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Olney Medal Address

The Developing Uses of Radiation in Industry

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ABSTRACT

During the last two decades high energy radiation processing techniques have come of age and have proven themselves in the production of such special products as coatings on wood, plastics and metals. These successes point squarely to uses in the textile industry. This paper reviews briefly the progress already made and points out some of the advantages foreseen for radiation technology, particularly in finishing.

KEY TERMS

Curing
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Radiation

ABOUT 20 years ago, when thoughts concerning industrial uses for high energy radiation began to appear, we wrote the following (*1*): "The development of new products for the textile industry through radiation chemistry, at least in the near future, appears unlikely." Today the situation is somewhat different; during the ensuing years, radiation techniques have come of age—through research efforts of a purely chemical nature, through the development of machines for the irradiation of sheet materials, through the needs of a cleaner environment, and most recently because of apparent advantages in an energy crisis. While final prognostications may still contain an element of daydreaming, the successes of radiation techniques for the production of special products in other industries—e.g., the curing of coatings on wood, plastics and metals—point squarely to uses in the textile industry.

The name of the game is the creation of marketable products of improved end-use performance, efficiently and economically. Radiation technology has the potential for increasing productivity, for savings in energy, and for the manufacturing of new and better products. Successful utilization of this technology should also provide the textile industry with additional ways to meet the growing demands of state and federal governments and consumers for safer products and even better working conditions at the manufacturing level.

Over the past two decades, extensive basic research has been done on the application of radiation to textiles, particularly for initiating useful reactions of chemicals with fibrous materials. It is the purpose of this paper to review this period, not comprehensively, but briefly and to cite findings along the way that encouraged us, as well as others, to find new means to engineer fiber and fabric properties. An in-depth review (to 1967) dealing with the uses of radiation for the modification of textile fibers may be found elsewhere (*2*).

Our own interest in radiation applications began in 1953. In September of that year, N. C. State University achieved a "first" in the field of nuclear engineering. At that time, the Raleigh Reactor, the initial one on a college campus outside of the Atomic Energy Commission, went critical. During its operation, as in any reactor, the unit produced heat and radiation, the latter consisting primarily of neutrons and γ-rays, both potentially useful as sources of high energy. The value of the reactor as an energy source was immediately recognized, and heavy demands for its use in all kinds of research arose overnight. For

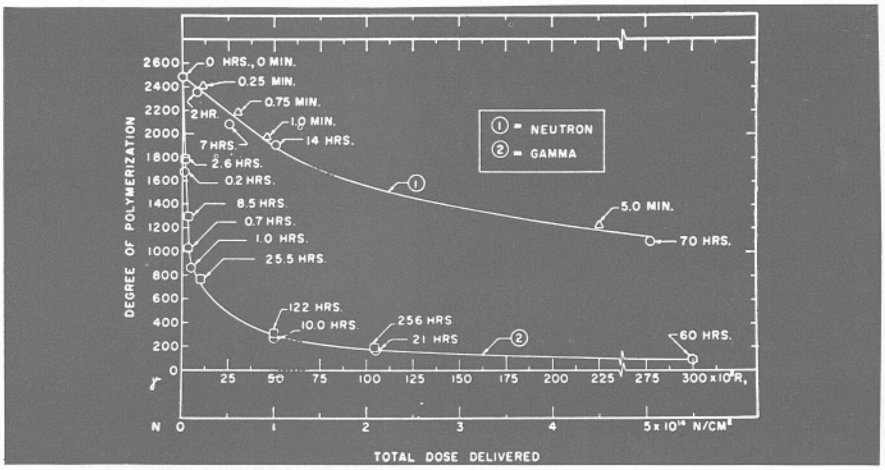


Fig. 1. Dependence of change in degree of polymerization of cotton on total dose of radiation.

the most part, the work was directed toward learning something of the nature of the interaction of reactor-produced radiation with matter, but more particularly how the properties of matter might be changed by such interactions.

In addition, the notion persisted at that time that we would some day have at our disposal large quantities of radioactive waste products from power reactors that might be of use in industry. It was this idea that prompted the U.S. Atomic Energy Commission to support several projects with the objective of finding industrial applications for radioactive isotopes. Our first major program—funded by the USAEC, Burlington Industries, Cone Mills, Reeves Brothers and J. P. Stevens & Co.—was directed toward the textile industry.

As early as 1954 the behavior of a wide variety of plastics and elastomers toward nuclear radiation was reported by Bopp and Sisman (*3*). With some reservations as to the exact order, they ranked polymer stability toward radiation according to chemical structure. It was clearly demonstrated that hydrocarbon long-chain polymers as such, or bearing no side chains other than phenyl groups, were predominately crosslinked. Thus, materials such as polystyrene and polyethylene showed the greatest stabliity toward radiation, and the changes in physical properties suggested crosslinking. Cellulose, of special interest in the field of textiles, and materials containing fluorine or chlorine showed little resistance to chain cleavage and were near the bottom of the list with respect to radiation stability. Polyesters and polyamides showed intermediate orders of stability.

In extending this work to organic textile fibers, all of which are polymeric materials, it was therefore expected that the general effects of radiation would be at least twofold. The substance might be improved with respect to certain properties through the medium of crosslinking or be degraded because of scission of its long-chain molecules. Early experimental work confirmed this view (*4-8*).

During this period some interesting data relative to the effects on various fibers of particle radiation, i.e., thermal neutrons vs. electromagnetic radiation, specifically, γ-rays, were revealed.

The data shown in Fig. 1 are representative of the behavior of cellulosic fibers when exposed at different dose rates to either thermal neutrons or to γ-rays (*8*). In this case, illustrative of the behavior of other fibers, the degree of polymerization of cotton as a function of total dose of radiation delivered is shown. Considering either type of radiation, it is clearly seen that the change in degree of polymerization was a function of total dose only and had no relation to the rate at which the dose was delivered. For example, the effect obtained after 256 hr in the case of γ-rays at a low dose rate was identical when an equivalent amount of radiation was delivered in only 21 hr. Similarily, a 5-min exposure to thermal neutrons at the fast rate was equivalent to about 70 hr at the slow rate, and the change in degree of polymerization of the cotton was nearly identical. Data obtained with rayon and acetate were consistent with the findings on cotton. Other investigations (*9*) have shown that the mechanisms of some radiochemical reactions are influenced by dose rate. It is fortunate, as will be indicated later, that desirable chemical modifications of textiles may be made at high dose rates, thus placing radiation procedures in the realm of economic practicality.

Subsequently, it was shown that the exposure of all textile fibers to nuclear radiation alone generally led to degradation, but that the rates of degradation were not the same among the fibers (*10*). This is illustrated in Table I (*11*) and in Fig. 2.

Of the chemically different types, polyester was the most stable. The other fibers followed in the order: acrylics, wool, synthetic polyamides, acetate and cellulosics. Draw ratio was also shown to influence the nature of the response of polyesters and acrylics. In some cases, the ambient conditions (e.g. oxygen) had a noticable influence on the rate of change in polymer properties, particularly in the case of polyamides. Overall, however, it was concluded that radiation alone had little potential for significantly improving the properties of fibrous materials.

In the meantime, considerable interest developed in the possibility of modifying fibrous materials by graft polymerization utilizing free-radical chemical reactions (*12, 13*). Because high-energy radiation can induce the formation of free radicals in organic materials, a number of investigators turned their attention toward another way, i.e., the radiation route, for the modification of materials by grafting (*14-16*). It turned out that when fibers were exposed to several types of radiation in the presence of certain chemicals they behaved very differently than when exposed to radiation alone (*16*). Figs. 2, 3, and 4 illustrate the point. The relative breaking loads of various textile yarns were determined as a function of duration of irradiation in

Table I—Radiation Tolerance of Textiles in Air Below 95F[a]

	Dose (Mrad)		
	Where loss in strength becomes significant	Where viscosity is changed significantly	First complete destruction of fibrous properties[b]
Cotton	0.1	0.055	30
Rayon	0.8	0.5	80
Acetate	1	1.3	100
Wool	5	—	100
Nylon 6 or 66 (polyamides)	2	1.1	100
Dynel (modacrylic)	4	—	—
Orlon (acrylic)	8	—	1,000
Dacron (polyester)	25	—	10,000

[a] Data of Bolt and Carroll (*11*).
[b] Estimated by extrapolation; values may not be realistic.

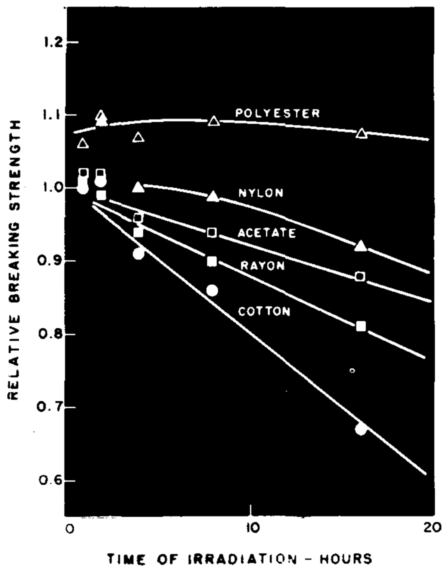


Fig. 2. Breaking loads, relative to unirradiated materials, of yarns after exposure to γ-radiation for different periods of time in an atmosphere of nitrogen saturated with water at 70F. Dose rate, $3x10^5$ r/hr.

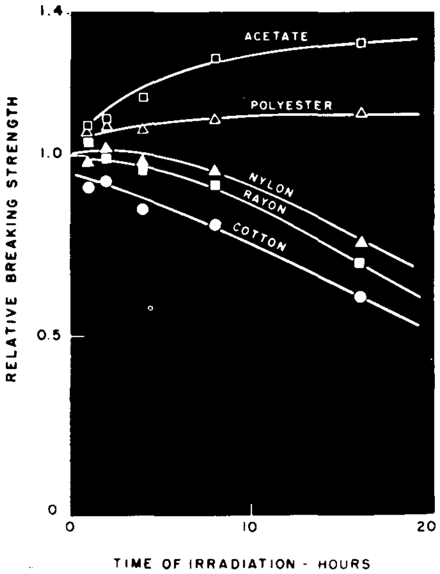


Fig. 3. Breaking loads, relative to the unirradiated materials, of yarns after exposure to γ-radiation for different periods of time in an atmosphere of nitrogen containing 10% acrylonitrile and 2.2% water at 70F. Dose rate, $3.8x10^5$ r/hr.

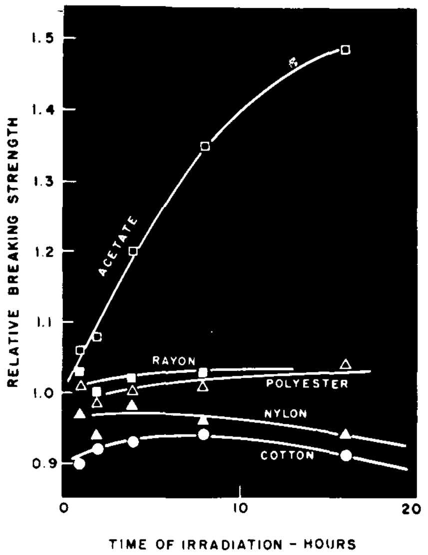


Fig. 4. Breaking loads, relative to the irradiated controls (no acrylonitrile), of yarns after exposure to γ-radiation for different periods of time in an atmosphere of nitrogen containing 10% acrylonitrile and 2.2% water at 70F. Dose rate, $3.8x10^5$ r/hr.

the presence of a vinyl monomer, acrylonitrile. Fig. 2 shows the effect of irradiation alone in the absence of monomer and in an atmosphere containing nitrogen saturated with water. The breaking load shown on the ordinate is relative to the unirradiated yarn. Figures 3 and 4 indicate the effect of the addition of different amounts of acrylonitrile on the breaking loads of the yarns relative to the unirradiated and the irradiated samples, respectively. It is obvious from Figs. 3 and 4 that the load required to break an acetate yarn was greatly increased by the addition of acrylonitrile and that some protective effect from radiation was given to all the materials by the presence of the vinyl monomer.

Further studies (*16-18*) of the behavior of several of the common fibers in the presence of a variety of monomers both monofunctional and difunctional with respect to unsaturation revealed the following.

Relatively small amounts of acrylonitrile grafted (or added as homopolymer) to cotton by the radiation procedure produced a material extremely resistant to cellulose-destroying microorganisms without loss of esthetic qualities. Polypropylene could be made dyeable with disperse dyes by the "grafting" of small amounts of methyl acrylate. Divinyl or vinyl-allyl monomers that were anticipated to be effective as crosslinking agents for cellulose under the influence of radiation failed for the most part to act in this way. On the other hand, materials less sensitive than cellulose toward chain scission by radiation, such as nylon, could be crosslinked with only a small amount (less than 2%) of allyl acrylate. Nylon filament yarns were made unmeltable at a relatively low dose of radiation (1 Mrad) in the presence of this difunctional monomer. Another observation that turned out later to be of practical significance was that monomers which contained, in addition to a vinyl group, a group chemically reactive toward cellulose hydroxyls offered the possibility of polyfunctional crosslinking agents. Examples were: acrylic acid ($CH_2{=}CHOOH$), with a carboxyl group; glycidyl acrylate ($CH_2{=}CHOOCH_2\overline{CHCH_2{-}O}$) with an epoxy group; and methylolacrylamide ($CH_2{=}CHCONHCH_2OH$), with an *N*-methylol group.

These results, as well as many others not cited, made it clear, then, that the potential of high-energy radiation in the processing of textiles, did not lie in its use alone, but rather in adjunct with the proper chemical substances, especially those containing unsaturation. Thus, during the period 1962 to 1965, the principle became well established that the properties of textile fibers could be altered by the use of radiation techniques. With the availability of the proper chemicals, i.e., those that would respond to free-radical reactions, the finishing of fibers for specific and uses could be envisioned. Even dyeing, did not seem out of the realm of possibility.

In this same period, there was a flurry of interest on the part of the textile industry in the possibility of using radiation in finishing processes, perhaps largely brought about by a few successes in other industries. Added impetus was provided when in 1965 a paper appeared in the literature that reported the possible use of radiation as the final step in a delayed-cure process for cotton (*17*). This investigation was extended, and in 1966 the details of a process thought to be practical were announced (*19-20*). It was shown that methylolacrylamide could be reacted through its *N*-methylol group with cotton by pad-dry-cure procedures normally employed in textile finishing mills. At this stage [I in Eq. (1)] the fabric could be washed free of unreacted chemicals and made into garments without the attendant nuisances experienced with the normal fabrics prepared for post-cure processes. The fabric had an infinite shelf life, being sensitive only to radiation. Electron irradiation of the garment in a machine (II) or exposure to γ-radiation in a ^{60}Co source quickly induced the structural changes required (crosslinking, III) to produce durable-press characteristics without the need of ellevated temperatures or long periods of curing. Eqs. (1)-(3) describe these reactions, although the chemistry of the crosslinking step is not clear.

The effect on crease recovery angles of the addition of different amounts of methylolacrylamide to cotton twill and with subsequent irradiation to different levels is shown in Fig. 5. Permanent creases were achieved with all fabrics that had crease recovery angles of 240° or higher.

From 1967 to 1971, Cone Mills Corporation thoroughly investigated this process for the manufacturing of durable-press garments, but chose finally not to go into commercial production. The reason for this decision was not revealed, but neither the economics nor the success of the process seemed to be in the prohibiting factors, at least from our vantage point.

Also in 1966, Deering Milliken announced a new process for the production of a soil-release fabric. To the best of our knowledge, the same monomer was used in this process, but, unlike the radiation system just mentioned for making durable-press fabrics, the compound was reacted with the fabric with the use of radiation as the first step. Durable-press properties were imparted by a subsequent normal post-cure procedure utilizing high temperatures in an oven.

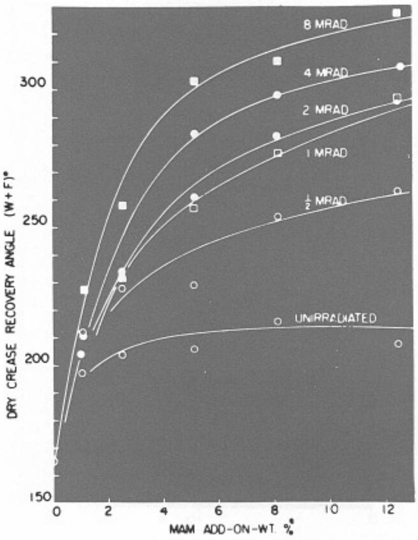


Fig. 5. Variation of dry crease recovery angle with add-on and electron radiation dose.

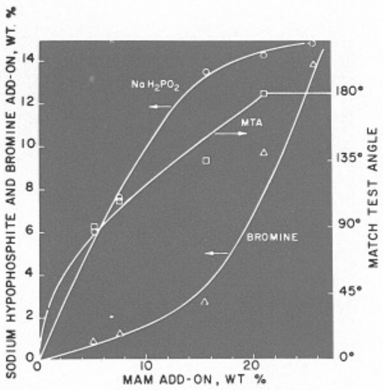
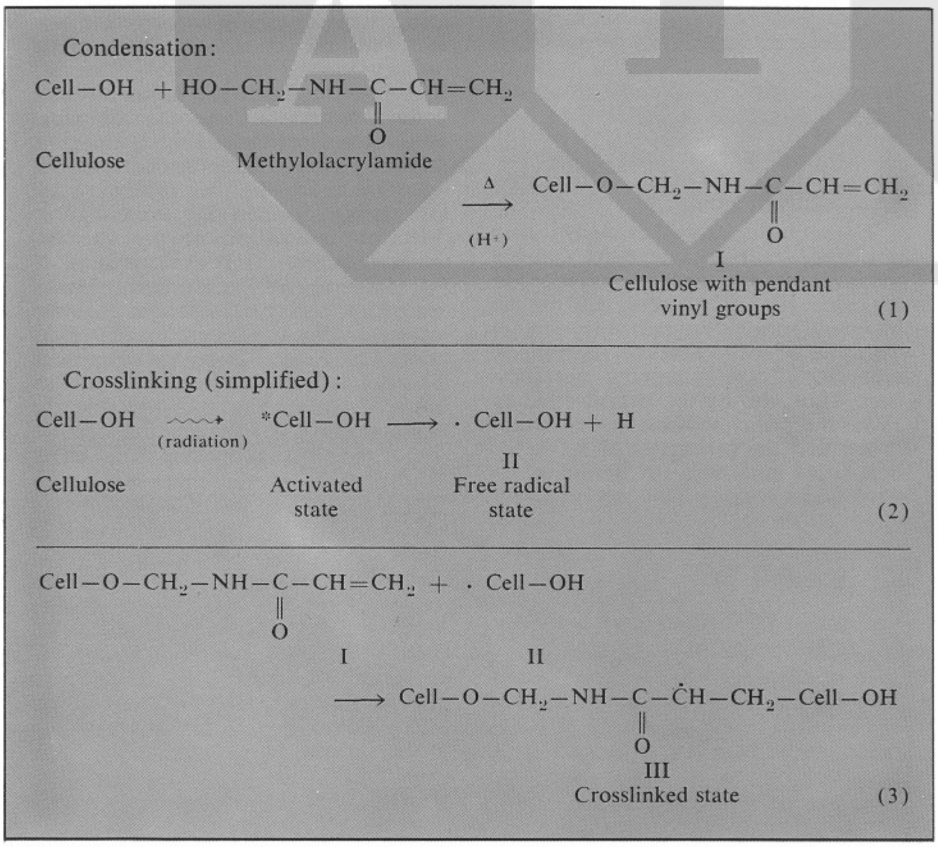


Fig. 6. Addition of sodium hypophosphite and bromine to 4 oz/yd^2 viscose shirting with various amounts of methylolacrylamide (MAM). Padded with 48% NaH_2PO_2, irradiated 1.3 Mrad in air, and brominated.

In the instance cited (Fig. 5), irradiation was done in a 500-V insulated-core transformer accelerator (High Voltage Engineering Corp.). It was interesting to note that essentially identical curves were obtained at equal doses, when γ-radiation from a ^{60}Co source was used, even though the dose rate in the γ-source was smaller by a factor of 8000 than in the machine. A surprising feature of the curves in Fig. 5 is the lack of a well-defined leveling-off of crease-recovery angle with increasing add-on or radiation dose. Crosslinking, responsible for rises in crease-recovery angles, is presumed to occur by a free-radical polymerization of the double bonds in short chains (*21, 22*). The small chain length results from the fact that these bonds are locked in place on the cellulose backbone and cannot diffuse. When a polymerization chain is initiated by addition of a free radical to a double bond, only the neighboring ones can participate in it. When a growing chain cannot reach another double bond, it stops. It appears that 10-15% of the original double bonds cannot be removed by any reasonable radiation dose (20 Mrad), and at doses adequate for permanent press (3-4 Mrad), almost half of the double bonds are unused (*21*).



Condensation:

$$\underset{\text{Cellulose}}{\text{Cell}-\text{OH}} + \underset{\text{Methylolacrylamide}}{\text{HO}-\text{CH}_2-\text{NH}-\overset{\displaystyle O}{\overset{\|}{\text{C}}}\!-\text{CH}=\text{CH}_2} \xrightarrow[(\text{H}^+)]{\Delta} \underset{\substack{\text{I}\\ \text{Cellulose with pendant}\\ \text{vinyl groups}}}{\text{Cell}-\text{O}-\text{CH}_2-\text{NH}-\underset{\displaystyle O}{\underset{\|}{\text{C}}}-\text{CH}=\text{CH}_2} \quad (1)$$

Crosslinking (simplified):

$$\underset{\text{Cellulose}}{\text{Cell}-\text{OH}} \xrightarrow[\text{(radiation)}]{\rightsquigarrow} \underset{\substack{\text{Activated}\\ \text{state}}}{{}^*\text{Cell}-\text{OH}} \longrightarrow \underset{\substack{\text{II}\\ \text{Free radical}\\ \text{state}}}{\cdot\ \text{Cell}-\text{OH}} + \text{H} \quad (2)$$

$$\underset{\text{I}}{\text{Cell}-\text{O}-\text{CH}_2-\text{NH}-\underset{\displaystyle O}{\underset{\|}{\text{C}}}-\text{CH}=\text{CH}_2} + \underset{\text{II}}{\cdot\ \text{Cell}-\text{OH}} \longrightarrow \underset{\substack{\text{III}\\ \text{Crosslinked state}}}{\text{Cell}-\text{O}-\text{CH}_2-\text{NH}-\underset{\displaystyle O}{\underset{\|}{\text{C}}}-\dot{\text{C}}\text{H}-\text{CH}_2-\text{Cell}-\text{OH}} \quad (3)$$

In a recent paper (*23, 24*) the results of efforts to take advantage of these double bonds by reacting them during or after irradiation with small molecules were presented. Cotton and rayon fabrics were condensed with *N*-methylolacrylamide to give products with various degrees of unsaturation. Radiation-induced free-radical addition to the double bonds in these fabrics was accomplished with carbon tetrachloride, bromoform, chloroform, bromotrichloromethane, polyethylene oxide, chloral and bromal hydrate, and sodium hypophosphite. Stannous and stannic chloride were also reacted by what seemed to be a different mechanism. Direct bromination of these fabrics was also described. In some cases, significant flame retardancy was obtained without alteration of hand, because the reactions were apparently limited to the inside of the cellulose fiber (*21*). Strong antibacterial activity was also found in the samples that were brominated. Fig. 6 is a typical example of the flame retardance that can be obtained by the combination of radiation free-radical induced addition of sodium hypophosphite followed by bromination of residual double bonds from a solution of bromine in potassium bromide. The rayon fabric reached a 135° match-test angle at about 2% bromine in the presence of the hypophosphite (ca. 12%), where 8% bromine alone was required.

Turning back again to the time when it became obvious that radiation could be used in adjunct with chemicals to modify fiber properties (1962), the textile industry, as well as other

Table II—Estimated Energy Requirements for Processing Fabric (8 oz/yd^2, 60 in. width, 100 yd/min)

Equipment and Initial Cost	Energy Consumption	Energy Cost ($/hr)
Electron Accelerator ($250,000)	1-5 Mrad 8-40 kW	0.05-0.24
Ultraviolet ($50,000-100,000)	100 kW	0.60
Curing Oven ($50,000)	1.5x10^6 BTU/hr 440 kW	1.00
Tenter Frame ($250,000)	3-6x10^6 BTU/hr 880-1760 kW	2-4

industries, showed some reluctance to investigate new processing techniques involving radiation for a number of reasons. One, the idea of trying new and unproven techniques with the concomitant high development costs did not have any appeal. There was no motivating force to induce a textile finishing plant, for example, to embark upon a totally new method of processing to get an end product that might be obtained by conventional methods of chemical finishing. Secondly, the radiation sources generally thought of at that time were nuclear reactors and γ-sources such as ^{60}Co, neither of which had any appeal for obvious reasons. Moreover, it became obvious that industrial uses for the energy-producing radioactive byproducts of power reactors were impractical.

The development of machine irradiators to produce accelerated electrons or to emit high intensity ultra violet radiation capable of treating sheet materials continuously at high dose rates provided the practical answer for industrial applications. These began to appear during the period 1957-1962. From 1962 to the present, tremendous advances have been made in irradiation technology. The costs of machines have dropped significantly, equipment reliability has greatly improved, there are self-shielded units that are compact and efficient, very high dose rates are achievable, and penetration can be controlled to obtain surface treatments without adverse effects on substrates.

Comparisons of the costs of radiation "curing" of textile materials as opposed to normal heat-curing processes show in favor of the former by a considerable amount. One estimate of comparative costs, including the purchasing and amortization of equipment (10 years), operation costs (2 shifts, 4000 hr/yr), etc., have indicated $5.70 vs. $19.30 per hour of operation. When it is considered that radiation processing can take place at high speeds, the cost per unit of material being processed by radiation is considerably below $5.70. Speeds of processing in accelerators with high dose rates or irradiation in high intensity ultraviolet systems, for example, can be from 500 to 1000 ft/min. Estimated comparisons of energy costs are given in Table II.

Two additional factors have contributed to our belief that there is a good future for the radiation finishing of textiles. One, which is important but not directly related to radiation technology, is that attitudes toward the use of radiation have materially changed. No longer is radiation something in a black box to be feared (and associated with atomic bombs) but instead is considered as another source of energy, highly controllable, that can be cut on and off at will, and is almost completely lacking in environmental problems. The other factor is the most important one, particularly from a technical point of view. It has finally been recognized that we cannot pull existing chemicals off the shelf and use them in adjunct with radiation to produce materials of the best end-use properties. At last chemicals are being developed with radiation sensitivity in mind. A typical example of a substance that responds to radiation that can be used to obtain flame retardance in cellulosic materials is bis (2-chloroethylvinyl) phosphonate or an oligomer of this material. In future developments we must also think in terms of polymer chemistry and its related areas and not in terms of radiation chemistry. We now look upon radiation as merely the energy source to initiate more or less normal polymerization or graft polymerization reactions.

The successful use of radiation requires, as we have indicated earlier, chemical substances specially prepared for the purpose. As a matter of fact, a total systems approach to each individual process is needed, i.e., one where the chemicals, the radiation source, and the materials handling equipment would be developed for each particular case. Only with this approach can the relative economics of radiation systems be judged meaningfully. The uncertainties involved in the comparisons shown in Table II are therefore recognized, but there is a definite indication for some degree of optimism in favor of radiation.

Radiation technology is presently being used to produce heat-shrinkable films and tubes, the manufacturing of polyethylene foams that are easily blown, the crosslinking of insulation in electrical applications, the vulcanization of rubber, the curing of organic coatings on wood, metals and plastics, and for the sterilization of medical disposables. It is estimated that 300 to 500 million pounds of materials per year are now being radiation processed.

In the textile field, experimental programs are underway to assess the value of radiation for the fixation of flame retardants in textile fibers, for the curing of adhesive bonding systems (nonwoven materials), for the crosslinking of carpet yarns to improve resilience and bulk retention, for the reaction of surface modifiers on textiles (water repellents, soil-release agents and anti-static additives) and the fixation of dyes and curing of pigment prints. The practicality of radiation for the crosslinking of cellulosic fibers for permanent-press characteristics has already been demonstrated.

When we look at the several commercial successes already achieved by the use of radiation, we visualize a good future for it in the textile industry. The forces that may mitigate for the changes are not clear. Substantial savings in energy and processing costs as well as environmental considerations, all of which are highly important in today's society, should not be discounted.

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