 cotton-polyester in a 4 oz/yd<sup>2</sup> print cloth from Springs Mills. All fabrics were scoured and bleached before further treatment.

Triallyl phosphate was from Borden Chemical, N-methylol acrylamide was furnished by American Cyanamide Co., and Stauffer Chemical furnished bis( $\beta$ -chloroethyl) vinyl phosphonate and Fyrol 76.\*

Radiation from an electron accelerator and a plasma arc was used in these experiments. The electron accelerator, manufactured by High Voltage Engineering Corporation, has a maximum beam current of 20 mA and was operated at 500,000 V (from an insulated core transformer) for all experiments. This equipment utilizes a horizontal beam scanned to 48 in. (vertical) by approximately 6 in. The samples are hung vertically on a conveyor, which carries them in front of the beam twice in each pass through the equipment so that the samples received half of their total dose from each side. All irradiations were carried out in ambient air or in dry air-filled Ziploc polyethylene bags from Dow Chemical Corporation.

The plasma arc is a Linde PARS-102 laboratory/quality control unit. The radiation is produced by an arc in an argon-filled quartz tube. Argon passing through the tube is cooled in a water-jacketed heat exchanger and used for inerting the conveyor path for 1 ft ahead of and behind the irradiation chamber. The total radiant power

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\*Trade names of chemicals are given as part of the experimental conditions and not as an endorsement of any product over another.

delivered to the sample is  $7500 \text{ W/ft}^2$  for the operating conditions specified by the manufacturer. The delivered UV power (i.e., below  $4000 \text{ \AA}$ ) is  $560 \text{ W/ft}^2$ . The speed of the conveyor, which holds samples up to 6 in. in width, is variable from 60 to 540 ft/min, and the direction is reversible, so rapid, multiple passes under the light are feasible.

## RESULTS AND DISCUSSION

Rayon shirting previously reacted with N-methylol acrylamide to give a weight increase of 18.0% after washing was padded with 25% triallyl phosphate in methanol, dried, conditioned, and irradiated in air at a beam current of 3.1 mA and variable conveyor speeds. The weight gains after thorough and repeated washing in methanol are shown in Fig. 1. The sluggishness of the allyl groups, even in the presence of the fixed N-methylol acrylamide, can be seen in the low rate of reaction. Triallyl phosphate alone padded on untreated rayon did not polymerize it at all, as was shown by Miles et al. [2]. This monomer contains only 14.2% phosphorous, so match test angles of the treated fabrics only reached  $80^\circ$  at the highest add-on ( $\sim 0.6\%$  phosphorous). It has been this laboratory's observation that match angles approaching  $180^\circ$  are necessary to pass the Federal Sleepwear Standard (DOC FF3-71).

The bis( $\beta$ -chloroethyl) vinyl phosphonate, similarly treated, was more reactive, even with its single vinyl group, as may be seen in Fig. 2, but match test angles did not surpass  $120^\circ$  (at 1.5% phosphorous).

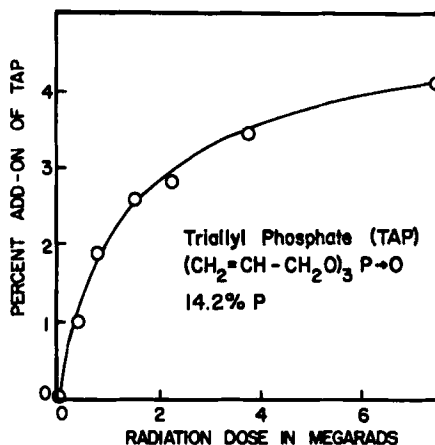


FIG. 1. Addition of triallyl phosphate to rayon with 18.0% MAM.

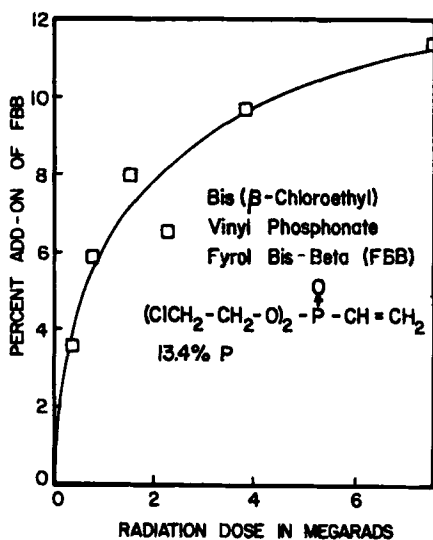


FIG. 2. Addition of bis( $\beta$ -chloroethyl) vinyl phosphonate to rayon with 18.0% MAM.

This monomer also did not polymerize in the absence of the N-methylol acrylamide.

Fyrol 76 (previously carrying the experimental designation of E-7176) is said by Stauffer Chemical Co. to be a condensate of bis( $\beta$ -chloroethyl) vinyl phosphonate and another phosphorous ester and to give a product containing 22.5% phosphorous. There are multiple vinyl groups per molecule, giving it greater reactivity, as shown in Fig. 3. The monomer was applied to cotton and rayon from a 25% water solution (the first two monomers are not water-soluble). The higher fraction of phosphorous in the molecule was also evident in the fact that 180° match test angle was reached at 12% add-on for the rayon (2.6% P) and 9% (2.0% P) for the cotton twill.

In all these treatments the phosphorous-containing monomer was copolymerizing with MAM groups that were attached to the cellulose backbone. This gave the fabrics high crease recovery, presumably because the copolymer formed involved MAM groups on more than one cellulose chain. These resilient fabrics had strength losses common to such fabrics (e.g., about 50%), so it seemed profitable to attempt to fix the flame retardants without cross-linking. The first two monomers would not polymerize in the absence of the previously reacted MAM, but the Fyrol 76 was fixed to a higher degree when applied alone, to untreated fabric, as shown by the uppermost point in Fig. 3.

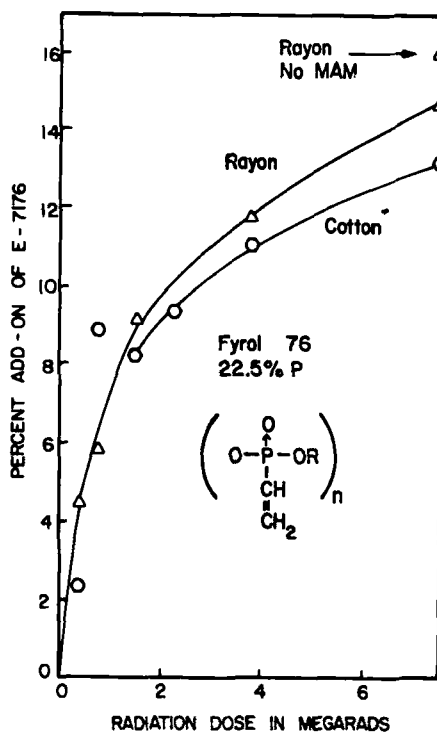


FIG. 3. Addition of Fyrol 76 to rayon with 18.0% MAM and to cotton with 8.7% MAM.

This monomer (or oligomer), since it is multifunctional, forms an insoluble gel when polymerized beyond a very low conversion. For this reason a conclusion as to whether it is or is not grafted cannot be made and the question is, in fact, moot. It was, however insolubilized inside the fiber, and is, for all practical purposes, grafted.

It was then decided to investigate more fully the polymerization of this monomer alone and in combination with N-methylol acrylamide—not reacted but applied in the same pad bath and copolymerized without cross-linking the cellulose. Cotton twill was padded with a series of mixtures of the two monomers to give roughly the same solids add-on, but varying percentages of Fyrol 76 and MAM. The results of irradiating these fabrics are shown in Fig. 4 as the fraction of the total solids applied (35% add-on) that were unextractable in one wash.

As the ratio of MAM to Fyrol 76 is varied, the yields did not vary greatly, but there was a broad maximum at around 50% MAM-50% Fyrol 76. The acrylamide group has a much higher polymerization

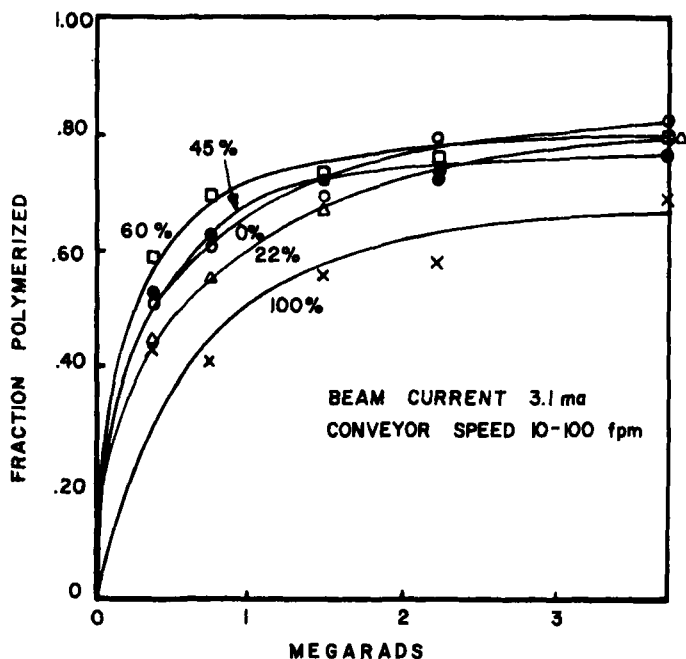


FIG. 4. Addition of N-methylol acrylamide and Fyrol 76 to cotton twill. Figures refer to percent Fyrol 76 in the mixture with MAM (on a solids basis). Total solids on fabric about 35%.

rate than the vinyls on Fyrol 76, but adding the latter increases the average double bonds per molecule and, since it is liquid at room temperature, the mobility and diffusion rate are also increased. In highly restricted polymerization systems an increase in mobility at first increases  $k_p$ , the polymerization rate constant for monomer addition to the growing chain, increasing the overall polymerization rate. Further increases in mobility then cause increases in  $k_t$ , the termination rate constant for the growing chains, and a decrease in polymerization rate occurs [3]. The maximum in overall rate occurs as one of these effects takes control from the other.

Another effect of mobility restrictions on polymerization kinetics is that, since radical termination is reduced, the familiar square-root relationship between dose rate and polymerization rate no longer obtains, and nearly linear plots are often observed. The beam current in the electron accelerator was varied by a factor of 3, keeping the conveyor speed constant, and conversion curves were obtained for two

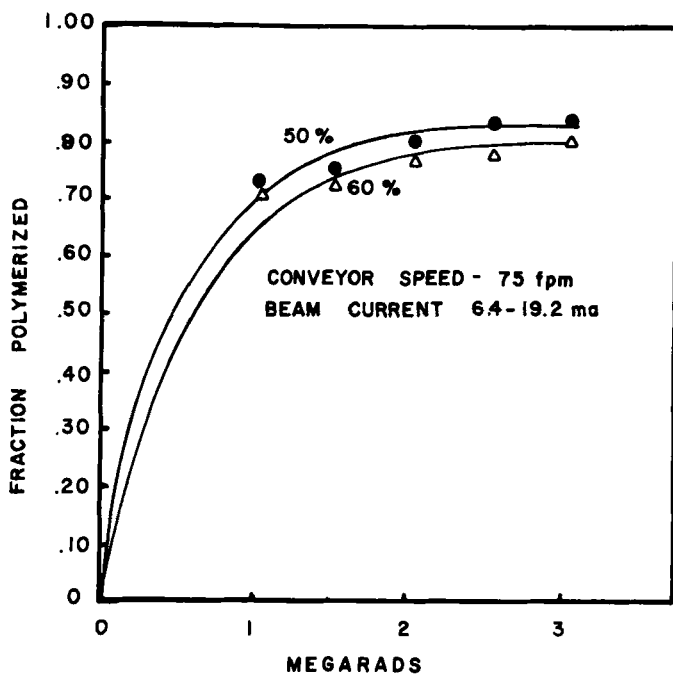


FIG. 5. Conversion curves for 50% and 60% Fyrol 76 in MAM on cotton at constant conveyor speed and variable dose-rate.

MAM-Fyrol 76 ratios similarly to the experiment just described. The data, shown in Fig. 5, were not greatly different from those obtained at constant dose rate, indicating that, within the fairly restrictive confines of this experiment, dose-rate changes did not affect the conversion efficiency.

Since a maximum was observed as the ratio of MAM to Fyrol 76 was varied, it was of interest to examine the conversion rates at low percentages of MAM. Figure 6 shows conversion data for Fyrol 76 containing 0, 2, and 10% MAM, and demonstrates strikingly the MAM's high reactivity and its ability to increase the overall polymerization rate in a copolymerization. Fractionation is likely in such a system, and the percent nitrogen is probably different in the copolymer than in the pad bath solids, but the increase in overall conversion rate is too high to be accounted for by the additional MAM alone.

The same treatment was given to 50/50 polyester-cotton print cloth (4 oz/yd<sup>2</sup>), and the comparable conversion curve is shown in Fig. 7. In both the 100% cotton and the blend there were 45% solids



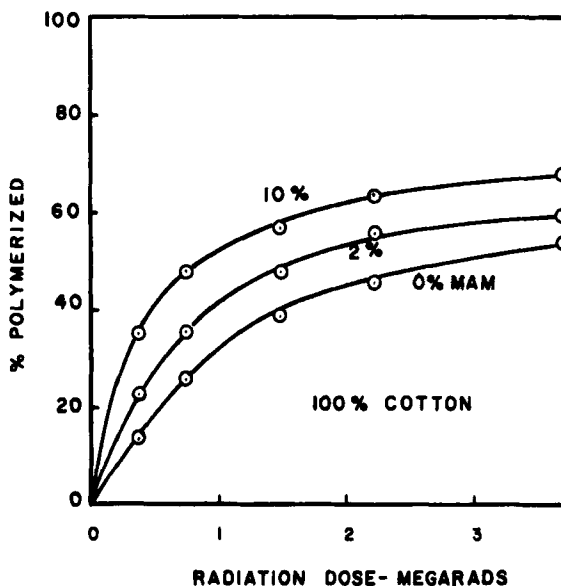


FIG. 6. Conversion curves for Fyrol 76 containing 0, 2, and 10% MAM on cotton twill (8.0 oz/yd<sup>2</sup>). Total solids on fabric: 45%

on the fabric during irradiation. In both cases a significant fraction of the add-on was outside the fibers, but this fraction must have been considerably higher in the case of the blend, since the polyester is not penetrated. Comparison of the conversion curves for these two fabrics reveals that the 100% Fyrol polymerizes more slowly on the blend than on the cotton fabric, but that addition of MAM decreases this difference, and at 10% MAM the curves are almost the same. Presumably the increased mobility of the monomer outside the fiber reduces its polymerization rate due to increased termination, but addition of MAM helps to overcome this liability.

It was also observed in these experiments that the conversion for 100% Fyrol 76 was lower than previously observed (compare Figs. 4 and 6). Since all irradiations were in air at ambient conditions, and the fabrics in Fig. 6 were irradiated on a day when humidity was high, moisture was suspected to be playing a role. To test this hypothesis, the polyester-cotton blend was padded with Fyrol 76 (40% on fabric) and irradiated at different conditions. One group was oven dried at 70°C, put quickly in Ziploc polyethylene bags, and flushed thoroughly with dry (R.H. < 1%), medical breathing air. Another was oven dried and allowed to condition before irradiation (at 75% R.H.). The third

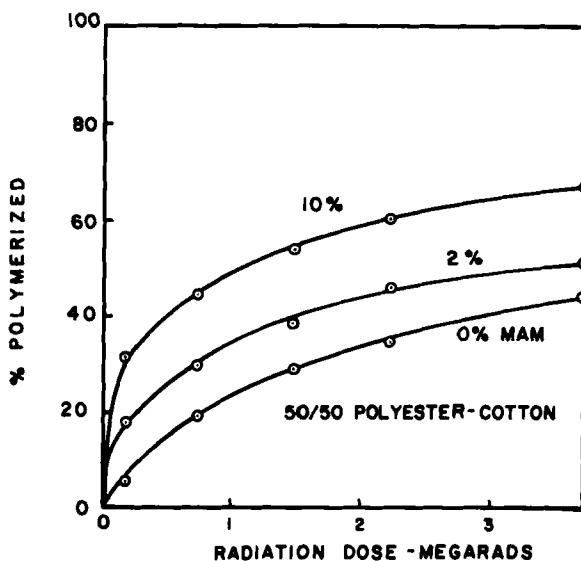


FIG. 7. Conversion curves for Fyrol 76 containing 0, 2, and 10% MAM on 50/50 polyester-cotton print cloth (4 oz/yd<sup>2</sup>). Total solids on fabric: 45%

group was air-dried (22°C, 75% R.H.) and then irradiated. The striking effect of moisture on the conversion curves for these fabrics can be seen in Fig. 8. Even the hysteresis moisture in the air-dried fabrics was effective in reducing the polymerization rate.

The moisture can affect the polymerization by increasing the overall mobility (and chain termination) and by increasing the fraction outside the fiber, which should increase both mobility and oxygen inhibition. The fraction outside the fiber can be varied by simply varying the add-on, and this technique was used on a 50/50 polyester-rayon fabric, which was then irradiated 2.25 Mrad, either in dry air or conditioned at 65% R.H. The results are shown in Fig. 9. Up to about 10% add-on (20% on the rayon), no effect of moisture can be seen. Above this add-on, as will be shown in a subsequent publication, monomer begins to be deposited outside the rayon fiber in significant quantities where its mobility is increased and where it is less protected from air inhibition.

It was also of some interest to assess the possibility of using UV radiation to induce these reactions. Both the cotton and cotton-polyester fabrics used in the prior experiments were padded with a mixture of MAM and Fyrol 76 taken near the optimum from the mixtures shown in Fig. 4, i.e., 60% Fyrol 76, 40% MAM (solids basis). This mixture,

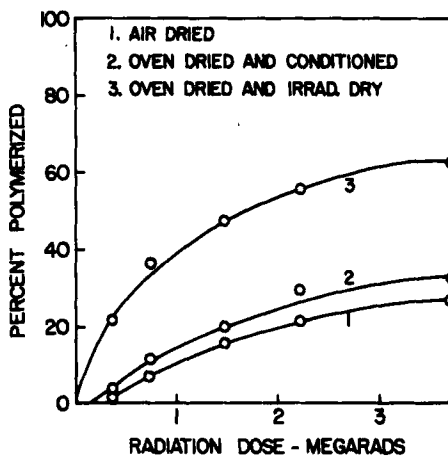


FIG. 8. Conversion curves for Fyrol 76 (40% add-on) on 50/50 polyester-cotton irradiated in dry (< 1% R.H.) air and at ~75% R.H.

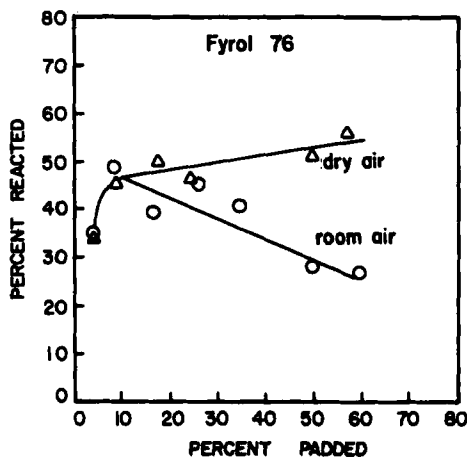


FIG. 9. Polyester-rayon (50/50) padded with various add-ons of Fyrol 76 and irradiated 2.25 Mrads in dry (< 1% R.H.) or ambient (~65% R.H.) air.

in pad baths containing 1 or 3% anthraquinone-2,6-disulfonic acid, sodium salt (ADS), was applied to the fabrics to give total solids addition of 22%. These fabrics, dried and conditioned, were irradiated in the plasma arc, passing them under the beam at speeds from 60 to 545 ft/min. Some were passed several times through the beam. The results are shown in Figs. 10 and 11. Examination of Fig. 10 reveals that yields on the polyester-cotton blend are about twice those on the cotton fabric, in direct contrast to the results obtained from electron-beam irradiation. Samples irradiated in the plasma arc are swept with dry (99.996%) argon during irradiation, but these were conditioned before irradiation, and it is doubtful that any significant dehumidification occurred during the rapid sweep through the inerting chamber. Thus a higher fraction of solids should have been outside the cellulose fiber in the blend, giving it a lower yield. The difference observed here must have been due to the fact that the cotton fabric was dyed (khaki) and was twice as heavy. The ADS showed a noticeable color change on irradiation, and this was not as noticeable on the underside (away from the light) of the fabrics, even in the 4 oz/yd<sup>2</sup>, white print cloth. Obviously, the lack of complete penetration was a major factor in determining the yields of these irradiations. Tripling the photoinitiator concentration increased the yields by about 30% (Fig. 11) but the difference between the fabrics was not altered (no polymerization at all was observed in the absence of photoinitiator). It is

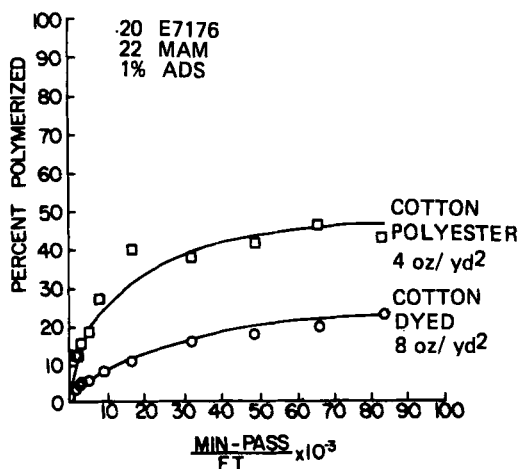


FIG. 10. Conversion curves for fabrics padded with 60% Fyrol 76 and 40% MAM (solids basis). Pad bath contained 1% anthraquinone-2,6-disulfonic acid, sodium salt. Total solids on fabric: 22%.

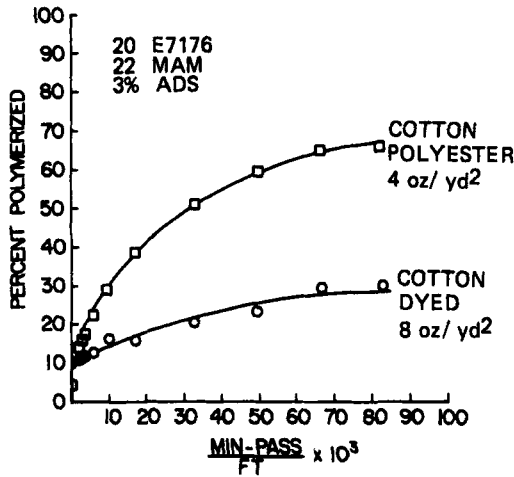


FIG. 11. Same as Fig. 10 but the pad bath contained 3% anthraquinone-2,6-disulfonic acid, sodium salt.

equally certain that irradiation of both sides of the fabrics would have improved the yields and probably narrowed the contrast between the two fabric weights.

### SUMMARY AND CONCLUSION

Bromination of unused double bonds after addition of flame retardants to acrylamidomethyl cellulose was found to be unnecessary when a copolymerization reaction with the pendant MAM groups was used instead of chain transfer addition. Good flame retardancy and permanent press was obtained by using a multifunctional vinyl phosphonate oligomer with high phosphorous content (Fyrol 76). Polymerization of this monomer alone and copolymerizing it with uncondensed N-methylol acrylamide eliminated the cross-linking. This reaction was inhibited by moisture when it took place outside of the cellulose (where it does not graft, but forms a cross-linked coating). The use of electron beam irradiation to fix these compounds is rapid enough to be entirely feasible from a practical standpoint. The durability of the products and economic comparisons with thermally cured fabrics will be the subjects of ensuing publications.

A photoinitiator was found to be necessary for UV light induction of the copolymerization reaction and the rate was highly dependant on fabric weight, indicating lack of uniform penetration. For these reasons

and based on this preliminary study, it seems doubtful that UV is as practical an alternative to thermal curing as is electron beam irradiation.

#### ACKNOWLEDGMENTS

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